

DOI: http://doi.org/10.52716/jprs.v13i3.718

# Corrosion in Crude Oil Distillation Units (CDUs) and a Study of Reducing Its Rates by Changing Chemical Injection Sites

Samer N. Shattab<sup>1\*</sup>, Wissam S. Khudair<sup>2</sup>, Mohammed A. Mohammed<sup>3</sup>, Majid A. Kahthim<sup>4</sup>

Ministry of Oil / Midland Refineries Company/ Najaf Refinery, Iraq <sup>1\*</sup>Corresponding Author E-mail: <u>sameralbabily7@gmail.com</u>

<sup>2</sup><u>wissamhsse12@gmail.com</u>, <sup>3</sup><u>mohammedaulhassanmohammed@gmail.com</u>, <sup>4</sup><u>majidadmajd@gmail.com</u>

Received 20/11/2022, Revised 18/01/2023, Accepted 24 /01/2023, Published 10/09/2023



This work is licensed under a Creative Commons Attribution 4.0 International License.

# Abstract

The injection of chemicals is one of the most important treatment steps used to reduce the effect of corrosion factors in crude oil distillation units in oil refineries. As a result of the availability of suitable conditions for the formation of the main corrosion agents, namely acids (HCI,  $H_2S$ ). It has become necessary to neutralize the effect of these factors in distillation units and towers by changing the sites of adding chemicals, where oil refineries use anti\_ corrosion film and caustic soda (NaOH) as well as neutral amine to control and limit the effect of chloride ion, iron rates, salts and the (PH) values.

As a result, the research paper is interested in developing a study of adding and changing chemical injection areas (points) of adding chemicals, especially (caustic soda and neutralizer amine) at different specific points, and as it is well known, crude oil passes through a number of different heat exchangers to raise its temperature in preparation for refining. It was found that changing the addition of the neutral amine in the striper tower area of the kerosene section (drops that are returned to the main refinery tower) has a significant effect in controlling the stabilization of pH values between (5.5-6.5) and reducing the iron ion concentration at a rate of (1% ppm), While the injection of caustic soda depends on the temperatures of the crude oil, so it is changed into two lines. The first is before the heat exchangers, that is, when the temperature (65-90) c, it has a significant effect in reducing the concentration of the chloride ion at a rate of (1-5 ppm) present in the form of chloride salts dissolved in the crude oil.

**Keywords:** Corrosion in distillation towers, control of corrosion, injection of chemical treatments, Chemical injection points in refining units, Control of (PH).



# التأكل في وحدات تقطير النفط الخام (CDUs) ودراسة تقليل معدلاته عن طريق تغيير مواقع حقن المواد الكيمياوية

#### الخلاصة:

يعد حقن المواد الكيمياوية واحد من اهم خطوات المعالجة المستخدمة للحد من تأثير عوامل التأكل في وحدات تقطير النفط الخام في المصافي النفطية. ونتيجة لتوافر الظروف المناسبة لتشكيل العوامل الرئيسية المسببة للتآكل ،و هما الأحماض (HCI، H<sub>2</sub>S). اصبح من الازم تحييد تأثير هذه العوامل في وحدات وأبراج التقطير من خلال تغيير مواقع أضافة المواد الكيمياوية حيث تستخدم المصافي النفطية مادة مانع التأكل الغشائي والصودا الكاوية كذلك مادة الامين المحايد للسيطرة والحد من تأثير ايون الكلورايد ومعدلات الحديد والاملاح والسيطرة على قيم (PH).

نتيجة لذلك تهتم هذه الورقة البحثية في وضع دراسة أضافة وتغيير مناطق (نقاط) حقن المواد الكيمياوية خاصة (الصودا الكاوية والأمين المحايد) في نقاط محددة مغايرة، وكما هو معروف جيدًا، يمر النفط الخام عبر عدد من المبادلات الحرارية المختلفة لرفع درجة حرارته استعدادًا لعمليات التصفية. وجد أن تغيير إضافة الأمين المحايد في منطقة الراجع من برج التثبيت مقطع الكيروسين (القطفات التي يتم إرجاعها إلى برج المصفاة الرئيسي) له تأثير كبير في السيطرة على تثبيت قيم الاس الهيدروجيني بين (6.5-5.5) وتقليل تركيز أيون الحديد بمعدل (ppm %1). بينما يعتمد حقن الصودا الكاوية على درجات حرارة النفط الخام لذا يتم تغييرة الى نظري المبادلات الحرارية أي عندما تكون درجة حرارة النفط الخام - 35) درجة مئوية، الثانية بعد أن يصل النفط الخام إلى درجة الحرارة (65 - 90) درجة مئوية، له تأثير كبير في تقليل تركيز ايون الكورايد بمعدل (1-5 ppm) لموجود على شكل املاح الكلورايد الذائبة في النفط الخام.

