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Formation of Gas Hydrates in the Field of Crude Oil Refining: Najaf Refinery (Unit 2)/ Case Study

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Abstract

Gaseous hydrates are defined as (clathrates) consisting of three basic components (crude liquid, gas, and water). When the gas (guest) is liberated from the raw liquid by the concepts of dynamic and thermal movement of gas and liquid, the (gas) is confined inside the cage of the evaporating water bubble (the host) to form gaseous hyder due to the conditions of heat and pressure in the form of a spherical crystalline structure linked by hydrogen bonds under the van der Waals force effect. Hydrates, when they occur, cause total or partial blockage and obstruction of the flow of crude oil and loss of operational capacity. It depends on the type of gaseous hydrate formed and the nature of the local conditions. Therefore, gaseous hydrates are considered one of the most important local scientific problems that crude oil refineries suffer from, especially in the two locations, starting from the primary heating area - heat exchangers package (EX-211ABC) all the way to the heating area Secondary - (the unit's furnace). The present study discusses in detail the. most important scientific and practical solutions, and through the results it was found that the technical practical steps adopted by the operators of the refining units cause future damage and reduce the design life of the unit, in contrast to the scientific solutions.
The paper discusses the most important issues and related analyzes that predict the occurrence of hydrates to reduce or limit the impact of the occurrence of gaseous hydrates by relying on the following checks (Rvp, salt content, sediment and water). In short, the aim of this paper is to identify behaviors and discuss problems and solutions gas hydrates in crude oil refineries (Najaf Refinery - unit 2) specifically in the second heating area (Branch-B 105 thermal unit furnace), the paper shows complete information in a concise form for operators and engineers of the crude oil refining sector.

Keywords: Gas hydrates, clathrates, crude oil pipelines, refining sector, applications of gas hydrates.

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تكون هيدرات الغاز في مجال تكرير النفط الخام: مصفى النجف (unit 2)/ دراسة حالة

الخلاصة:

تعرف الهيدرات الغازية بأنها مركبات (clathrate) تتكون من ثلاث مكونات أساسية (سائل خام، غاز، ماء). عندما يتم تحرير الغاز(الضيف) من السائل الخام بفعل مفاهيم الحركة الديناميكية والحرارية للغاز والسائل، يتم حصر(الغاز) داخل قفص فقاعة الماء المتبخرة (المضيف) ليتكون الهيدر الغازي بفعل ضرفي الحرارة والضغط على شكل هيكل بلوري كروي مرتبط بروابط (أواصر) هيدروجينية تحت تأثير قوة فان دير فال تسبب الهيدرات، عند حدوثها، انسدادًا كليًا أو جزئيًا وعرقلة لتدفق النفط الخام وفقدان للطاقة التشغيلية. يعتمد ذلك على نوع الهيدر الغازي المتكون وطبيعة الضروف الموقعية، لذا تعتبر الهيدرات الغازية واحدة من اهم المشاكل العلميه الموقعية التي تعاني منها مصافي تكرير النفط الخام خاصة في الموقعين، أبتداً من منطقة التسخين الأولية - حزمة المبادلات الحرارية (EX – 211ABC) وصولاً الى منطقة التسخين الثانوية– (فرن الوحدة).

وضعت الورقه اهم الحلول العلمية والعملية، ومن خلال النتائج تبين ان الخطوات العمليه الفنية التي يتبناها مشغلي الوحدات التكريرية تسبب اضرار مستقبلية وتقلل من العمرالتصميمي للوحدة، على العكس من الحلول العلمية بأستخدام مثبطات الهيدرات.

تناقش الورقة أهم القضايا والتحليلات ذات الصلة التي تتنبأ بحدوث الهيدرات لتقليل أو الحد من تأثير حدوث الهيدرات الغازية من خلال الاعتماد على الفحوصات التالية (Rvp، content salt، sediment and water)، باختصار، ان هدف الورقة الوقوف على سلوكيات ومناقشة مشاكل وحلول حدوث الهيدرات الغازية في مصافي تكرير النفط الخام (مصفى النجف - unit 2) تحديداً في منطقة التسخين الثانية (فرن الوحدة الحراري Branch-B 105)، تظهر الورقة معلومات كاملة في شكل موجز لمشغلي ومهندسي قطاع تكرير النفط الخام.

1. Introduction:

Gas hydrates are defined as solid clathrates consisting of three primary compounds (crude liquid, gas and water) upon liberation of gas molecules (guests) such as carbon dioxide, nitrogen (N_2), hydrogen (H_2), methane (CH_4) and other gases or hydrocarbons imprisoned in a cage of (host) water molecules (H_2O) bound together by hydrogen bonds [1], [2]. Hydrates are formed under specific thermodynamic and kinetic conditions, including temperature and pressure, whereby these gases are trapped in a cage composed of water bonds, and form a solid crystal agglomerate that grows into polygonal shapes of various types, with great surface tensile strength, which precipitate on the walls of pipelines carrying crude oil in the most common locations (primary heating stage - heat exchangers, secondary heating stage - thermal furnace of the refining unit). Before the crude oil enters the refining operations inside the atmospheric distillation tower, and for gas hydrates to occur (liberation and formation), two basic conditions must be met (temperature and pressure), as they are formed at low temperatures under certain conditions and in other cases at high temperatures and pressures High. The optimum temperature for hydrate formation depends on the gas components [4].

There must be 3 basic materials for the formation of hydrates, namely (methane - ethane - carbon dioxide, the availability of a sufficient amount of water), and the temperature at which the

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hydrates are formed is called the temperature of the hydrate [5].

In addition, the presence of some phenomena increases the possibility of its formation, namely:

1. Flow turbulence and high speed, which makes throttle valves the ideal place for hydrate formation due to the temperature difference according to Joule-Thomson law, in addition to the high speed resulting from valve stenosis [6].

2. Mixing or agitation (contamination): Mixing through vessels or heat exchangers promotes hydrate formation. The formation of hydrates is enhanced in places where the formation of the solid phase or the liquid phase occurs, and this occurs in pipes such as welding points or some accessories such as (bends - the letter T in pipes - valves) or the presence of dirt and rust [7].

