

## Results and Solutions for Unit Corrosion Breakdowns

Done by Eng. Essa M. A. Alruwaieh

*Engineer in the Public Authority for Applied Education & Training.*

Assisted Eng. Tareq Ibrahim Alnkhailan.

*Mechanical Engineer in the Public Authority for Applied Education & Training.*

*Specialized trainer member in the Instate of Civil Structural Training.*

### ABSTRACT

Corrosion is commonly defined as the degradation of a substance or its qualities as a result of an interaction involving its environment. In certain environments, the majority of materials corrode. For example, water wears away stone, iron, and even wood as they rot. Although corrosion cannot be prevented, it can be slowed down or momentarily stopped. The following search paper clarify how to prevent corrosion and provide a cause study for the oil and gas process. In addition, the paper shows a complete understanding of the corrosion in the process.

**Keywords:** CORROSION BREAKDOWNS , Heat Exchanger Corrosion, corrosion control in vacuum

Date of Submission: 02-04-2024

Date of acceptance: 13-04-2024

### I. INTRODUCTION

It is essential to compile corrosion occurrences and construct "banks" out of them. It is crucial to gather these incidents and establish (banks) of troubles and degradation in the Petro - chemical and oil industries. assist in identifying concerns with corruption and oxidation. Such broad generalizations have been made. Although the case is known and has been incorporated into certain reports and publications, other of them are not being reported at all and are just known informally. In my professional deep expertise with petroleum refining including Petro - chemical machinery, I came across about 10–14% of corrosion events that weren't frequently described. This fact suggests that seasoned specialists as well as the younger ones of engineers cannot always realize and understand all of the problems that arise. Even if I am aware of 1000 cases of corrosion, always there is the instance 1001 that I am not aware of. There are both usual and uncommon corrosion failures with Petro - chemical and oil refinery machinery, which is another issue. There are supporting resources and facilities for auxiliary processes. At oil refineries and petrochemical businesses that make fuels and organic chemicals, there are related infrastructure and medium in auxiliary processes. These facilities include a power plant with the ability to generate steam and boiler feed water, a cooling water system, a firefighting system, and units dedicated to dealing with environmental concerns including

cleaning the water, air, and land as well as disposing of petroleum waste. Construction of devices and equipment that absorb acid gases was prompted by stringent guidelines to prevent air pollution. (Hydrochloride, Hydrogen sulfide, and Nitrogen oxides), causing corrosion issues that had never been seen before. As an illustration, corrosion-cavitation caused the alloy Hastelloy B-2, which was regarded as the ideal material for an ejector (a Venturi scrubber) in the CCR unit to collect acid gases, to fail after 9 months of duty [1-5]. Another illustration is the elimination of dangerous NO<sub>x</sub> from atmospheric gas emissions. Currently, an inhibitor solution that decomposes is injected into petrochemical, electricity, and oil refinery plants to reduce NO<sub>x</sub> emissions. From water vapor to ammonia, see how it reacts with NO gas to create N<sub>2</sub>, which is the primary element of the atmosphere. Only stainless steel should be used in this device since carbon steel is not urea resistant. This device may have problems with cavitation and erosion in addition to choosing the right corrosion-resistant materials. There is occasionally confusion in identifying the causes of corrosion episodes when many corrosion phenomena take place at the same time or when various causes result in equivalent manifestations and failures. among other things, advances. Pitting can be brought on by dissolved oxygen, chlorides, naphthenic acids, acid dew erosion, sediment erosion, and cavitation. On the carbonyl group, caustic, H<sub>2</sub>S, or polythionic acid assault takes

place. The issues with both old and new ships will be discussed in this chapter. There are sometimes answers. Additionally, the proper correlation between corrosion concerns and dangers, as well as the adoption of a new corrosion management approach, [6-7].

### 1.1 DISTILLATION SYSTEM IN VACUUM

Water vapour, H<sub>2</sub>S, HCl, and sometimes weak organic acids are all present in the vacuum distillation overhead stream. Vacuum bottoms include significant levels of sulfur compounds and naphthenic acids. As a result, the vacuum distillation apparatus may encounter the two main corrosion problems listed below: Condensers, valves, and pumps can corrode from acid at low temperatures; pipes can corrode at high temperatures (\*340–350 °C) if naphthenic acids and sulfur compounds are present in the vacuum bottom. Similar to how they do in the air column, H<sub>2</sub>S and HCl dissolved in condensed water induce corrosion in the vacuum distillation unit's overhead. About 90% of the MgCl<sub>2</sub> and 10% of the CaCl<sub>2</sub> in desalted crude are hydrolyzed, and the HCl that is produced rises to the top of the pre-flash and crude columns. The atmospheric residual, consisting of 90% CaCl<sub>2</sub> and 10% MgCl<sub>2</sub>, is delivered to the vacuum heater where it interacts with the steam to form HCl gas. Additional sources of chlorides in the vacuum overhead might be entrained saltwater containing chloride salts and tanker-transported waste products that contain organic chlorides. Along with the same corrosion elements (HCl and H<sub>2</sub>S) as the ambient overhead system, there are specific corrosion challenges. Further oxidation of sulfur compounds by air entering the vacuum system can result in the production of both inorganic (H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) and organic (acetic) acids, both of which are damaging to carbon steel. When naphthenic acids and high molecular weight aliphatic acids break down, acetic acid can also be produced. Some N-organic compounds in residual air can be converted to ammonia in the vacuum heater, and ammonium chloride can be generated in the vacuum above when HCl is present. Amine neutralizers are occasionally added to the vacuum above to adjust pH. As a result, HCl amine salts may also form. Both salts are present in the separator drum and dissolve in the roof condensate. Vacuum overhead can also make it difficult for steam ejectors to erode due to corrosion. The most frequent causes of erosion are high steam velocity and the formation of water droplets in steam (droplet impingement). Temperatures for steam exhaust should range from 120 to 150 degrees Celsius. If the temperature is low, the steam is wet.

#### 1.1.1 SYSTEM FOR CORROSION CONTROL IN VACUUM OVERHEAD

The choice of building materials is influenced by the sulfur and naphthenic acid concentration of air waste. Carbon steel is often utilized at T 230 °C if the sulfur content is less than 1 wt percent and the TAN is less than 0.5 mg KOH/g. If the temperature is over 230 °C and the sulfur content is more than 1 weight percent, low alloy 5Cr steel is advised. When TAN > 0.5 mg KOH/g and T > 230 °C, SS 316L or SS317L is advocated.

Vacuum columns usually have 12Cr SS internals, as does the column itself. Aluminum can be used since it is resistant to both sulfur compounds and naphthenic acids (as well as to other organic acids). Condenser tubes can be manufactured of Ti Gr.2 and Admiralty brass CDA 443.

The first steps in managing corrosion in both atmospheric and vacuum overhead systems are tank settling, desalting, and caustic injection to desalted oil. The vacuum overhead system does not have wash water put into it as atmospheric overhead does. The main method of preventing corrosion in vacuum overhead is the injection of a neutralizer, which maintains the pH of the water condensate in the separator between 5.5 and 6.5. As a neutralizer, steam can be injected with morpholine, cyclohexylamine, or diethylaminoethanol. This suffices in a lot of situations.