## 1. Introduction:

Despite the scientific and technological development and modern control mechanisms to control the rates of corrosion occurring in oil and industrial equipment. Oil refineries in particular are still suffering from huge practical and financial losses. As a result, it has become necessary to carry out periodic maintenance of refining equipment in crude oil distillation units (CDUs) due to obstacles and problems caused by corrosion. Therefore, scientists and researchers specialized in this regard have come up with specific solutions and special deals to neutralize corrosion problems. [1].

The first stage is dealing with corrosion issues in the area where crude oil enters the refinery, i.e. when removing crude oil salts and reducing them, in addition to injecting caustic substances to convert unstable salts into relatively stable ones, while the second stage is represented in the area over head distillation tower and is represented by the injection of neutralizing amines and corrosion inhibitors to reduce corrosion rates [2].

These chemical additives are very effective when it comes to corrosion control. Additives are used by taking periodic samples of acidic condensed water from the system at the top of the distillation tower as well as desalination equipment to determine the levels of pH and chloride ions, and to indicate the extent of corrosion activity by measuring iron ions. However, due to the

high variability of acidity in the upper system due to the effect of local level difference, it can be difficult to determine the most appropriate use of chemical additives and injection amounts, [3]. This is due to the fact that crude oil contains a group of chloride salts with opposite solubility, and these salts are (NaCl, MgCl<sub>2</sub>, KCl, and CaCl<sub>2</sub>). As it is known, the amount of each salt in the crude varies greatly depending on the reservoir or source of the crude oil. For example, there are chloride salts in varying proportions: MgCl<sub>2</sub> 80-95% and 10-15% CaCl<sub>2</sub>, while calcium chloride and CaCl<sub>2</sub> decompose during the heating of crude oil in heat exchangers. The following equations show the decomposition of salts in water at extreme temperatures for each salt. (noting that the study of this research paper was approved at the Najaf refinery site).

$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCL$	at 120	
$CaCl_2 + H_2O \rightarrow Ca (OH)_2 + 2HCl$	at 205	
$NaCl + H_2O \rightarrow NaOH + HCl$	at 480	[8].
$Fe+2HCl \rightarrow FeCl2 \text{ (soluble)} + H_2$	at >Dew point	
$Fe(Cl)_2 + H_2S \rightarrow FeS + 2HCl$	at >Dew point	

In addition, the area of OVHD is affected by a number of factors, including temperature and the amount of unsolved salt ions. Figure (1) shows the effect of temperature on erosion rates, as the higher the temperature, the higher the erosion rate [16].

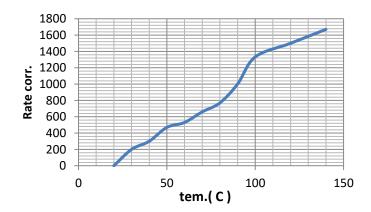


Fig. (1): The effect of temperature on corrosion rates [5].

The crude oil distillation unit is distinguished by its containing salts deposited in the pipes or heat exchangers, so when desalinating and washing the crude with a desalination device, if the



use of magnetized water is adopted as a substitute for normal fresh water, the best performance will be obtained for treating inorganic chloride salts and increasing their removal ability, thus reducing the ion values chloride [8]. Studies show that dissolved salts and hydrochloric acid form different forms of corrosion in distillation tower metal, depending on the temperature gradient (boiling point values) and concentration. The wear of the oil and gas production tray area differs from that of Tray 24 and tray 28 as shown in Figure (2). Table (1) Also shows the areas and the cause of corrosion for each area.

Picture









## Tray 28- Monel (APS)

The stairs are in an advanced state of wear.

It can be seen as a full hole of the tray. The size of the valve openings became worn out, causing the valves to malfunction and the tray to work fully. Salts can be seen stuck to the walls of the tower and the tray. The precipitation of sulfur produces yellow products, while the precipitation of ammonia salt produces white calcifications.

Comments

#### S.S- 410 tray 24

The corrosion process left large holes in the tray. The dimensions of the valve ports are completely gone. The function of the valves in the first tray was lost during the production of light naphtha fuel. The valves in the drawer lost their efficiency and effect, which led to a decrease in the production of light naphtha, and thus weak condensation and the appearance of vapors and gases.

#### kerosene tray 15

The effect of corrosion is visible, and this area is partially clogged. This crack occurs due to the presence of a large number of salt products in the intake canister. The red circle depicts the shape of the crater. Therefore, it is preferable to put a treatment at this point, as it is the first point at which the phases change significantly Between gas oil and kerosene.

#### Exchanges [211, 217]

Corrosion appears clearly in these areas, as hydrochloric acid increases the activity in these exchanges, (211) the temperature of the crude oil rises before entering the de-salter, while the exchange (217) reduces the heat of the light naphtha product through the exchange with water.