3. The presence of free water the presence of free water in the crude liquid promotes the formation of hydrates, and the boundary between water and gas associated with crude oil is very helpful in its formation.

Another important issue is the presence of solids, where the hydrates move in the tube with the liquid phase and tend to collect in the same places where the liquid collects, and the problem lies in the places where the hydrates collect, especially in existing tubes in which the multiphase flow occurs, where the accumulation leads to hydrate eads to complete or partial blockage of the pipe, depending on the type of hydrate formed in the area. The presence of gaseous hydrates obstructs the flow of crude oil so much that in extreme cases the oil pipeline becomes 100% blocked. This has significant implications and risks for crude oil atmospheric distillation unit operations [9], [10].

The process of formation of gas hydrates is a phase transformation process of the first order, and the process does not involve the occurrence of any chemical reaction, even the mechanism of formation of these hydrates is still not completely clear,[10] . The first to document the description of gas hydrates in 1810 [11]. When performing annual or emergency maintenance operations, it is best to use skimming of the oil pipes in the direction of the operating unit. Skimming is a suitable method for removing hydrates from pipes. The scraping equipment or brush must be of the same diameter as the pipe and pushed by pressure to remove all solid materials from it (such as hydrates - wax - dirt… etc.) in addition to reducing corrosion. And to provide a smooth flow. Figure (1) shows the gaseous hydrates [12], [13].

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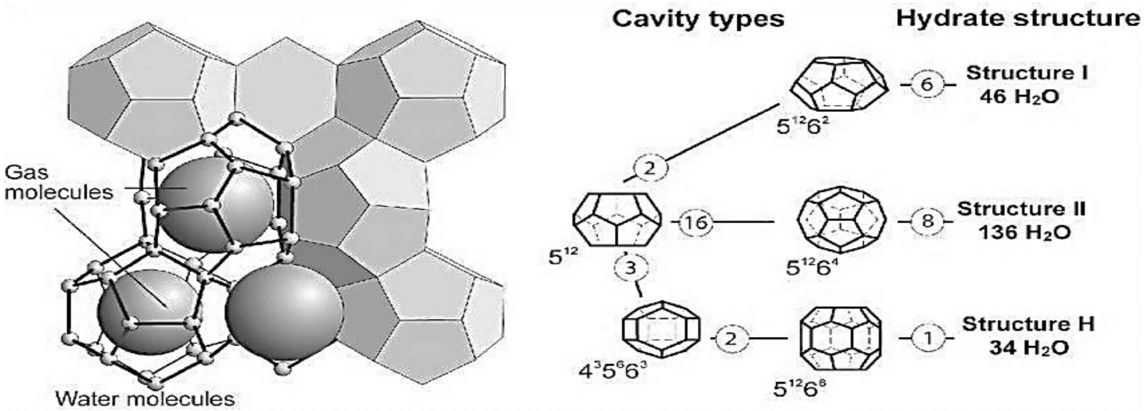

Fig. (1): The structure of gaseous hydrates and the common types of gaseous hydrates [20]

The formation of hydrates depends on the points below:

1- Crude density	7- temperature (T)
2- viscosity	8-Time (t), location (x)
3- Corrosion of the inner lining of the pipes	9- spread (d)
4-Presence of biological bacteria in the lining of the tubes	10- Heat transfer coefficient
5- Presence of mineral deposits in the ore The amount of salts associated with crude oil	11-The presence of gas in different forms (dissolved, conjugated, resulting from the processes of movement and heat)
6- The amount of water in the crude (conjugated, free, dissolved)	12-the high value of the vapor pressure of crude oil.

Gas hydrate lumps usually cause serious problems for oil and gas pipelines and processing facilities. Obstruction of flow threatens the safety of personnel and unit equipment to the point of explosion in oil pipelines [15].

The formation of gas hydrates begins after the release of gas in the form of weak bubbles. These substances accumulate, forming a larger crystalline agglomeration that grows more and more over time with conditions of pressure and temperature. And the high temperature rates, the greater the liberation of gas, as well as the increase in the evaporation of water, so that the whole gathers in the formation of a crystal cage that imprisons the gas molecule inside it [16].

Oil refineries, especially the Al-Najaf refinery, suffer from the formation of gaseous hydrates in two locations, which are the most common [17].

The first location: Heat exchanger area (EX - 211), where the flow type is turbulent, gaseous hydrates occur, but this can soon be seen by sudden rises in exchanger temperatures and

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tightness of the flow. Weak flow can be seen through the valve of the main unit (FCV - 101) in extreme cases, when a complex type of gas hydrate occurs, the gas gap is confined to one of the corners or corners of the heat exchanger (shell) and once it occurs in the (tube) region. Therefore, the operators in this situation are forced to carry out immediate treatment after taking the necessary directions. The technical processors start by closing the unit completely and starting to unload the raw material. This process takes about 12 hours or more, depending on the unit's operating conditions. What should be noted is the great loss of operating energy, refining process, and operators' efforts. In fact, this is a very big problem caused by gaseous hydrates.

The second location: in the unit's furnace area, the flow type is streamline, where gas hydrates form in one or both of the two flow lines exiting the convection furnace. Weak flow and a decrease in the second line as a result of the accumulation of ore. This appears through transmitters (FI-104, FI-105) and the on-site readings of temperature and pressure gauges. In this case, unit operators are forced to follow the applicable technical procedures by keeping temperatures in the furnace lines. This is done by extinguishing the flames of the convection oven (gradual extinguishing), in extreme cases, the operators of the unit Turn off the furnace completely. Figure (2) shows the two sites (first and second location).