Injections, though, occasionally combine the neutralizer and amine corrosion inhibitor. Amine neutralizers shouldn't be injected into dry overhead wires to prevent the creation of hydrochloride salt deposits and subsequent corrosion. A surplus of neutralizers can result in higher pH levels (>7), the formation of deposits, and more corrosion. Air leaks must be prevented since they can cause corrosion. Helium testing can be used to find leaks.

Injections, though, occasionally combine the neutralizer and amine corrosion inhibitor. Amine neutralizers shouldn't be injected into dry overhead wires to prevent the creation of hydrochloride salt deposits and subsequent corrosion. A surplus of neutralizers can result in higher pH levels (>7), the formation of deposits, and more corrosion. Air leakage must be prevented since they can cause corrosion. Helium testing can be used to find leaks.

#### 1.1.1 CASE STUDIES

Five corrosion examples are presented and examined in this section.

### 1.1.2.1 First vacuum condenser corrosion

Conditions: Steam, hydrocarbons, and acid gases (mostly H<sub>2</sub>S) flow into a vacuum condenser shell at 40°C after the vacuum distillation column. Cooling water containing chemicals (corrosion blockers, flake agents, and biocides) passes through towers at 30-35°C and 4-5 bar. The equivalent is typically injected in top vacuum installations (about 5 years).

--- The building's components are 90/10 copper-nickel tubes (CDA 706). A515 Gr. 70 ASTM carbon steel sheet and tube 10 mm thick tube-sheet that is coated with copper-nickel 90/10 (from water side). ASTM A285 Gr. C baffles made of carbon steel.

--- Six years of service were provided prior to the breakdown.

--- Visual inspection and findings: Grooves, cracking, dryness, and sponginess of the surface

were found on carbon steel dividers and tube-sheet from the processing side (Fig.1).

When carbon steel came into touch with copper-nickel tubes, it too corroded. Additionally, the exterior of copper-nickel tubes was found to have pits.

Acid, pitting, as well as galvanic corrosion are the failure phenomena. ---

• Failure's root cause and justification: And per the morphology of failed surfaces of baffles and tube-sheet, light organic and inorganic acids (including H<sub>2</sub>S) impacted carbon steel surface areas in the form of separating (delamination), porosity, sponginess, and cracks. Attacks of this kind were caused by nascent hydrogen atoms that were liberated during the cathodic process and spread through carbon steel (see Fig.1). Once hydrogen sulfide (H<sub>2</sub>S) came into contact with copper-nickel tubes' outer surface, pits were created.

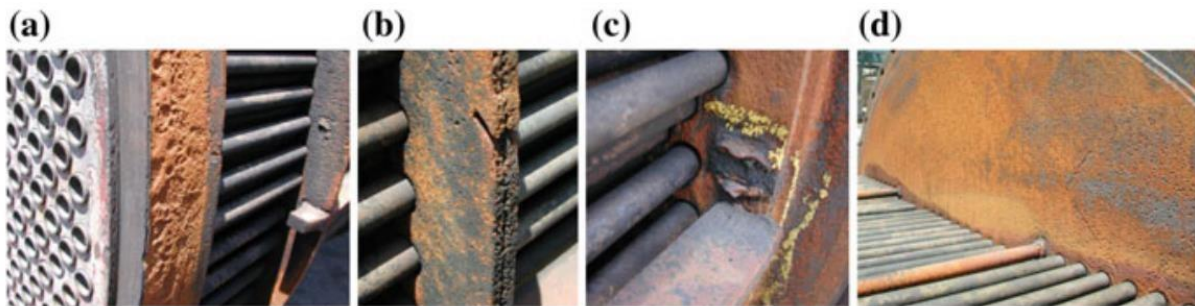


Figure 1(a) bulkheads and corrosive steel sheets (process side). (b) erosion baffle. (c) A weld that is completely rusted and ruined. (d) The tubular plate's etched surface (process side)

### Alternatives and suggestions:

- Carbon steel that has been harmed by hydrogen produced as a result of an acid-corrosion reaction cannot be repaired.
- Tube panels and baffles constructed from A516 or killed steel.
- Injecting the acid corrosion inhibitor into the vacuum distilling system's top.
- Carbon-nickel-copper tubes, as corrosion inhibitors based on iron are used to treat coolant water and corrosion-resistant alloys are not necessary.

### 1.1.2.2 Failure of the Vacuum Condenser Boot in the First Step

Conditions: The first stage vacuum condenser is used to cool a combination of water is used to cool hydrocarbons. Water vapor and hydrocarbons were expelled from the vacuum distillation column. When the condensate left the condenser, its temperature was 20 degrees Celsius. The neutralizer was not pumped into the vacuum overhead system for the first four years, which caused the bottom of the condenser (which covers

30% of the unit) to severely corrode. An amine neutralizer (4 ppm) was fed into the vacuum condenser's intake during the course of the final four years before the failure. The streams from the first, second, and third vacuum condensers are merged in the tank The first condenser's actual state was not captured by the corrosion coupons put at the condensate tank's entrance for corrosion monitoring.

Building structural elements: tube slabs, titanium grade 2 shell, Carbon steel.

Years of service prior to repeating: 8

• Optical inspection as well as results: In the initial step of visual inspection, the hole (diameter 10 cm) was observed. vacuum condenser boot, or bottom (Fig. 2). The upper portion of the condenser, which is where water vapor and hydrocarbons enter, was severely corroded. The titanium tubes seemed to be in good shape. Deposits deposited on the outer surface of titanium tubes. The chemical make-up of the aquatic condensation in the condensation vessel was assessed once per week. pH values fluctuated between 3.6 and 4.1 (all through the year prior

to the collapse; alternately, 5.5 and 6.5 are stated) and pH = 8 to 9.8 at times. The amounts of chloride ions ranged from 42 to 56 parts per million (instead recommended 10 ppm maximum). Only the condenser's input saw carbonate scale emerges

from titanium tubing. The sacrificial anodes worked well. On the other end of the condenser, the coolant water outflow was in good shape. The performance of aluminum sacrificial anodes was excellent.