Fig. (2): Some forms of corrosion inside the crude oil distillation tower [9]



P- ISSN: 2220-5381 E- ISSN: 2710-1096

Location	Corrosion compounts
Tank	HCl, H <sub>2</sub> S, dissolve
Preheat exchange	HCl, H <sub>2</sub> S
Furnace	H <sub>2</sub> S, S-compount
Flash zone	H <sub>2</sub> S, S-compount and organic
Middle zone	H <sub>2</sub> S
Top zone	HCl and H <sub>2</sub> O
Tower overhead system	HCl, H <sub>2</sub> S and H <sub>2</sub> O
Bottom exchange	H <sub>2</sub> S, S-compount

Table (1) Location of corrosion and types at the refining unit [17]

The paper shows that the chloride content, if its value exceeds 20 ppm, has the ability to precipitate NH<sub>4</sub>Cl chloride salts, in addition to increasing the iron ion values to less than 30 ppm [9]. As a result, corrosion scientists have devised several strategies to mitigate the effects of the corrosion problem, including corrosion inhibitors, cathodic protection, and coating-based corrosion inhibitors. The majority of corrosion inhibitors used are organic compounds. These inhibitors acquire the ability to form a protective barrier between the metal surface and the corrosive environment through an adsorption process, thus delaying metal corrosion, [12]. Organic inhibitors are effective at all acid concentrations and do not affect refining catalysts [10]. In the petroleum industry, the inhibitory action is not sufficient to reduce corrosion without the addition of neutral amine and caustic soda, therefore according [17] of placing injections of amines and inhibitors above distillation towers, and soda injection in preheating oven stages. Weakly neutral amines neutralize existing acidic species such as hydrochloric acid. As a result, the PH value rises, and the activity at the top of the tower becomes less acidic. Note that the pH value must be between (5.5 - 6.5) in oil refineries, locally and globally.

While the corrosion inhibitor acts as a protective barrier as previously mentioned, the caustic soda partially adsorbs the acid hydrochloride ion formed from the decomposition of the salts (NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub> and KCl) to reach the latter along with the NaCl product, which will be expelled to the outside of the distillation unit. [11, 12].

The aim of the research paper is to find a study of changing areas of adding chemicals to reduce the effect of corrosion in distillation towers, furnaces, heat exchangers and condensers in atmospheric distillation units by effectively controlling the pH values.



## 1.1 Relationship of (H<sub>2</sub>S, HCl) With (pH)

The pH value is the best way to find out the cause of the corrosion (H<sub>2</sub>S, HCl). Hydrochloric acid is formed when water vapor condenses in the upper system of the distillation tower due to the presence of some decomposing organic salts, resulting in pH between (1-3.5). With increasing temperature, the pH value decreases in the direction of extreme acidity, which causes the water at the top of the distillation tower to evaporate, which leads to higher unit pressure, and the corrosion of hydrochloric acid increases. As a result of increased amounts of acid vapor. Figure (3) shows the effect of hydrochloric acid on the corrosion rate. (The higher the concentration of hydrochloric acid, the higher the corrosion rate value).

While sulfuric acid is the most prevalent cause of corrosion, the lower the temperature, the higher the PH value between (7.5 -12), the higher the corrosion rate. Figure (4) shows the effect of sulfuric acid on the corrosion rate (the higher the concentration of sulfuric acid, the higher the rate of corrosion). Figure (5) illustrates the relationship between both acids and shows that as the pH values increase in the direction of acidity, the cause is acid (HCl), while if the pH values are in the direction of basal, the cause of the apparent corrosion by the ionic value (Fe<sup>-2+3</sup>) is sulfuric acid (H<sub>2</sub>S) [15].

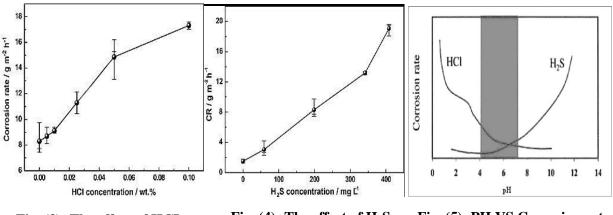


Fig. (3): The effect of HCL on the corrosion rate.

Fig. (4): The effect of H<sub>2</sub>S on the Corrosion rate.

Fig. (5): PH VS Corrosion rate

#### 1.2 Chemical additives caustic soda and neutral amine (Neutralizer Corrosion Inhibitor)

Sodium hydroxide solution, which is prepared in different concentrations as needed by dissolving sodium hydroxide crystals in water, comes to the water refining units before injecting it into the crude oil pipeline, where it dissociates the dangerous salts MgCl<sub>2</sub> and CaCl<sub>2</sub> and turns them into the most stable sodium chloride. It should be noted that when the salt content in the



crude oil rises more than 30 parts per million by weight or (10 pounds per 1000 barrels), the effect of the sodium hydroxide solution is weak in reducing the effect of these salts, so the increase in injection leads to damage to the equipment.

Treating the effect of salts by adding a caustic soda solution has many risks, especially in the case of an increase in injection beyond the required limit, which requires continuous monitoring in terms of the concentration at which the solution is prohibited in the unit and the real injection rate, confirming this rate and comparing it with the content of salts in crude oil, and the indicator The important influence on the injection rate is the percentage of chloride ions that appear when analyzing the water of the system above the distillation tower, which should not be less than 1 ppm and not more than 10 ppm.