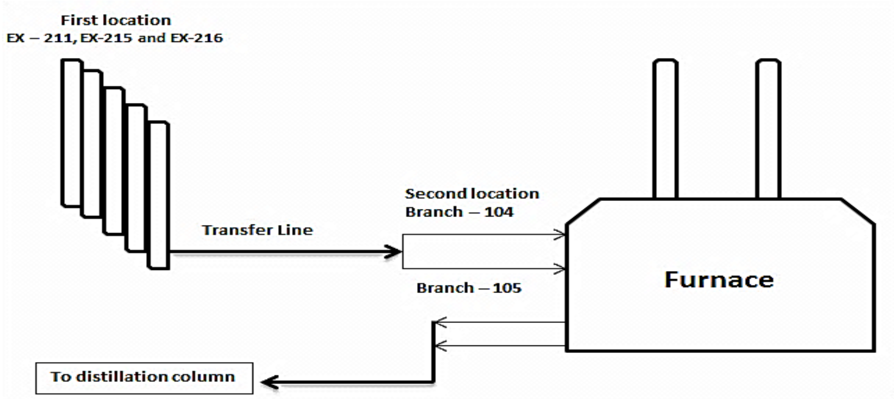

Fig. (2): Shows the first and second locations

Therefore, different research groups worked in a large number of scientific centers in the oil and gas sector to study gaseous hydrates and their formation factors. The results of these studies show that the formation of gaseous hydrates changes significantly due to the formation of hydrates of different shapes and sizes depending on the type of gas released in the oil pipeline. The three crystal structures of gaseous hydrates are structure I (SI), structure II (SII), and structure III (SH). In the first structure there are cages arranged in the mid-body bundle which are large enough to contain methane, ethane, and other gases of similar molecules of large

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diameters such as carbon dioxide and hydrogen sulfide. In the second structure packed like diamond, the cages are large enough to contain not only methane and ethane but also large gas molecules such as propane and isobutene. Whereas the Type III SH hull required both components from the accumulation of both the previous types. The three types at the site - the Najaf Refinery - can be seen in the following description [18].

If a narrowing occurs in one of the crude oil lines exiting the convection oven and lasts for 30-60 minutes, and it disappears. This indicates that the gaseous hydrates are of type I (SI) (weak structure). And that the flow is capable, due to pressure and temperature factors, of destroying the crystal form and dissolving the hydrates inside the flow stream, when there is a narrowing in the flow of one of the furnace lines, and this narrowing will last between 60-120 minutes without changing anything, which forced the refinery operators to take measures A process, for example (narrowing the flow on one of the flow lines to enhance the flow push to the second line that contains gas hydrates while reducing the heat and circulation from some furnace torches after applying these procedures [3],[19]. After more than an hour and a half, the blockage was opened and the pipe returned to its normal position and the amount of flow This description indicates that the type of gas hydrate is the second type (SII), but in the case of applying all procedures without any change, the operators of the units were forced to turn off and reduce the heat completely. This indicates that the type of gas hydrate is of a complex type (SH), as show in Fig. (1) Above.

The physical properties of non-gas hydrates come from the flow of crystalline solids that are denser than typical liquids of hydrocarbons and the gas molecules they contain are effective and mineral plankton - dangerously compact, which leads to the emergence of many applications of hydrates in wide fields and many different effects. Returning to the objective of the paper, which is the analytical review and study in the various important areas related to gaseous hydrates in the oil and gas refining industry [19].

2. Hydrate issues in crude oil refining systems

2.1 Water desalination equipment problems

One of the most important factors for the presence of gaseous hydrates within oil refinery systems is the operation and efficiency of the de-salter equipment. The oil is transported from the oil fields to the main strategic line, preceded by the crude oil stabilization operations and the preliminary treatment of water and salts. By the action of heat, flow and friction of the liquid

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through the pipe, a hydrate is produced, so it must be treated to prevent serious problems.

Crude oil is received at the first refinery with desalination equipment to get rid of salts and suspended matter by the desalting system. After the oil passes through the heat exchangers (EX 216, EX 211 A) to raise the crude at a temperature of 80-90 ° C, the salt remover begins to wash the crude oil with water, the volume of wash water (1-3) m^3 is pumped with a mixing pressure of (0.4 - 0.5) bar. We have shown in previous research that the use of magnetized water in improving the treatment of crude oil salts is the best use and a wonderful alternative to plain water [8], an emulsifying agent is injected to reduce the value of salts associated with crude oil, loosening bonds and breaching complex emulsions (0.1 per hour), the oil is returned to heat exchangers. It was transferred to the secondary heating stage (the convection furnace of the distillation unit) to start the secondary heating processes at a temperature of 295-300°C. Hence, the role of the salt remover appears in the disposal of the hydrates formed by transport. The design capacity of the desalination equipment at the Najaf refinery is 25 cubic m^3. The Najaf refinery follows the working system of the combined remover betweenْ two units (the first refining unit and the second refining unit - in one remover located in the second unit). Therefore, the oil is similar between the two units in terms of the influencing factors. It is preferable to place desalination equipment for each unit to avoid poor work and poor efficiency, and to get rid of salts dissolved in water, the third component of gaseous hydrates.

2.2 Flow assurance issues in refineries

Crude oil enters the refining units by the turbulent flow type. Therefore, one of the most important issues that engineers and operators of crude oil refining units deal with is ensuring process flow, continuity of flow, and changing the type of flow from turbulent to smooth crude oil without any obstacles. This is done through:

1- Monitor the operation of the unit p-311 main feed pump and its driving force. Therefore, operators are concerned about the pump pressure and driving force and its safety from mechanical disease.

2- Ensure the heat exchangers work. This is done by following the preheat and temperature in each exchanger. In the event of a weakness in the heat exchange of the exchangers, maintenance operations must be initiated to ensure that the exchangers are freed from crude oil deposits (mineral or deposited).

3- Ensure that the FCV-101 crude oil main valve is in good working condition and that the flow

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reading between the position and the controller is consistent. After these flow assurance steps, we ensured that the crude oil moved from the primary heating stage to the secondary heating stage, and in case of failure to ensure the flow process, this would completely indicate a disturbance and obstruction in the flow stream [26].

2.3 Crude Oil Specification Issues

1- The deposition of asphaltene: it is one of the matters of concern to the specifications of crude oil, as its high percentage indicates poor quality of the oil and vice versa. Asphalt decomposes in certain conditions that depend on pressure, temperature and viscosity. Asphaltene is usually described as a fraction of crude oil that is insoluble in alkanes (such as n-heptane or n-pentane) but soluble in aromatic solvents (toluene or benzene). Its presence in the ore promotes the formation of gaseous hydrates. For example, depressurization can lead to unwanted asphalt deposits and build-up in pipes and tanks. Asphalt precipitation / accumulation leads to damage to the pipes, stable emulsions that are difficult to separate, as well as partial / complete blockage of the pipe. The deposition of asphaltene depends on several factors, including temperature and pressure. Similarly, the deposition of asphaltene in the tube can depend on the flow rate and the interaction between the particles and the inner tube lining [21].