**Failure phenomenon: Acid corrosion. ---**

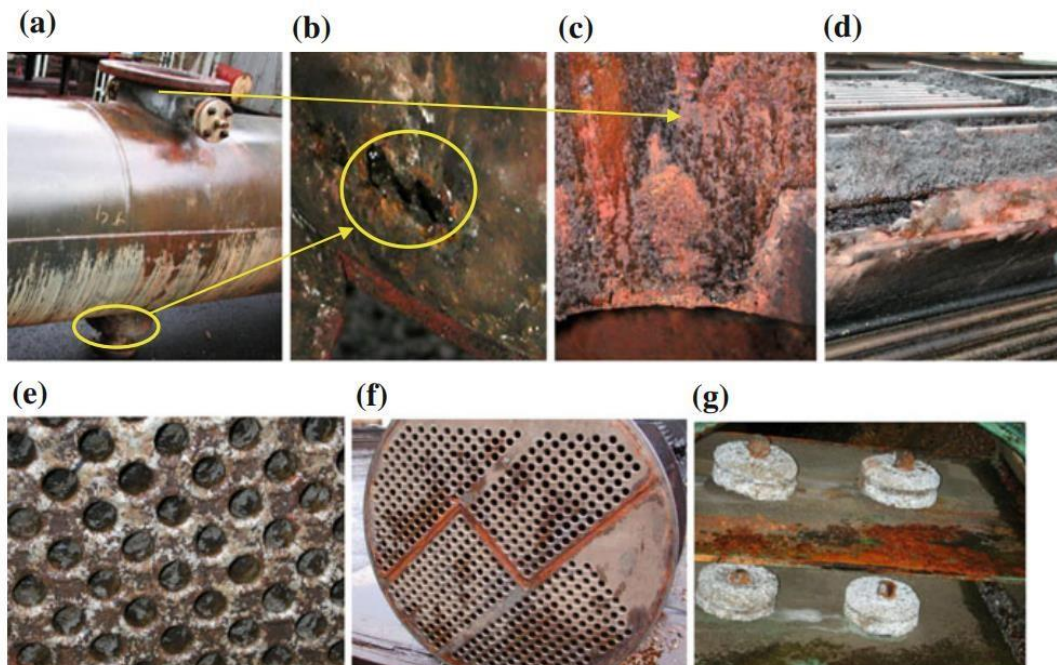


Figure 2 (a) The first vacuum capacitor as seen from above. (b) The hatch at the bottom (10 cm) (luggage compartment). (c) The condenser's rusted top portion. Sedimentation on the condenser's titanium tubes' exteriors. (e) The scale is on the tube sheet and within the titanium tubes (cooling water side). (f) The adversary (cooling water). (g) cooling water with aluminum anodes used as sacrifices (inlet channel).

• **Failure's root cause and justification:** Induced by an aqueous acid solution that contains chlorides. The first vacuum condenser's internal structure has suffered from significant, widespread corrosion. The dose of amine neutralizer given was inadequate. In every case, overdoses occasionally happened, causing the aqueous condensate to have a pH of 8.0 to 9.8, which caused salt deposits to form.

**Alternatives and suggestions:**

- a) Ti Gr.2 coating the inside surface of the first vacuum condenser
- b) As an alternative, epoxy-ceramic coating (600 lms thickness) or epoxy vinyl ester coating (3 mm in thickness).
- c) Coupling the injection of a corrosion inhibitor and neutralizer.

d) Continuous pH and corrosion rate measurements should be made.

**1.1.2.3 The Two-Step Vacuum Condenser Corrosion**

Requirements: Following vacuum operation at 40 °C in the second-stage casing of the Steam, hydrocarbons, acid gases (mostly H<sub>2</sub>S), and vacuum condenser were all generated. The cooling water containing chemicals (corrosion inhibitors, flake makers, and biocides) passes through. At 30-35°C and 4-5 bar. The neutralizer was not introduced into the vacuum distillation column's overhead for a considerable amount of time (about 4 years).





Figure 3(a) shows the second vacuum condenser's shell's damaged inner surface. Localized corrosion from the second vacuum condenser can be seen in (b,c) close to the water condenser.

Shell-carbon steel ASTM A515 Gr. 70-copper and nickel 90/10 are the materials used in construction (CDA 706).

- Years of service prior to repeating: 5
- Optical investigation as well as findings: Near the water condenser, there was widespread area erosion (shallow pits). second vacuum condenser (Fig. 3).

- Under sediment erosion, there is a failure phenomenon.
- The cause and justification for the failure: The acid deposits were brought on by it.

• **Solutions and Recommendations:**

a) Weld drill to fix it.

P) Take out the fire with a race from the fire.

c) Install ER sensors to monitor wear status.

2.4.1.1 Heat exchanger tube plate and baffle corrosion

- condition: it is usually cooled on August 20th. Hydrocarbon gases have a temperature of \* 50 ° C. Cooling water at 30-35 degrees and 4 bar across the tube

• Building Materials: Admiralty CDA 443 (70Cu-30Zn) copper tubes. Carbon

steel baffles and tube plates in contact with cooling water, placing Admiralty copper cladding lay on tube plate. They contain a shell (hydrocarbon gases containing water vapor and H<sub>2</sub>S).

- Years of service prior to repeating: 4

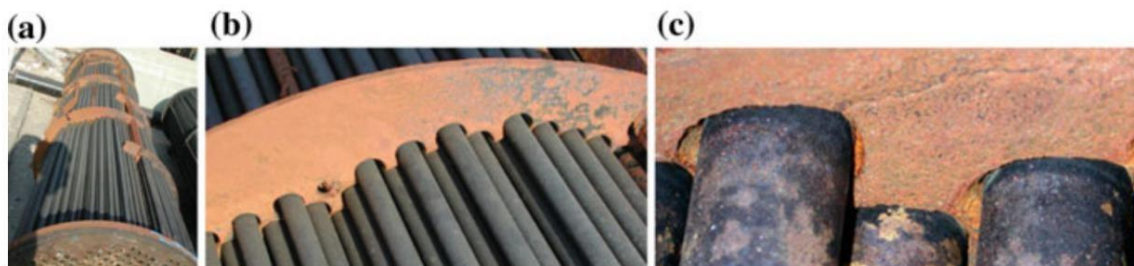


Fig. 4 (a) Overhead condenser (vacuum unit). (b) an Admiralty brass tube and a baffle made of corroded carbon steel. (c) Carbon steel tube-sheet corrosion due to galvanic contact (positions of interaction with Admiralty brass tubes). Brass tubes corroded due to moist H<sub>2</sub>S, resulting in the formation of black copper sulfides.

- **Optical inspection and outcomes:** localized tube sheets and baffle corrosion in locations where they come into contact with Admiralty brass tubes on the process side (Fig. 4). Black copper sulfide scaling coated the outside surface of Admiralty brass tubes.

- **Failure phenomenon:** Low-Temp sulfidic corrosion, galvanic corrosion.

**Source of failure and its clarification**  
 Hydrocarbon gases were discovered to include H<sub>2</sub>S and water vapor, which explains why the system failed. When the water phase condensed, H<sub>2</sub>S that had been dissolved there began to destroy the brass tubes used by the Admiralty. Galvanic corrosion manifested itself where carbon steel baffles and tube sheets came into contact with Admiralty brass tubes.

- **Resolutions and suggestions:**

a. A raw material to substitute chemicals with Ti Gr.2 search machines. This resistance has proven resistant to the medium present in the discharge. There can be a solid stream of air. The baffles shall be prepared of SS 316 As SS 316 and Ti Gr.2 have virtually similar electrode prices and no galvanic corrosion risk, the baffles must be manufactured of SS 316.

b) If refrigerants are employed.