While The acid equivalent anti-corrosive consists of more basic polyamine-type amino compounds, which are mixed in varying proportions. Water forms a solution that smells like ammonia, the boiling point of primary amines is higher than that of secondary amines, and so on. As for its chemical properties, it is considered one of the weak bases for the presence of a free pair of electrons in the molecule, because of which amines can interact with organic and inorganic acids, neutralizing them, and forming substituted amine salts, which are characterized by their solubility in water and do not precipitate with water.

This substance is used in refining units, and the addition of this substance comes as a complementary step to adding caustic soda, which could not dissolve all harmful salts. Therefore, an acidic medium is created in the upper system as a result of the formation of HCL acid in addition to the naphthenic acids originally present in crude oil, in addition to sulfuric acid, which is formed from the decomposition of sulfur compounds such as  $H_2S$ , mercaptans, thiophenes, and others. The material is diluted with water and injected into the steam pipe coming out of the top of the distillation tower in order to desalinate the tower top system.

The injection rate is in such a way as to keep the pH of the sample taken from the distillation tower system water in the range between 5.5 and 6.5, where the lowest rate of corrosion occurs in the minerals.

One of the most important characteristics of the pH neutralizer is that it does not contain an ammonia compound because it leads to the formation of ammonium chloride salts that do not dissolve in water and settle in the tubes, and that the effect on the pH is calm and not severe, and that it gives the best results at the lowest injection rate, and that it begins to condense before Evaporation of water to provide an alkaline medium ready for acid neutralization.



# 2. Method and Materials

Preparation of chemicals begins in the petroleum refinery and preparation for injection, each according to its type, into the refinery units. Where these chemical preparations depend on the following requirements:

- Concentration required.
- Determine the amount of injection by means of a special pump for the substance.
- The effectiveness of the substance to be used and its expiry date.

## 2.1 Preparation the neutral amine

It is known that the amine is highly soluble in water because it contains polybasic amino compounds that like to bind with water in short chains, so the preparation of the neutral amine begins by adding (10 liters) of crude amine to (57.5 cm) pure water. To produce a solution with a smell similar to ammonia, this amine containing a pair of free-moving electrons reacts with organic or inorganic acids to form the substituted amino salts, which is characterized by being soluble in water and not precipitating.

#### 2.2 Study of changing the injection point of the neutralizer amine.

The research paper presents the investigation of the injection of a neutralizer amine as shown in Figure (6).

As it is known that the distillation tower consists of a number of separation trays, and that the crude oil is separated depending on the boiling point, so the separation of kerosene begins in tray No. 15, where the separation of kerosene begins and its conversion by gravity to the stripper tower (stabilization tower) for the purpose of stabilizing kerosene and removing the pickings then the kerosene is withdrawn by the suction pump to production.

At tray No. 15, the chloride ion separation activity begins, and thus hydrochloric acid is one of the main causes of corrosion. Therefore, the research paper suggested that the injection point of the neutralizing amine be changed in the return area of the stripper tower to the main tower to ensure the effectiveness of the amine away from potential condensation sites at the top of the tower, which allows the longest life of the work of the amine equivalent and more effective and with the lowest quantity, since this injection point will treat the chloride ion from its first liberation site at a temperature between (190 - 210) °C down to the formation of hydrochloric acid at the top of the distillation tower at a temperature ranging between (110 - 120) °C.

Open Access No. 40, September 2023, pp. 143-161



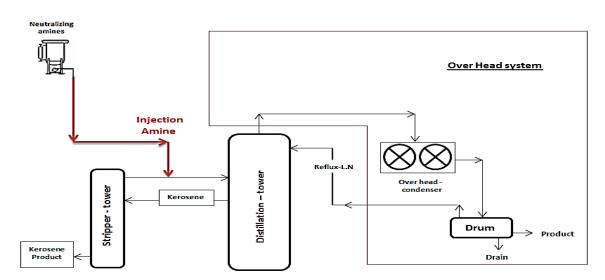


Fig. (6): Schematic representation of the neutralizing amine injection area [by researcher]

#### 2.3 Preparation Caustic Soda

Crude oil refineries use caustic soda of the dry type, which is in the form of oval-shaped granules packed in special preservative bags of a specific weight. Preparation begins with adding 25 kg of caustic soda to 1000 liters of pure water with continuous stirring, in addition to operating the evaporator for the purpose of good mixing as well as for the purpose of creating a warm space for preparation. The following equation explains the nature of the preparation.

 $NaOH + nH_2O \rightarrow (NaOH) nH_2O.$ 

#### 2.4 Cases study injection points for caustic soda.

Before proceeding with the study of the approved injection cases in the research, it is necessary to clarify the place and location of the study of these cases, as the oil refinery under study and research uses the design of a group of heat exchangers, which are called exchangers No. {(211 a, b, c), (216), (215)} Each exchanger has a special location and role, as these exchanges are concerned with raising the temperatures of the crude oil entering the refining unit, which is the initial stage in heating the crude oil before starting the refining process And entering the main distillation tower. The location of these heat exchangers and injection points will be shown in Figure (7). The paper suggests studying two cases of injecting caustic soda to reduce the role of corrosion in distillation units by increasing the effectiveness of using caustic soda to reduce the effectiveness and activity of chloride ion in salts and converting salts into more stable salts and facilitates Separate it later.