2- Wax effect: Hydrates can form at certain pressures and temperatures in a liquid system containing water and heavy and light hydrocarbons. The thermodynamic behavior of a solid may be affected by the composition of another solid. On the other hand, the formation of wax can remove heavy hydrocarbons, which leads to an increase in the concentration of light components in the liquid. Temperature and pressure affected the wax, which in turn affected the formation of gaseous hydrates. As wax is a key element in flow issues, wax provides the necessary sites and promotes hydrate formation and emulsification in pipelines from flow processes, and that the presence of wax increases hydrate growth under conditions of high pressure and temperature [22].

3. Hydrate Occurrence Prediction Analyses.

It was found that the most important analyzes that would predict the occurrence of gaseous hydrates or contribute to alerting the staff of the operational unit to the occurrence of gaseous hydrates before they occur. They are arranged as follows.

1- RVP analysis of the vapor pressure value indicates the abundance of light hydrocarbons and

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volatile gases dissolved in crude oil: From this point of view, we can say that the rise of (RVP) is one of the most important issues that would determine the occurrence of gaseous hydrates in the later stages of oil industry operations.

2- Analysis of the percentage of salts entering and leaving the de-salter for crude oil: The presence of dissolved salts is related to the presence of water (solute and solvent). In the event that the value of the salts rises as a result of poor performance or failure of the salt remover, this tells us that the water containing the salts can evaporate to form a lattice and crystal cage (the host). For the gas that can be liberated (guest) to be the two main factors for the formation of gas hydrates in the crude oil pipeline, in the secondary heating stage under the condition of maintaining the flow regime.

3- Water and sediment: The analysis of water and sediment indicates the amount of sediment escaping from the treatment when desalting the salts or the amount of prepared sediment that remained with the crude oil, sometimes due to the high rates of heat in the heat exchangers and depending on the specifications of the crude oil, the sediment rates are more than they were before treatment Because of the increase in sedimentation, because the salts present are insoluble, their sedimentation increased in the crude oil refining systems.

3.1 Mineral Hydrates

Through the on-site phenomena, it was found that there is an important phenomenon in addition to gaseous hydrates, which are mineral hydrates. The formation of this type of hydrate depends on the presence of mineral compounds such as (mineral salts, mineral impurities, sand and clays, iron ratios ... etc.), this type of hydrate is considered dangerous Very, and when it occurs, the operators of the refining units are forced to perform emergency maintenance. Maintenance operations for this type of hydrate are carried out by means of special tools, including the brush for cleaning pipes (Rolling- cleaner) [23]. This type of hydrate is very solid and causes a complete obstruction of the flow stream. The hydrates are in the refineries close to the oil fields, as they are the closest to preserving the mineral residues. Figure (3) shows the form of hydrates in the pipelines carrying crude oil within the refinery systems.

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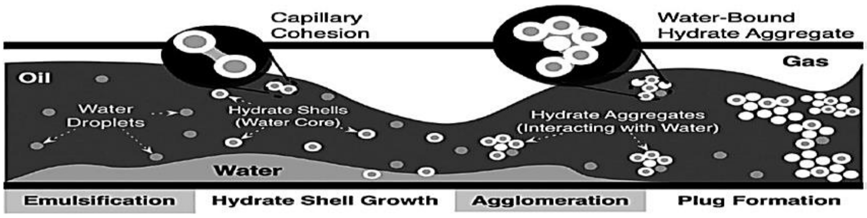

Fig. (3): Right, shows the shape of the mineral hydrates locally [24]
Left, shows the shape of the hydrates inside the pipeline carrying crude oil [25]

4. Hydrate Inhibitors

Thermodynamic inhibitors (THI) are the industry standard for preventing hydrates despite their high cost, environmental and operational concerns. Alternatively, less expensive "low-dose hydrate inhibitors" (LDHI) can prolong the period by preventing agglomeration of the initial hydrate molecules and maintaining regularity of flow [25].

Hydrate inhibitors are used to reduce the formation temperature of gas hydrates, control the Rvp value, and release hydrocarbons and light gases. Another type of industrial hydrocarbon hydrate inhibitors, methanol and ethylene glycol, are the most widely used inhibitors in industry due to their acceptable costs compared to (THI), (LDHI) inhibitors. Figure (4) shows the effect of gaseous hydrates in preventing the formation and dispersal of the mixture of hydrate components.

Methanol and ethylene glycol have a low molecular weight and thus have the ability to handle substances with low molecular weights easily according to their physical nature. Table (1) lists some of the properties and characteristics of methanol and ethylene glycol and the most preferred ones for use in hydrate inhibition.

Gas hydrate inhibitors are usually added together with corrosion inhibitors, in order to prevent equipment corrosion due to the frequent lack of immediate compatibility of the hydrate inhibitor [26]. As for the Najaf refinery, an anti-corrosion membrane is injected at the top of the distillation tower, and this does not serve the work of a hydrate inhibitor, so the research paper suggests injecting an anti-corrosion membrane if this is expected to happen. In the area after the FCV-101 valve and before the unit's furnace.