**1.1.2.4 Check valve corrosion**

□ **Circumstances:** In the overhead vacuum system, two valves were in use. At 50 degrees Celsius, hydrocarbon gases, hydrogen sulfide

(H<sub>2</sub>S), and water vapor passed through two valves. Corrosion inhibitor was not always used, and neutralizer was not always administered.

**Building components:** ASTM A216 WCB carbon steel Afore the failure, there was a one-year period of service. Visual inspection and conclusions in the body of two valves, two holes (12 and 2 mm in diameter) were discovered (Fig. 5). Inside two valves, black iron sulfide corrosion yields were discovered on the exterior of the moving disc, bolt, pin, and other fittings. After condensation, the pH of the water ranged from 3.8 to 7.8, although it was usually around 4.

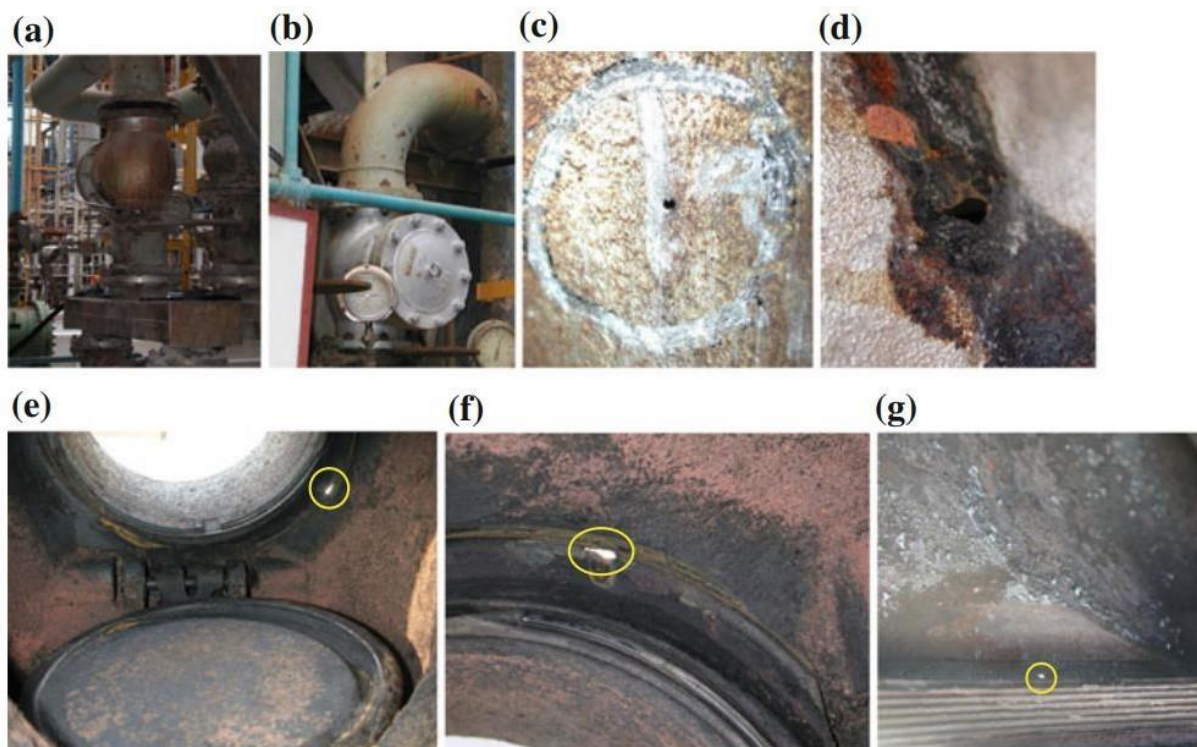


Figure 5 (a,b) Positions of faulty valves in the vacuum unit (a,b). the valve body has perforations caused by corrosion (outside view). e- an interior view of worn holes and rusted internal components.

□ **Failure phenomenon:** Low-temperature sulfidic corrosion and wear.

□ **Reason of failure and its justification:** Sour water with a pH of \* 4 was generated by dissolved H<sub>2</sub>S in water condensate. H<sub>2</sub>S attacked the internal surface of carbon steel valves besides other components of valves. When the dimensions of the moving disc shrank due to corrosion, contact between the disc and the valve body was inadequate, resulting in no tautness. The unrestricted motion of the disc led the internal surface of the valve's figure to wear away, and the bulk's wall thickness eroded from 12.5 mm to zero (until the formation of holes).

□ **Resolutions and suggestions:**

a) Injecting the neutralizer and corrosion inhibitor at the proper amounts into the refinement vacuum system's overhead.

b) Exchange carbon steel in the valve and internal components with H<sub>2</sub>S-resistant low-alloy steel (5 percent Cr).

• **1.2 HYDRODESULFURIZER (HDS)**  
 H<sub>2</sub>S is the most corrosive chemical found in HDS devices (see Chap. 1). Besides being corrosive, H<sub>2</sub>S may be corroded to generate SO<sub>2</sub>, then SO<sub>3</sub>, and eventually sulfurous and sulfuric acids in the existence of water vapor. At HDS units, corrosion is also a concern due to hydrogen invasion and

ammonium bisulfite. Oxidization at HDS units is caused by incorrect structure, poor functioning procedures, and solution uncleanness, just as it is at other units.

**1.2.1 Case Studies**

This section designates and evaluates six examples.

**corrosion in air coolers**

Circumstances: Thermostat temperature in the upper stabilizer 60-80°C. The inlet benzene contained 400ppm of H<sub>2</sub>S, while the outlet contained 200ppm of H<sub>2</sub>S. As a result, being a stabilizer. The installer has been working for 20 years. He was a defender of naphtha; he was a

defender of naphtha. During the eight returns, the feed was infected with FCC Gasoline. At this time, effective means were used enclosures.

- Construction materials: carbon steel.
- Failure phenomenon: general wear.
- The cause of failing and its clarification:

In the presence of washing water, air was damaged in the oxidation of hydrogen sulfide and the formation of sulfuric/sulfuric acids. At a temperature of 60-80 degrees, two acids corrode the carbon steel trays in the tower. Of great importance are the temperatures.