## 2.5 First injection case at crude oil temperature (20-35) °C

In the area before the heat exchangers {(216, (211a, b, c)} (first preheating) in the crude oil input line, this injection point is used for purposes next.

• Increasing the surface area of dissolving chloride salts and their interaction with caustic soda to form a somewhat stable salt by injecting caustic soda and increasing its solubility along the ore line to the desalting stomach.

• Ensure better activity and keep the pH between (7-9) in de-salter.

#### 2.6 Second injection case at the temperature (65-90) °C

In the area after the exchangers [(216, (211a, b)] before the crude oil enters the de-salter equipment for the following purposes:

• It is considered close to the stomach vessel, so the effect of the injection is clear.

• Ensure that there is no contamination or accumulation of salt in the exchangers [(216, (211a, b)].

• Reducing and controlling the amount of injections.

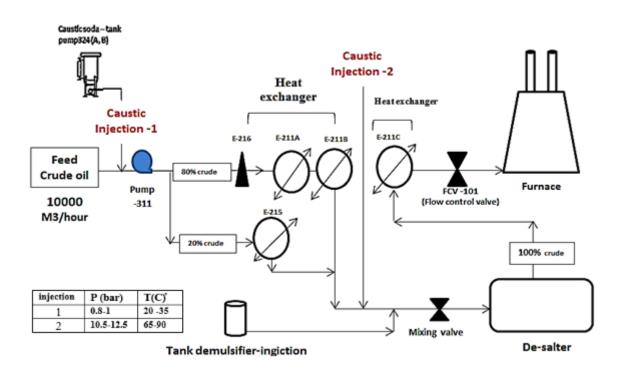


Fig. (7): A complete schematic representation of the entry of crude oil through the heat exchangers to the de-salter The drawing shows the areas of injection of caustic soda (1, 2) [By researcher].



# 3. Results and Discussions

Oil refineries generally rely on some important chemical laboratory readings for crude oil and products after distillation, and through these, we determine the injection quantities of chemical injection treatment materials for the purpose of the required specifications and PH values as well to preserve the industrial oil unit from corrosion.

Therefore, in our time, we will rely on these mentioned readings, taking into account the rates of salts accompanying crude oil. The research paper will discuss the quantities of chemical injections of the equivalent amine before and after in terms of dependence on

- Injection quantities neutralizer amine.
- Effect of injection rates on **pH** values.
- The effect of injection rates on the of chloride ion  $CL^{-1}$  values.
- Effect of injection rates on  $Fe^{+2+3}$  values.

The approved results will be studied before and after changing the injection points for the chemicals proposed in the research paper, as our study will depend on two sites, the first in Al-Najaf Al-Ashraf refinery and the second an oil refinery with a volume feed 10,000 m3 / hr. for one unit, which was reached in particular by the Saudi Arabian Oil Company - Aramco, and we will compare the results On the same conditions with some research modifications. The results of monitoring the injection of the neutralizing amine were taken for different periods ranging from **10/16/2021 to 11/25/2021** (in (location-1), which depends on the injection of the neutralizing amine at a common point between it and the anticorrosive film at the top of the tower Distillation is an approved point and designed by design.

The results were reached in (site -2) within close limits to the previous time period after making a change in the injection site of the neutralizing amine, which is suggested by the research, as it will be, as we mentioned in the body of the research, in the return site from the stripper tower towards the main tower and as shown in the Figure (6) We will study the results and the differences through the results of Table (2).



## P- ISSN: 2220-5381 E- ISSN: 2710-1096

Date	Average injection site amine-1 <u>(before change)</u>	Average Salt contents	Fe <sup>+2+3</sup>	CL-	рН	Average injection site amine-2 (after change)	Fe <sup>+2+3</sup>	CL-	рН
16/10/2021	1.1	92.2	10.8	7.0	7.0	1.0	10.0	11.5	5.2
20/10/2021	0.8	79.7	7.0	56.8	6.7	0.6	3.0	9.2	5.5
24/10/2021	0.9	48.9	9.6	10.6	4.6	0.7	7.6	7.7	5.6
28/10/2021	0.3	94.6	17.2	57.9	3.4	0.4	7.2	9.8	4.4
1/11/2021	1.2	50.6	13.8	18.7	8.3	0.9	11.8	13.4	6.3
5/ 11/2021	0.5	61.7	16.2	10.6	6.0	0.4	10.4	10	5.2
9/11/2021	0.6	20.4	5.0	35.5	7.3	0.5	3.5	8.8	6.3
13/11/2021	0.7	20.0	6.2	77.2	6.5	0.6	4.4	11.3	6.5
21/11/2021	1	24	1.2	20.1	5.5	0.9	9.18	Nile	5.8
25/11/2021	0.8	34.2	0.4	Nile	7.6	0.6	0.3	Nile	6.7