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Table (1): Chemical properties of methanol and ethylene glycol [28]

Property	Ethylene Glycol	Methanol
Molecular weight	62.10	32.04
Boiling point at 760 mm Hg, °F	387.10	148.10
Vapor pressure at 77°F, mm Hg	0.12	94
Specific gravity at 77°F	1.110	0.7868
Specific gravity at 140°F	1.085	–
Pounds per gallon at 77°F	9.26	6.55
Freezing point, °F	8	−144
Pour point, °F	-75	–
Absolute viscosity in centipoises at 77°F	16.5	0.55
Absolute viscosity in centipoises at 140°F	5.1	0.36
Surface tension at 77°F, dynes/cm	47	22
Specific heat at 7°F, Btu/lb/°F	0.58	0.27
Flash point, °F	240	0
Fire point, °F	245	0
Decomposition temperature, °F	329	0
Heat of vaporization at 14.65 psi, Btu/lb	364	473

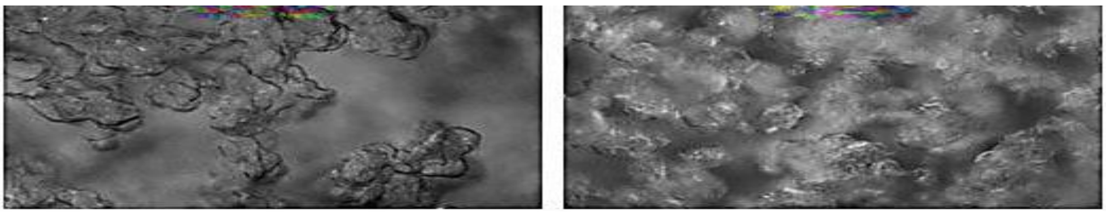

Fig. (4): Shows the effect of gaseous hydrates in preventing the formation and dispersal of the mixture of hydrate components [27].

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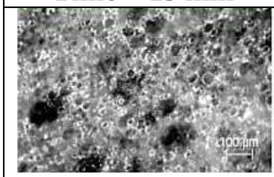
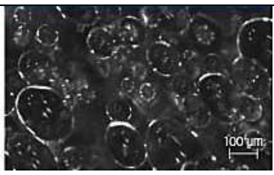
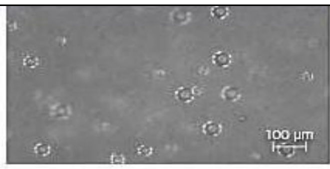
5. Materials and experiments

In this section, unit joints that have a direct influence on the formation of gaseous hydrates will be evaluated.

1- Evaluation of the performance of the chemical demulsifier injected into the desalination equipment is one of the factors that directly affect the formation of gaseous hydrates in the pipelines of the refining unit. The effectiveness of the used emulsifier is clear, but there is a technical problem, which is the injection quantity, as the Najaf refinery continues to inject the substance at a rate of (0.3) every three hours. This is because of the cost, but in fact the injection quantity is not enough because the crude oil has poor specifications. The bottle test was used to monitor the action of the oil demulsifier. For oil (API ~ 29), as shown in practical experiments that were carried out on de-salter with four stages according to time, Table (2).

Table (2): Four-stage bottle test to observe the effect of the demulsifier

Time = 15 min	**Time = 1 min**	**Time = 3 min**	**Time = 6 min**
			
t = 15 min: In the absence of a demulsifier, smaller droplets aggregate and undergo morphological rearrangements to form larger droplets.	t = 30 min: In the presence of the demulsifier, larger droplets are initially observed, without affecting the physical integrity of the droplets.	t = 45 min: Over time, the emulsion appears stable for the duration of the experiment.	t = 1 hr.: Eventually, large droplets separate, leaving behind small oil droplets in the crude that can be deposited and removed.

2- Evaluation of the activities of unit operators to break down gaseous hydrates. The engineers and operators of the refining units begin to perform several activities on site when gaseous hydrates occur, which are always located in the tubes of the secondary heating zone (104, 105) and the primary heating zone (heat exchanger package EX - 211). These activities have their own problems as they shorten the operational life of the unit. High and low temperatures weaken the metal of the furnace tubes and increase corrosion rates, and thus the possibility of tube explosion and loss of unit energy and refining process. Therefore, it is best to take the necessary measures to prevent the frequent occurrence of gaseous hydrates. (Figures) The following charts (5, 6, and 7) show the results of this evaluation.

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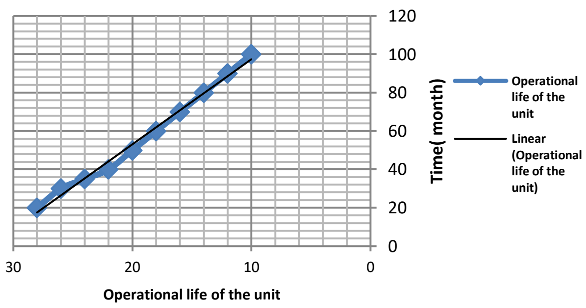

Fig. (5): Decrease in unit life over time

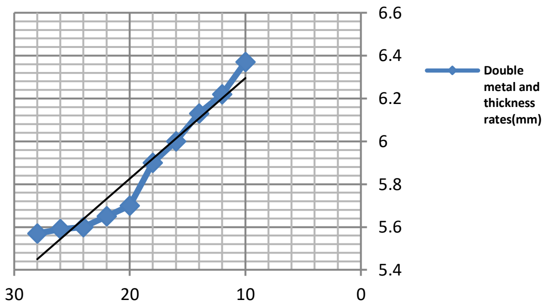

Fig. (6): The effect of metal and thickness of the unit through time

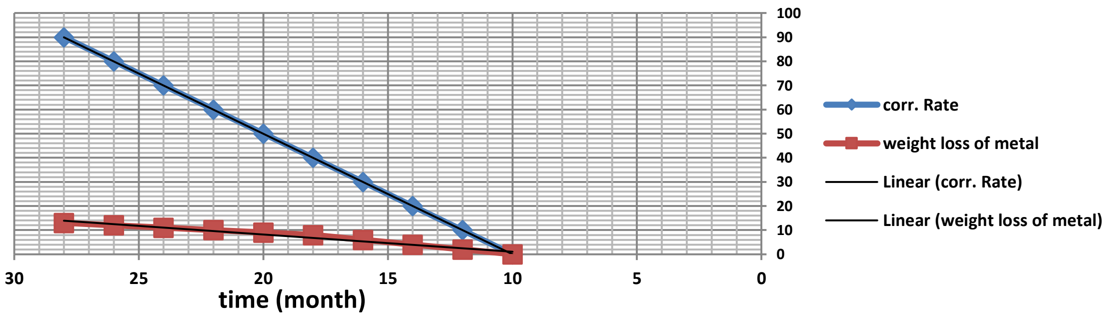

Fig. (7): The increase in corrosion rates and the decrease in the weight of the metal of the furnace through time

6. Results and Discussions

The current section aims to follow up the results of using the technical solution and the procedures approved by the operators and engineers of the second refining unit in the Al-Najaf Refinery, as they are technical procedures that have future damage and affect the design life of the refinery, as we have explained in detail. The results discuss the location of gas hydrates in the sites below.