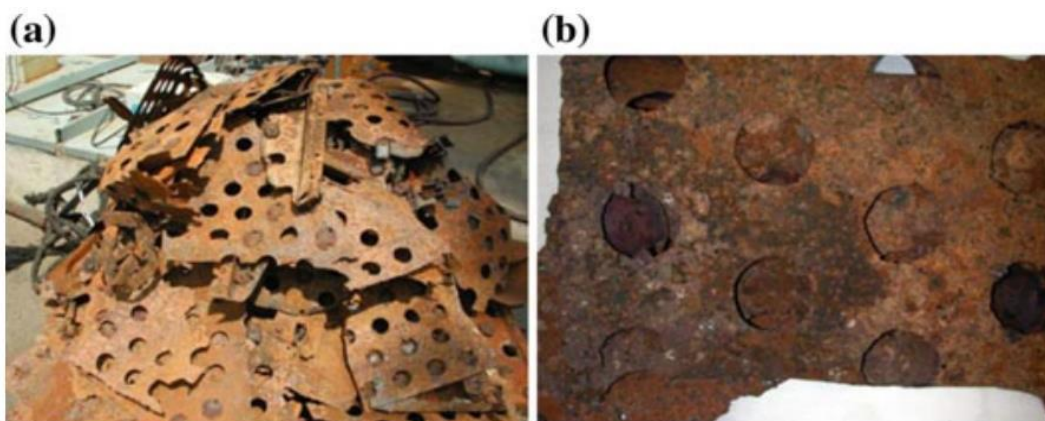


Figure 6 (a) shows rusted trays in a general perspective; Figure 6 (b) shows the image enlarged

□ **Resolutions and suggestions:**

- a) To swap out carbon steel trays for austenitic stainless-steel trays made of 20Mo-6 or 20Cb-3.
- b) Because sulfurous/sulfuric acids may form in this case, wash water shouldn't be utilized.

1.2.1.1 Corrosion of Air Cooler (SRU)

**State:** The quench water is cooled as it leaves the quench tower by the air cooler. Quench water with H<sub>2</sub>S and N<sub>2</sub> entered the air cooler at 80 degrees Celsius, and it exited at 50 degrees Celsius.

**Building elements:** carbon steel A516 Gr.70

Four months of service prior to the breakdown.

**Optical inspection and outcomes:** The hole in the header's center was made twice, two nozzles apart. When the carbon steel patch (12 mm thick) was initially fitted, the hole (4 cm in diameter) was reformed precisely in the patch's center after four months (Fig.7). 36 millimeters of corrosion occur per year at this pace. In the two months prior to the event, the pH of quench water varied between 2.2 and 3.0, according to PI data. Black deposits and a pipe blockage were found within the air cooler. The deposits contained corrosion byproducts such as iron sulfides and sulfates.

- **Failure phenomenon:** • Erosion and acid

corrosion (by turbulent flow).

• The presence of iron sulfides in deposits shows that carbon steel was badly corroded by H<sub>2</sub>S dissolved in water, **which is the cause of failure and its explanation**. Such a high rate of corrosion (36 mm/year) could only be brought on by the presence of H<sub>2</sub>S in the water. The production of two acids, H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, suggests that the reactor's gas SO<sub>2</sub> was not transformed to H<sub>2</sub>S, as evidenced by the formation of these two acids. At 80 °C, these two acids extensively damaged carbon steel. The corrosion rate of 36 mm/year only materialized in the presence of these acids at high temperatures (80 °C) or when erosion (turbulent flow of acidic solution) took place. Blocked pipes and nozzles allowed corrosion products from the stream to enter the air cooler. Pipes at the ends of the header were blocked in front of the quench water intake (two nozzles). In the center of the header, a turbulent flow of an acidic aqueous solution developed, speeding up corrosion. The laboratory measurements of 36-258 mm/year of carbon steel corrosion rates by H<sub>2</sub>SO<sub>4</sub> are evidence of this corrosive process (Table 5.1).



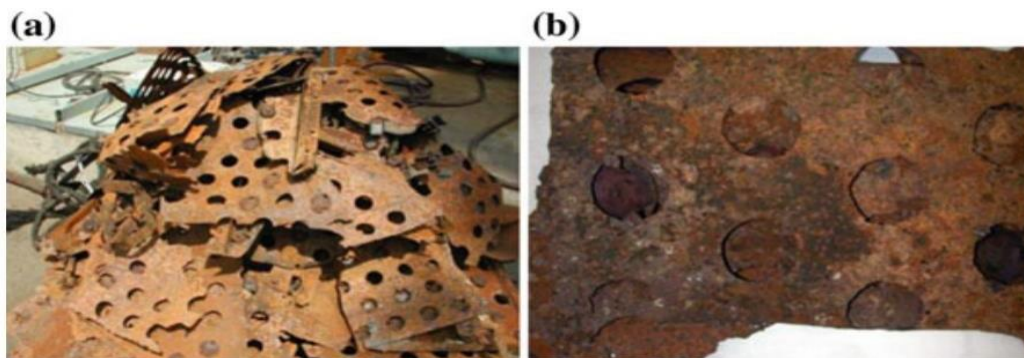


Fig. 7(a) the air cooler in broad terms. (b) The gap and repair

Table 1 the rate of corrosion of carbon steel in aqueous H<sub>2</sub>SO<sub>4</sub> solution over a period of 4 hours at 95 degrees.

| H <sub>2</sub> SO <sub>4</sub> (wt%) | pH  | Corrosion rate (mm/year) |
|--------------------------------------|-----|--------------------------|
| 0.05                                 | 2.0 | 36                       |
| 0.1                                  | 1.7 | 54                       |
| 0.2                                  | 1.4 | 117                      |
| 0.5                                  | 1.0 | 258                      |

#### Suggestions and remedies

a) Use water to thoroughly wash the pipes and interior surface of the air cooler to get rid of any residue.

b) To avoid an acidic solution building up inside the header box, install a drain valve there.

#### 1.2.1.2 Heat exchanger corrosion (SRU)

- Specifications: The heat exchanger is used to cool sour water coolant for the SRU unit. At \*40 C, sour water passes through the temperature. In the casing, the casing flowed cooling water at 30-35°C and 4 bar.

- Construction Elements: Tubes - SS 304L. Tubular Plate - A105 Carbon Steel Analyzed with SS316L (10mm thickness). Shell - A516 Gr.70 carbon steel coated with SS316L (3mm thickness).

- Duration of service before repetition: 3 years.

- Examination and results: Corrosion was found at the succeeding positions of the heat exchanger (Fig. 8):

(a) The wear of the tube plate is localized at the cladding. The shape of the damaged area is characteristic of acid assault (see Fig. 8c,d).

(b) Sour waterside, severe erosion of the channel extensions (see Fig. 8e-g).

(c) Unembellished erosion at the water inlet to the projectile sites (see Figure 8h). From the sour

water, corrosion yields (iron sulfide) were detected on the exterior of the tube plate.

Failure phenomena:

(a) Corrosion due to galvanic action (portion of the tube sheet in interaction with SS 316L clad).

(b) Erosion in common (the internal surface of the canal).

The pH of the acid should be between 0.5 and 3 over a period of several months, and it should have a pH of around 8. This is the reason and explanation for the failure. I want it to just contain weak acids like H<sub>2</sub>S, which cannot produce such pH levels. The pH can drop significantly (to 0.5-3) as a result of the creation of the acids H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> when the ratio of H<sub>2</sub>S/SO<sub>2</sub> at the HDS unit's outlet is off. This happens when the acidic gas SO<sub>2</sub> passes through the TGT reactor (tail gas treatment) and dissolves in the sour water. This often happens when acid gases enter the system and it is switched off. The reaction to sudden fluctuations in H<sub>2</sub>S concentrations can be managed under steady settings. The carbon steel was corroded by the sour, acidic water, which also interacted with the channel's inner surface. Acidic acid tapped into tube plates in the vicinity of carbonaceous material and stainless-steel type 316L and produced galvanic.