# Table (2) The results of the neutralizing amine injection points

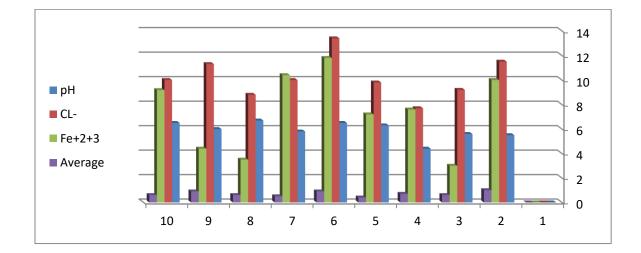
It is noted through the values of the table above that the effect of changing the injection of the neutral amine appeared clearly and distinctly in the second site. The reason is due to the fact that this point at the conditions and temperature of the air distillation tower contributed to showing the full effectiveness of the neutral amine the results are explained in the following points.

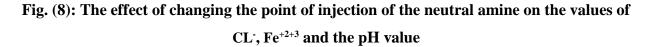
- ✤ Obtaining relative stability in PH values.
- ♦ Obtaining more acceptable values for the chloride ion CL<sup>-</sup>.
- Obtaining more acceptable values for the iron ion  $Fe^{+2+3}$ , thus reducing corrosion rate.
- Reducing the volume of injection of the neutral amine.
- Reducing the financial losses resulting from the large number of amine injections compared to the first site.
- Activate the work and complete the task of injecting anticorrosion agent into the distillation tower.
- ✤ Reducing corrosion rates in general.
- Reducing the activity and reducing the effectiveness of the sulfur ion.

The case of injection of the proposed equivalent amine in the research into the reflux area of the scrubber tower as shown in Figure (6), the injection point is close to the kerosene separation area in the direction of heavy naphtha separation in the fractional distillation tower and according to



the site conditions, the direct effect and the remarkable role make a difference Large, as this point is practically suitable for the emergence of the effectiveness of the equivalent amine injection in moderate quantities, so that the effect is directly evident in reducing corrosion rates as shown in Figure (8), which shows a significant change in the values of the ionic readings and the convergence of the ratios, which indicates obtaining a better treatment. This point is practically applied and studied in a Saudi Aramco refinery and has proven to be effective. And through scientific research and objective study, we found that its use under the practical conditions of the Najaf refinery can make a quantum leap in the field of chemical treatment injections, especially the neutralizing amine, and thus control corrosion rates. Until now, the research paper is still being studied and researched, as the nature of this research is theoretical with the main study due to the difficulty of application.





It is clear from the above figure to obtain the most stable iron and chloride ion values, thus controlling the PH values. This effect resulted from an increase in the efficiency of the injection of the neutral amine, whose effectiveness was evident due to the activity of the injection area, since this area is suitable through its temperatures and the formation of corrosive ions in it. It should be noted that this proposed area is under research and study, but it has been proven in practice in the applications of other refineries outside Iraq, and through our research we found that this could be applied practically in the future of the oil industry.

It should also be noted that increasing the effectiveness of the neutral amine depends on several



basic factors, including:

- ✤ Quality of preparation
- ✤ Type of neutral amine and date of manufacture
- ✤ The amount of injection
- ✤ Salts associated with crude oil
- Unit life and effectiveness
- Good distillation process in the main air distillation tower.

As for the change that occurred after adding the caustic soda injection point, as shown in Figure (7), the research paper studied the effect of the change and compared between relying on the first point only and adding the second point, it showed salt rates from 16/10/2021 to 01/11 /2021 The effectiveness of caustic soda in reducing the values of chloride ion and adjusting the values of PH and iron ion after adding the injection point suggested by the research and through the results of the values from Table (3).

We are not here to determine fixed values with great accuracy, but we are aiming to establish approximate theoretical practical results, since the nature of crude oil is variable and depends on the nature of the oil reservoir and the quantities of salts and accompanying water (dissolved or free) and that the laboratory examination lacks development and some practical obstacles and the difficulty of obtaining some Examination devices and boilers of the examining materials, so it was necessary to note.

Date	Salt contents (In – out )	Average Caustic soda injection (1) <u>before</u> <u>adding</u>	рН	CL-	Fe <sup>+2+3</sup> PPM	Average Caustic soda injection (2) <u>after</u> <u>addition</u>	рН	CL-	Fe <sup>+2+3</sup> PPM
16/10/2021	124 - 80	10	3.8	100	>30 over range	8	5.8	20	2.2
20/10/2021	245 - 150	10.5	4.3	170.4	>30 over range	9.5	5.3	30.3	3.2
24/10/2021	230 - 56	9.3	4.5	46.2	16.8	9.0	5.5	33.2	6.8
28/10/2021	245 - 48.6	12.5	4.9	156.2	19.0	2.5	5.9	10.12	9.0

Table (3) Results of the effect of adding caustic soda on the values of CL<sup>-</sup>, Fe<sup>+2+3</sup> and the PH.