The location in the furnace of the refinery (unit 2) type (box – type furnace) shown a blockage occurred in one of the thermal furnace lines. This was observed by a gradual decrease in line flow (Branch B-105), as indicated by the dispatcher on the unit's control panel. A sample was taken to examine the salts entering and leaving the desalination device, as well as examining the percentage of water, sediment, and vapor pressure values. The reason for this check is due to the fact that gas hydrates depend in their composition on salts, sediments, and vapor pressure. If the salts are of the potassium chloride (KCl) type, a temperature drop occurs in the flow stream. It greatly helped in the formation of gaseous hydrocarbons, because potassium chloride, in order to decompose, needs to absorb more thermal energy than the rest of the salts, as it is difficult to

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precipitate, except with the availability of high heat. To be absorbed from the surrounding environment.

Therefore, we notice a decrease in temperature and an increase in pressure, and this is in contrast to sodium chloride salts that do not need high heat and do not cause a significant decrease in temperature, because they contain small molecules that quickly dissolve in water. From this it is clear that potassium, calcium and iodine salts lead to the formation of gaseous hydrates faster than sodium salts. Sample readings were taken at 10:15 am, 12:00 pm, and 2:00 pm, respectively (when gaseous hydrates appeared, when on-site treatment started, when hydrate dissolved and blockage opened), Table (3) Shows the test readings.

Table (3): Results of the examination of the internal and external salts of the de-salter, the rate of water and sediment and RVP.

Time (min)	Test salt content mg/l		Water and sediment % vole		RVP
Test times	**In**	**Out**	**before it happens**	**during the occurrence**	**pa**
10:15 AM	277	272	0.05	0.1	**12.9**
12:00 PM	135	77.9	0.1	0.2	**12.7**
2:00 PM	287	27.3	0.2	0.2	**11.1**

The table shows the high percentage of salts leaving the desalination device, as well as the percentage of water and salt deposits at the beginning of the deposition of gaseous hydrates. It is also noted that there is a rise in the beginning of the formation of gaseous hydrates, followed by a decrease when the treatment processes are completed. The reason for this is due to the following:

- De-Salter is malfunctioning (or not working).
- Misuse or termination of the effectiveness of the emulsifier.
- Poor quality of the crude oil entering the unit and its specification
- API value less than 28
- High viscosity of crude oil.

After checking the water and sediment levels, salts and vapor pressure value before and during the blockage in the flow pipe, confirming the presence of gaseous hydrates, the unit operators started to take the necessary measures and prepare for on-site treatments. Documented readings

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were taken for both lines of the convection unit furnace. The results showed the location of the blockage as a result of the formation of gas hydrates of the complex type (SH) in (Branch B - 105), while the second line (Branch A - 104) continued to operate without obstructing the flow of ore oil. The results show the time when the blockage occurred from (10:00 am until 12:00 noon) and that the operating capacity is 60 m3 / hour, as shown in Tables (4) and (5).

Table (4): The site reading (Branch A-104) during the occurrence of gas hydrates

Branch A - 104			
Time(m)	**Temp.(ċ)**	**Press.(bar)**	**Flow (m^3/hr.)**
10:00 AM-10:15 AM	300	10.3	30.5
10:15 AM - 10:30 AM	295	10.0	32.0
10:30 AM - 11:00 AM	292	9.8	35.0
11:00 AM - 11:15 AM	288	9.5	37.5
11:15 AM - 11:30 AM	281	9.2	38.7
11:30 AM - 11:45 AM	275	8.8	39.1
11:45 AM - 12:00 PM	260	7.7	41.7

Table (5): Site reading (Branch B -105) during the occurrence of gas hydrates

Branch B - 105			Transfer line
Flow (m^3/hr.)	**Press.(bar)**	**Temp.(ċ)**	**Transfer line Temp.(ċ)**
29.5	9.8	305	300
27.5	10.0	310	302
25.0	10.2	315	305
22.0	10.5	320	301
18.0	11.3	327	307
13.0	13.9	335	310
12.0	14.7	341	303

At (12:00 pm) the refinery unit operators started to take the following measures to deal with the occurrence of gaseous hydrate in (Branch B - 105).

- The gradual tightening of the crude oil inlet valve in the second line (branch A - 104) in

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the hope of reversing the flow of crude oil by the principle of pressure and reverse flow on (branch B - 105) and attempting to open the blockage.

- Gradually reduce the oven temperature as shown in the reading (transmission line) until the temperature reaches 200°C.
- Opening the secondary passage of the main flow valve to increase the amount of operational energy entering the unit to reach the furnace, with the conversion to the most powerful pump for feeding crude oil to create a greater flow pressure.

These procedures, which the unit operators follow briefly, are considered a technical solution, and since the gas hydrates will deal with a decrease in temperature and pressure, the crystal structure of the hydrates will explode, and the pressure of the liquid becomes greater than the pressure of the gas so that the gas moves to dissolve in the liquid and open the line, and then start Operators to return according to the unit's normal conditions, operating power and required temperatures, which were completed at (02:00 PM). The following Tables (6) & (7) show the results of changing the circumstance in the branch that were read while following the procedures to remove the blockage.

Table (6): Reading of the situation when exercising the procedures in (Branch A – 104)

Branch A - 104			
Time(m)	**Flow (m^3/hr.)**	**Press.(bar)**	**Temp.(ċ)**
11:45 AM - 12:00 PM	**41.7**	**7.7**	**260**
12:00 PM - 12:15 PM	**39.5**	**8.0**	**262**
12:15 PM - 12:30 PM	**37.5**	**8.3**	**264**
12:30 PM - 01:00 PM	**35.5**	**9.0**	**225**
01:00 PM - 01:15 PM	**30.0**	**9.2**	**200**
01:15 PM - 1:30 PM	**32.1**	**9.8**	**245**
1:30 PM – 02:00 PM	**30.7**	**10.7**	**303**

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Table (7): Reading of the situation when exercising procedures in (Branch B - 105).