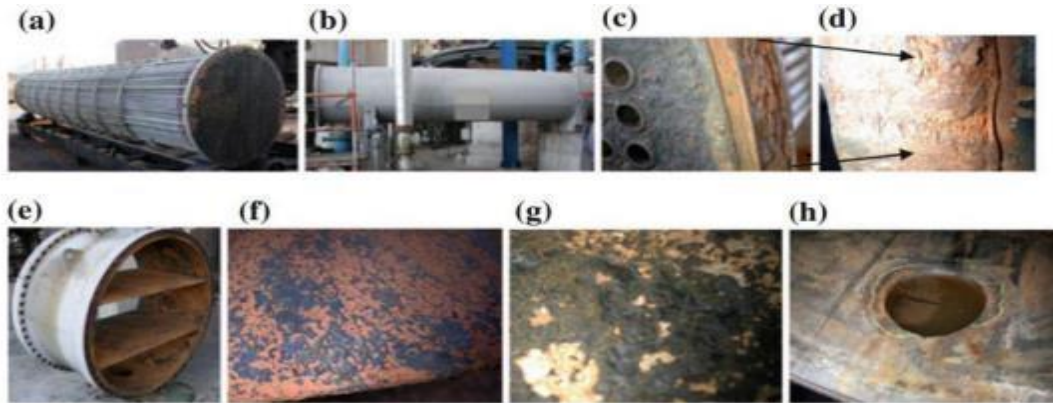


Figure 8 (a) The heat exchanger bundle as a whole (HDS unit). the cortex (b). (c) Corroded tube sheets in close proximity to the stainless steel 316L cap. (D) Enlarge the picture. (e-g) the degraded canal's interior surface (sour water). (h) The shell inlet's rusted inner surface (cooling water)

#### Solutions and recommendations:

- Replace soured water right away if the pH in the acidic region drops below 7 (pH).
- Keeping processing parameters consistent: making sure the H<sub>2</sub>S/SO<sub>2</sub> ratio at the HDS unit outlet is accurate.
- The temperature of the sour water is lowered by 5 degrees Celsius by this heat exchanger, which functions after the air cooler. Therefore, it's preferable to put it in bypass and only utilize it when the air cooler's performance or the load on it change.
- Rather than employing carbon steel for the tube sheet's cladding, the tube sheet should be made entirely of stainless steel 316L.
- To guard the channel against corrosion brought on by sour water, utilize sacrificial aluminum/zinc anodes and cover the interior surface with an epoxy coating resistant to acidic solutions.

#### 1.2.1.2 Corrosion in Heat Transfer Oil Heaters (SRU)

**Setting:** A combination of N<sub>2</sub>, water vapor, and acid gases H<sub>2</sub>S and SO<sub>2</sub> (H<sub>2</sub>S:SO<sub>2</sub>: 2:1) flowed inside the tubes. The gases ranged in temperature from 150 to 195 degrees Celsius, and occasionally even as high as 260 degrees Celsius. Heat transfer oil sprayed outside the tubes at 300 °C.

**Building components:** ASTM SA 214 carbon steel tubes with a 2.77 mm wall thickness. Shell: ASTM A516 Gr.70 carbon steel.

Two years of service prior to the breakdown.

**Optical inspection and outcomes:** Visual inspection reveals extensive corrosion on the tubes' acid gases side in three heat transfer oil heaters (Fig.8). There were pitting degradation symptoms in the welds. The wall thicknesses of the tubes and tube sheets decreased significantly. Large amounts of yellow-black deposits including iron, sulfur, and oxygen were found inside the tubes. After these deposits are dissolved in distilled water, the pH is 3.2. High levels of sulfates were discovered in this solution. Under thermal insulation, it was also found that heat transfer oil heaters outside surfaces were corroding (Fig. 9).it was also found that heat transfer oil heaters outside surfaces were corroding (Fig. 9).

Acid dew point corrosion (inner surface of tubes and tube sheets) **is the failure phenomenon;** corrosion underneath a thermal barrier (outer surface of heat transfer oil heater).

**Failure's root cause and justification:** Water vapor existence caused sulfur oxides (SO<sub>2</sub>, SO<sub>3</sub>) to condense at 150–180 °C hence producing the acids H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. These two acids significantly damaged the internal surfaces and tube sheets of carbon steel tubes.

#### Proposals and remedies:

- HASTELLOY C 276 or FERRALIUM 255 duplex steel tubes should be used in place of carbon steel tubes.
- Coating the outside of heat transfer oil heaters to prevent corrosion under thermal insulation.

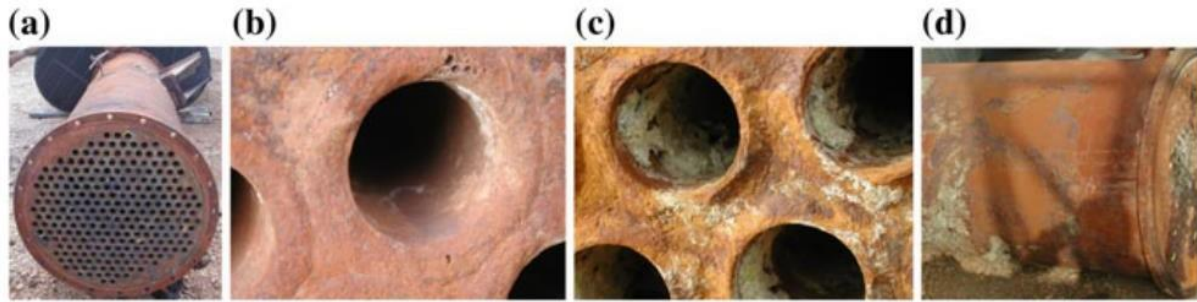


Figure 9(a) an overall view of a failed heat transfer oil heater. (b) The tube sheet's general and pitting corrosion. (c) The tube-sheet and tubes' severe corrosion (deposits are accumulated inside the tubes; the ends of the tubes are out from corroded tube-sheet). (d) Corrosion of the heat transfer oil heater's exterior surface underneath thermal insulation

### 1.2.1.3 Heat exchanger corrosion (SRU)

**Circumstances:** Remains of the gases N<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, water vapors, and sulfur were found inside the tubes after the Claus process. The temperature of the gases was 130 °C at the inlet and 290 °C at the outlet. Heat transfer oil flowed at 310–320 °C and 5 bar outside the tubes.

**Building Elements:** Tubes used in the construction are made of carbon steel and have a 2.77 mm wall thickness. Carbon steel ASTM A 516 Gr.70 for the shell

Two years of service prior to the breakdown.

**Optical analysis and conclusions:** At the gas input side, there was significant corrosion of the tube-sheet surface, particularly the welds and tubes end (Fig.10). In the place where the gases depart, the heat exchanger's surface very slightly rusted. Due to repeated interruptions, temperature frequently dropped to below 100 °C, according to PI data (Fig.11). During such outages, nitrogen would need to be cycled, but this circulation wasn't always achieved.