#### Journal of Petroleum Research and Studies

Open Access No. 40, September 2023, pp. 143-161



### P- ISSN: 2220-5381 E- ISSN: 2710-1096

1/11/2021	226.8 - 53	11	5.3	106.5	>30 over range	5.0	6.3	16.9	1.1
5/ 11/2021	165 - 39.6	8.5	6.4	20	>30 over range	6.5	6.4	20	1.2
9/11/2021	191.2 – 113	8.0	8.0	24.8	4.8	7.0	6.0	13.0	3.8
13/11/2021	232 - 99	7.0	6.9	17.7	11.3	6.0	6.4	22.0	1.4
21/11/2021	281 - 140	9.0	7.1	78.1	18.0	5.0	5.1	25.0	1.0
25/11/2021	103 - 86.7	7.5	6.2	21.3	2.6	6.5	5.2	20	6.6
16/10/2021	330 - 157	9.6	8.3	35.5	25.4	4.5	6.3	30.0	5.3
20/10/2021	107 - 80	11	5.5	35.5	2.5	8.0	5.5	22.6	3.5
24/10/2021	115.5 – 37.0	10.6	6.5	17.5	3.8	6.5	5.5	10.4	2.8
28/10/2021	257 - 36	11.0	7.9	17.7	10.4	9.0	5.9	11.8	1.4
1/11/2021	165 – 37	12.5	7.1	42.6	1.4	10.5	6.1	30.9	1.2

It appears from the table above that caustic soda, when injected directly into crude oil before the crude enters the first heating stage, achieves a work quality of less than 50%, because soda likes to work in a warm environment more than the usual environment in which crude oil enters, which has a temperature of 20 - 35 °C. Caustic soda absorbs moisture containing salt ions at temperatures below the dew point temperatures, bearing in mind that one particular point cannot be certain because the dissolution rates of salt in the ore are fundamentally unstable. The case can be diagnosed and approved by studying the dissolved salinity rates, the stability of their values, the age of the petroleum units and the quality of their work. As it is known to us, that caustic soda, if used in other than its normal quantities, and in the case of improper injection or a disturbance in concentration, will cause additional erosion, so injection at one point does not give relatively stable results, as shown in Figure (9), which shows the relationship between the injection of caustic soda .The injection rates are based on the above table and the corrosion rates, as it is clear that the corrosion rates increased as a result of the instability of the injection of caustic soda and the formation of the chloride ion.

#### Journal of Petroleum Research and Studies

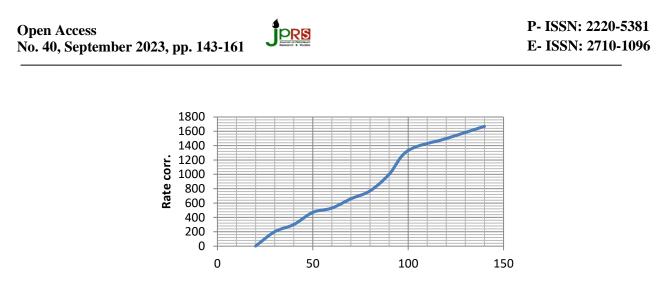


Fig. (9): (Rate corr.) VS. (time) before adding

While the case after adding the proposed point in the research shows a direct effect with a fixed value.

The injection rate is demonstrated to be stable and consistent over time with corrosion rates. This is because the injection point is after the heat exchangers, i.e. after the crude oil reaches a temperature of (65-90) c. The injection of caustic soda at this stage shows a significant improvement in controlling the liberated chloride ion, as well as a decrease in the concentration of hydrochloric acid formed as a result of the decomposition of salts. Also, caustic soda absorbs moisture and emits heat without affecting the work of the emulsifier, so the research suggests adding this point due to the necessity of its expected practical effectiveness. The following Figure (10) shows the rate of corrosion rates gradually decreasing over time.

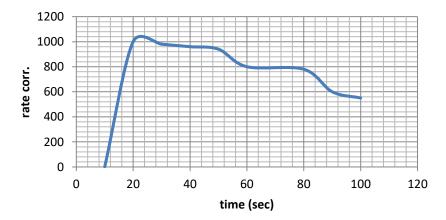


Fig. (10): (Rate corr.) VS (time) After adding



# 4. Conclusions

After evaluating the results of the operational context and scientific evidence to reduce corrosion in the refining units and the air distillation tower, it was found that changing the chemical injection sites has a significant effect in controlling corrosion rates by controlling the pH values and the values of chlorine and iron ions. As it is known that this study is a study of the analysis of the purpose and the main objective of which is to find the appropriate idea and scientific logic that would develop the work of chemical treatments used in crude oil refineries, and through the research paper it was found that the use of an additional injection point to inject caustic soda after the arrival of crude oil The temperature (65-90) c and the pressure (10.5-12.5) bar has a great effect in reducing the activity of the chloride ion, one of the main elements that cause corrosion, and converting it, by interaction with caustic soda, into a fixed and stable salt (NaCl) that can be controlled and expelled later outside the salt remover stomach. In oil refineries, also placing a different injection point for the neutralizing amine in the reflux kerosene area of the stripper tower has a great effect in controlling the pH values, and thus controlling in both cases the corrosion in general.