Branch B - 105			Transfer line
Flow (m^3/hr.)	**Press.(bar)**	**Temp.(ċ)**	**Temp.(ċ)**
12.0	14.8	341	300
15.5	13.1	330	280
17.8	12.8	310	265
18.0	12.5	280	230
30.0	10.0	200	200
29.0	10.7	240	250
29.3	11.0	298	305

It has become known that the high temperature of the raw liquid leads to an increase in the pressure of the flow or flow due to the dependence on the pressure of the feed pump (P-311) regardless of the friction loss during the flow, and thus the release of light gases and hydrocarbons in the space of the transport pipe, forming gas gaps in the event that The conditions for the production of gaseous hydrate have been achieved, and the most important condition is the high percentage of light hydrocarbons accompanied at the same time by the high percentage of water in the crude oil. Also from the bottom of the earth is the poor work and corruption of the oil companies contracted with Iraq, which are the licensing round companies, from which we have seen nothing but muzzling, opacity and poor quality. Hence, it should be noted that the increase in the rates of deposition of salts or the presence of mineral plankton and the weakness of the fixation of crude oil and processors, leads to the formation of another type of gaseous hydrates, which are mineral hydrates.

Figures (8) and (9) show the change in temperature values according to pressure and flow in the presence of gas hydrates. The table also shows the results of each of the two furnace lines (before performing technical treatments) (Branch A - 104) (Branch B - 105). Figures (10) and (11) show the initiation of on-site treatments. The change in temperature, pressure and flow can be observed.

It is clear from the Figures below (9 and 10) the amount of temperature change in the branch in which the blockage occurred (branch B - 104) as a result of the formation of gas hydrates and the amount of obstruction that caused a problem in the operational process, while the branch (branch A) - 104) is in operation, resulting in its temperature decreasing due to the accumulation of raw materials as a result of the reverse flow, the procedures show a change in values and conditions. This is illustrated by the two figures below.

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The occurrence of gaseous hydroxide in oil refineries in general, and the Najaf refinery in particular, being the site of our study, is a major problem. Those concerned and officials in the Iraqi Ministry of Oil and companies must pay attention to it and consider finding feasible solutions and focus efforts and follow-ups on the strategic line that carries crude oil from the oil fields and the work of the extractive companies.

The oil industry is the backbone of the Iraqi industry, and it is the main source of income. On oil, Iraq's financial budget is based. Therefore, the oil industry is the basis for all industries. Of this importance, we must have solutions and a concept to remove problems as much as possible from this large industry, support it with everything useful and useful, and develop its cadres. To be at global levels and this is not a big deal for the heroes of the Iraqi oil industry.

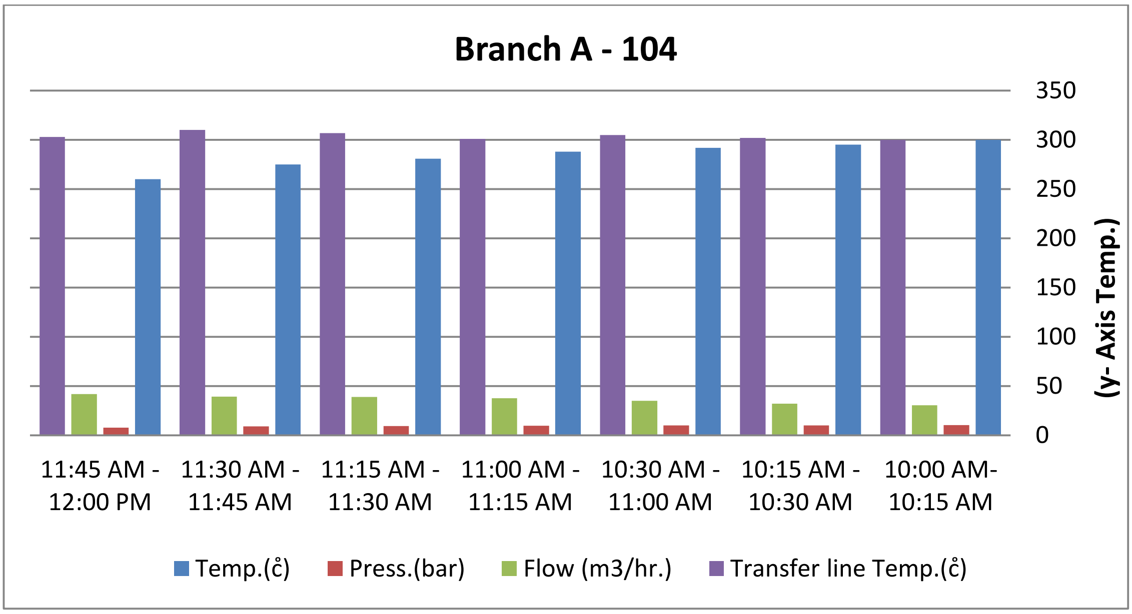

Fig. (8): (Branch A - 104) during hydrate formation

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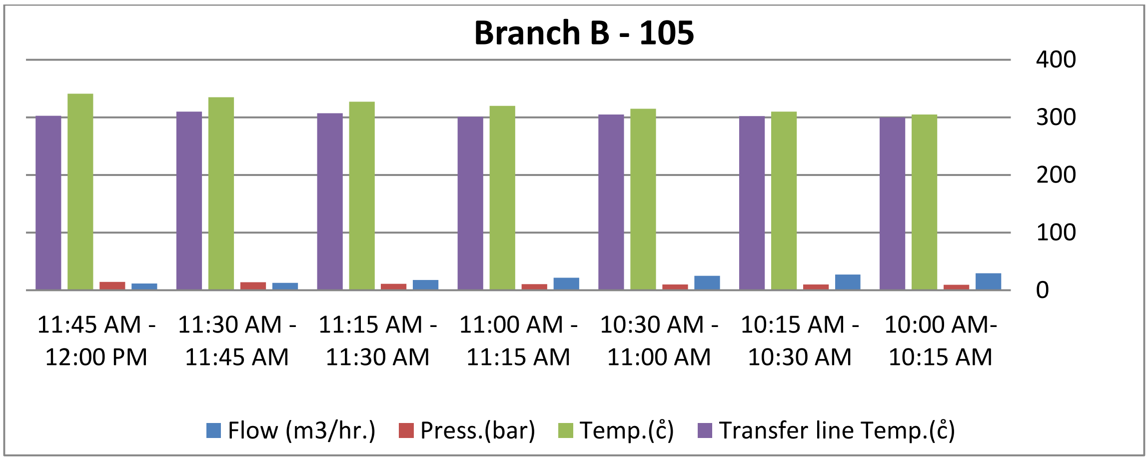