**Failure phenomenon:** Acid dew point corrosion.

**Failure's root cause and justification:** According to the results, acid dew point corrosion was found.

The reaction between SO<sub>2</sub> and H<sub>2</sub>O produces the liquid inorganic acid H<sub>2</sub>SO<sub>3</sub> when the temperature drops below 130 degrees Celsius (the acid dew point for H<sub>2</sub>SO<sub>3</sub>). The concentrations of SO<sub>2</sub> and H<sub>2</sub>O in the vapor phase really control the dew point temperature when an aqueous acidic solution is produced. The gas SO<sub>2</sub> is capable of being oxidized to produce SO<sub>3</sub>, and this often occurs in the presence of a catalyst, which decreases the activation energy of the oxidation. If SO<sub>3</sub> is produced even at T = 130–180 °C, it can combine with H<sub>2</sub>O to form the potent acid H<sub>2</sub>SO<sub>4</sub>. Once the heat exchanger is turned off, two liquid inorganic acids, H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, are produced when the gas temperature falls substantially underneath the dew point (130–180 °C). These acids destroyed the tube-sheet and tubes made of carbon steel. For acid dew point corrosion to take place, a few hours were sufficient.

• **Proposals and resolution:** In order to stop the development of liquid H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acids, a high temperature (above the dew point, T > 180 °C) must be maintained.

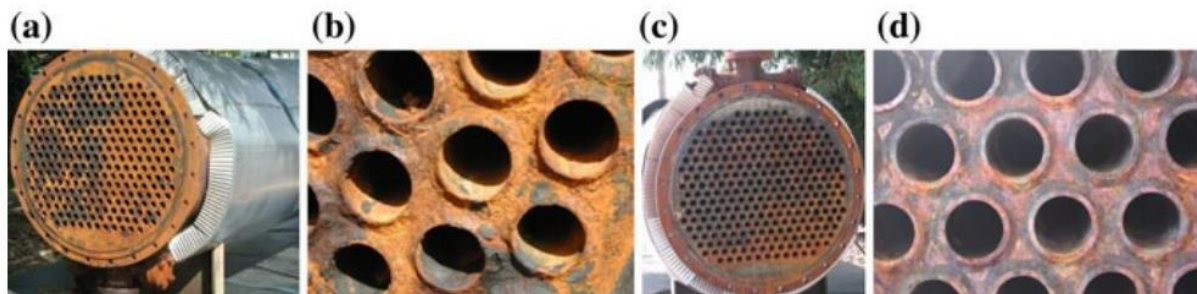


Fig. 10 Heat exchanger failure. (A, B) Gases entering (severely corroded area). (C, D) The gas discharge (slightly corroded area).

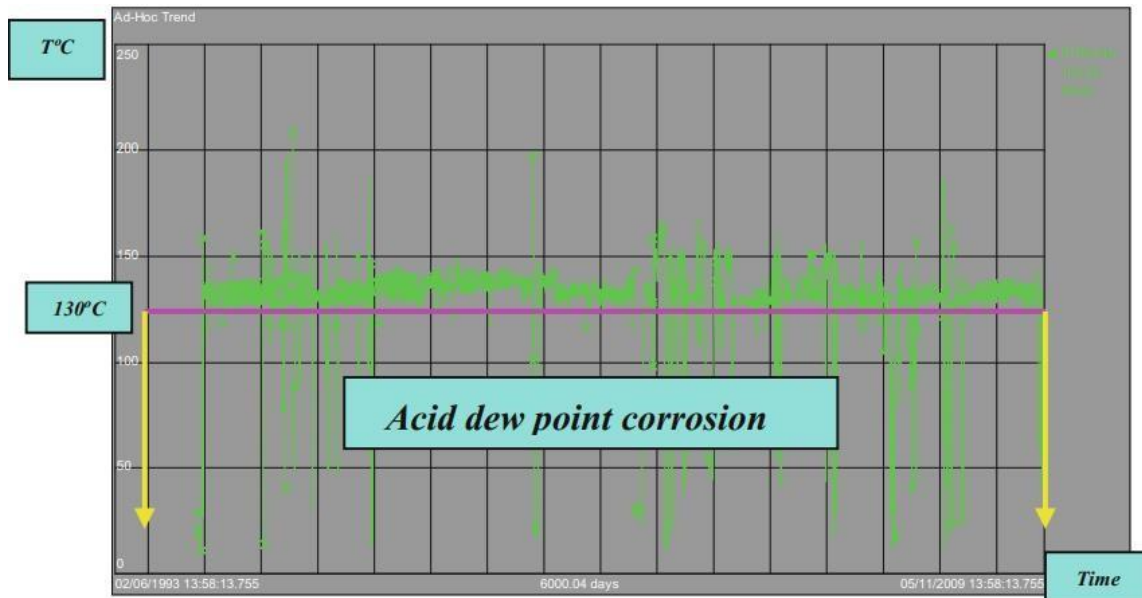


Fig.11 shows time-dependent temperature changes of the entering gases to the heat exchanger (green) (PI data).

#### 1.2.1.4 Corrosion of the Gas Transportation Tube (HDS Gas Oil)

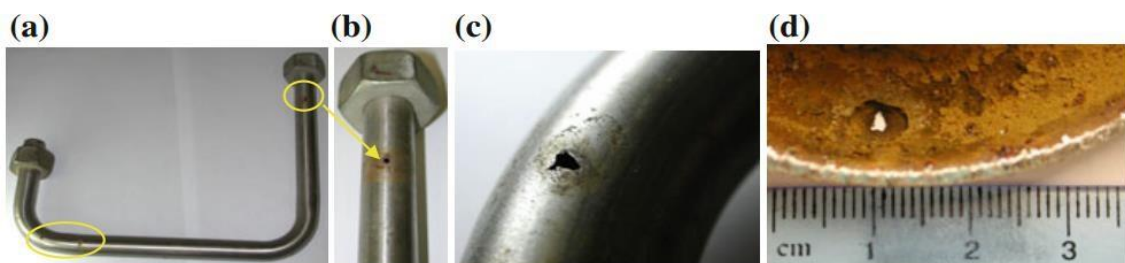
**Requirements:** The tube's function is to transport a gaseous mixture for use in the HDS gas oil unit at room temperature. H<sub>2</sub> (39.7 vol percent), CH<sub>4</sub> (16.3 vol percent), C<sub>2</sub>H<sub>6</sub> (18.7 vol percent), C<sub>3</sub>H<sub>8</sub> (14.7 vol percent), C<sub>4</sub>H<sub>10</sub> (7.4 vol percent), and C<sub>5</sub>H<sub>12</sub> were all present in the gaseous mixture (1.3 vol percent).

**Building elements:** SS 304. The tube's diameter is 12.5 mm.

One year of service prior to the breakdown..

**Visual inspection and outcomes:** reveal that the inner surface of the tube developed holes, and corrosion products were discovered (Fig.12).