In response to the study requests and controls, we would like to state the following through our study:

- ◆ There are no practical problems in the case of applying this study in practice
- There is no industrial pollution in case of changing chemical injection sites.
- By preparing this study and controlling the variables, it is possible to reduce the quantities of chemical injections, and thus reduce the money spent to purchase expensive chemicals.
- The study did not focus on acknowledging the accuracy of the practical results, since this study is in the process of research and development and needs experimental laboratories and large laboratories that are not easy to provide.



# **References**

- Petroleum Refining Industry, Application Data Sheet ADS 2900-01/rev, pH Control Reduces Corrosion in Crude Unit Overhead, August 2008.
- [2] S. R. Kunst, G. A. Ludwig, M. R. Ortega-Vega, and C. F. Malfatti, "The influence of adding corrosion inhibitor and pH on the electrochemical properties of hybrid films applied to galvanised steel", Ingeniería e Investigación, Vol. 33, No. 3, pp. 17-21, 2013.
- [3] A. Voice, F. Closmann, G. Rochelle, "Oxidative degradation of amines with high-temperature cycling", Energy Procedia 37, pp. 2118-2132, 2013. <u>https://doi.org/10.1016/j.egypro.2013.06.091</u>
- [4] Ari A. Ahmed, "Corrosion in Crude Oil Distillation Unit Overhead: A recent Case Study", The Scientific Journal of Koya University, vol. 9, no. 1, 2021. <u>http://dx.doi.org/10.14500/aro.10711</u>
- [5] Braden, Veronica K., Sugar Land, Texas(US), European Patent Office, EUROPEAN SEARCH REPORT Application Number EP 96 30 5555 Bulletin 1997.
- [6] Ali Fadel Mandeel, Auras Adnan Hatem, Ministry of Higher Education and Scientific Research, University of Al-Qadisiyah, Department of Chemistry, Corrosion Chemistry, 2018.
- [7] Bandar Seri Iskandar, Perak, Applied sciences, "Review on Corrosion Inhibitors for Oil and Gas Corrosion Issues", Appl. Sci.10(10), 3389, 2020. <u>https://doi.org/10.3390/app10103389</u>
- [8] S. N. Shatub, "The Utilization of Magnetized Water for the Improvement of Crude Oil Quality", Journal of Petroleum Research and Studies, vol. 12, no. 3, pp. 104-120, Sep. 2022. <u>https://doi.org/10.52716/jprs.v12i3.545</u>
- [9] A. J. Szyprowski, "Methods of Investigation on Hydrogen Sulfide Corrosion of Steel and Its Inhibitors", Corrosion, vol. 39, no. 1, pp. 68-81, 2003. <u>https://doi.org/10.5006/1.3277538</u>
- [10] S.A. Umoren, M.M. Solomon, "Recent developments on the use of polymers as corrosion Inhibitors-A review", Open Mater. Sci. J, 8, pp. 39–54, 2014. <u>https://doi.org/10.2174/1874088X01408010039</u>
- [11] S. A. Umoren, I. B. Obot, A. Madhankumar, and Z. M. Gasem, "Performance evaluation of pectin as ecofriendly corrosion inhibitor for X60 pipeline steel in acid medium: Experimental and theoretical approaches", Carbohydrate Polymers, vol. 124, pp. 280–291, 2015. <u>https://doi.org/10.1016/j.carbpol.2015.02.036</u>

- [12] Brylee David B. Tiu, Rigoberto C. Advincula, "Polymeric corrosion inhibitors for the oil and gas industry: Design graphic and mechanism", React. Funct. Polymer, vol. 95, pp. 25– 45, 2015. <u>https://doi.org/10.1016/j.reactfunctpolym.2015.08.006</u>
- [13] M. Goyal, S. Kumar, I. Bahadur, C. Verma, E. Ebenso, "Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review", Journal of Molecular Liquids, vol. 256, pp. 565–573, 2018. https://doi.org/10.1016/j.molliq.2018.02.045
- [14] M. Mobin, S. Zehra, M. Parveen, "L-Cysteine as corrosion inhibitor for mild steel in 1M HCl and synergistic effect of anionic, cationic and non-ionic surfactants", Journal of Molecular Liquids, vol. 216, pp. 598–607, 2016. https://doi.org/10.1016/j.molliq.2016.01.087
- [15] S. Lordo, A. Eisenhawer "Sensitivity analysis for modeling overhead chloride salt deposition and corrosion issues", Journal of Physics: Conference Series, vol. 1378, p.022089, 2006.
- [16] T. H. Abood, "The influence of various parameters on pitting corrosion of 316L and 202 stainless steel", A Thesis of Department of Chemical Engineering of the University of Technology. University of Technology, 2008.
- [17] D. F. Ahmad and M. H. Khalaf, "Studying of The Dynamic Behaviour and Control of Continuous Distillation Column", Tikrit j. eng. sci., vol. 21, no. 1, pp. 1–20, Jul. 2013. <u>https://doi.org/10.25130/tjes.21.1.07</u>