Fig. (9): (Branch B- 105) during hydrate formation

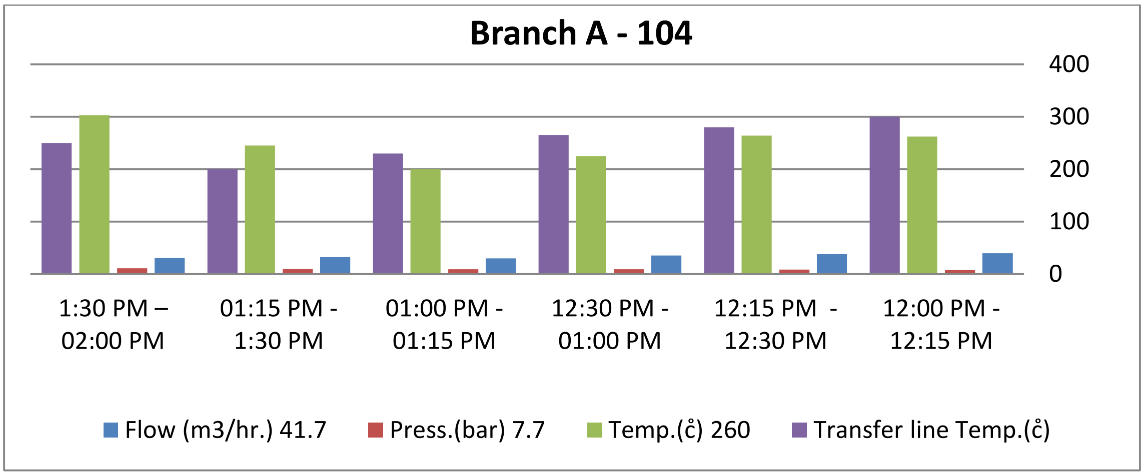

Fig. (10): (Branch A - 104) when exercising procedures

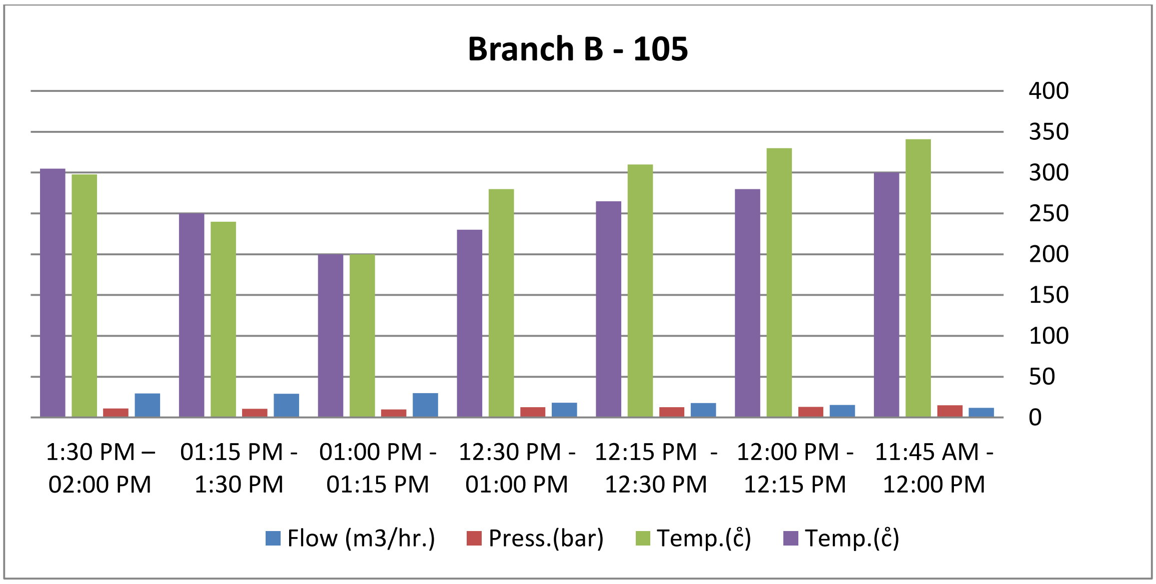

Fig. (11): (Branch B - 105) when exercising procedures

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Figures (10 and 11) show the amount of decrease in temperature accompanied by a change in the amount of flow and pressure, when the temperature drops from a stable level of (300) C^o to a sudden degree of (200) C^o. Even if it is gradual, it causes great damage to the life of the unit and the possibility of leakage in the furnace tubes as a result of the weak thickness. All these damages are caused by the poor level of heat treatment in the tube, which results in a weakness in the crystal structure of the nature of the metal manufactured for the furnace tubes.

7. Conclusions

The paper explained what gas hydrates are, how they occurred, and what are the most important issues and predictions that would address the occurrence of hydrates in the crude oil refining industry in general, and the paper discussed the proposed solutions in the joints of our study. Through the body of the research and the results, the paper concluded briefly as follows:

- Gas hydrates is a subject that has not been widely highlighted in the crude oil refining industry because it shows mishandling of the source of crude oil and companies operating in the oil fields. This is a problem in itself and needs follow-up to eliminate it completely.
- The continued use of technical solutions adopted by engineers and operators of refining units in the treatment of gaseous hydrates is extremely dangerous and causes a great loss in energy and the operational life of the unit, so the concerned authorities must take the necessary measures and provide hydrate inhibitors as much as possible.
- Hydrate inhibitors are the safest way to preserve refinery unit life and operational capacity as well as operators' efforts.
- The decrease in the unit temperature from 300 during a short period to less than 200 with the changes in the accompanying conditions has great future effects on the nature of the metal made for the unit tubes, especially the convection oven tubes.

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