• **D-XRF analysis** revealed that the corrosion products that had collected within the tube (in terms of weight percent) were Fe (68.6%), Cr (11.4%), Ni (8.7%), S (7.6%), and Cl (3). a review using chemical analysis of the gaseous mixture. The combination of gases conveyed inside the tube was found to contain H<sub>2</sub>, hydrocarbon gases, chlorides, and water vapor.



Pitting corrosion is **the failure phenomena.**

**Failure's root cause and justification:** Chlorides and water vapor in a gaseous hydrogen-hydrocarbon mixture led to pitting corrosion of the inner surface of stainless-steel tubes. Hydrogen chloride was produced as a result of the hydrolysis of organochlorine compounds.

#### 1.3 Vis-breaker

The vis-breaking procedure involves heating the feedstock (vacuum distillation unit waste) to 430–510 °C and lightly cracking it in a furnace [8]. S-organic compounds in residue decompose to H<sub>2</sub>S at these temperatures. High molecular weight organic acids can be converted into lighter organic acids. After leaving the furnace, the H<sub>2</sub>S- and

organic acid-containing cracking products (such as naphthenic acids) are next sent to a fractionation column. Gasoline, bitumen, gas oil, and LPG are all divided up in this column. The corrosion problems listed below affect vis-breaker units: NAC; sulfur compound corrosion at high and low temperatures. Column walls made of carbon steel fractionation can experience NAC at a rate of 9.6



mm per year. Typically, the gasoline and LPG leaving the column include H<sub>2</sub>S and water vapor. They are cooled to between 60 and 100 °C, and significant low-temperature corrosion from wet H<sub>2</sub>S can happen over the course of three to four years. This section analyzes two cases.

### 1.2.1 Case Studies: Corrosion of Heat Exchangers

#### 1.2.1.1 Cooling Gases

**Circumstances:** LPG, H<sub>2</sub>S, and water vapor are among the gases, that shoot out of the stabilizer, the heat exchanger is utilized to cool. The stabilizer may function as a splitter as well. Gases leaving the splitter had an exit temperature of 85–100 °C, whereas gases leaving the stabilizer had an exit temperature of 60–70 °C. Sixty tubes had leaks and clogs in their third year of use (Fig.13a). Cooling water was circulating within the tubes at 30-35 °C and 4-5 bar.

**Building elements:** The Admiralty 443 CDA brass tubes were used in the building, baffles made of carbon steel

**Service duration prior to failure:** Three years passed after the first analogous failure before the tube bundle was replaced (without conducting a failure study).

**Visual inspection and conclusions:** Scale and silt were found outside the tubes.(Fig.13b, c). The baffles have extensive corrosion. It was found that the outer surface of the tubes close to the impingement plate had holes, fissures, and grooves. Copper sulfide, which is dark, made up the scale. The deposits contained copper and iron sulfides. Corrosive assault on grain boundaries was discovered during **metallographic analysis**. (See Fig.13e–h).

**SEM analysis** revealed the presence of Cu, Zn, O, S, and Cl inside grooves.

Corrosion, including broad and intergranular, is a **failure phenomenon**.

**The reason for the failure and its explanation:** Hydrogen sulfide and water vapor present in hydrocarbon fumes significantly corroded the outside of the Admiralty brass tubes. Copper alloys cannot withstand hydrogen sulfide. Localized corrosion at grain boundaries caused grooves to develop. Carbon steel baffles were harmed by hydrogen sulfide and water vapor before they condensed to liquid at 100 °C.

The material in tubes and baffles will be replaced with Ti Gr.2, according to the **solutions and suggestions**. Ti Gr.2 tube sheets must also be used in place of those in contact on both sides with the cooling water and process stream (LPG).

#### 1.2.1.1 Light Naphtha

**Circumstances:** The heat exchanger is intended to cool light naphtha that was 85 degrees Celsius when it left the splitter. The naphtha had a \*100 °C or greater temperature. Cooling water at a pressure of 4-5 bar and a temperature of 30-35 °C raced through the tubes.

**Elements used in building:** Corrosion at the naphtha inlet and deposits on the exterior of tubes were found (Fig. 5.14). The deposits contained copper sulfides and sulfates. Rust, complete degradation of the epoxy covering, and separation were all visible in the channel (cooling water side).

**Visual Inspection and outcomes:** Corrosion at the naphtha inlet and deposits on the tubes' exterior surfaces were found (Fig. 14). In the deposits, copper sulfides and sulfates were discovered. Rust and complete breakdown of the epoxy covering were seen in the channel (cooling water side).

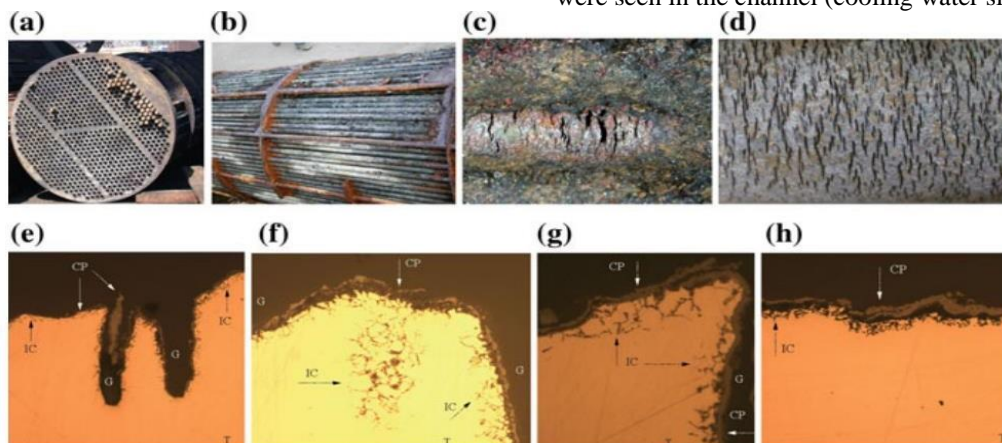


Fig. 13 The bundle of 60 obstructed tubes in (a). (b) Corroded carbon steel baffles and deposits on Admiralty brass tubes. (C, D) Surface flaws including holes, cracks, and grooves on the tube. (e–g) Different magnifications of a metallographic cross-section of grooves (e: x100, f: x200, g: x500): IC—Intergranular corrosion (corrosive assault on grain boundaries), CP—corrosion products, G—grooves, T—tube. (x100) Metallographic cross-section close to the grooves

**Failure phenomena** include epoxy coating breakdown at low temperatures and sulfidic corrosion.

**Failure's primary cause and justification:**

Admiralty brass tubes experienced severe corrosion on their outer surfaces due to the presence of H<sub>2</sub>S and H<sub>2</sub>O in naphtha deposits (copper sulfides and sulfates). Copper alloys cannot withstand H<sub>2</sub>S. The epoxy coating in the cooling water channel was damaged by high temperatures (\*100 °C and higher), which also extensively rusted the surface.

**Suggestions and remedies:** Replace Admiralty brass tubes with Ti Gr.2 tubes. Ti Gr.2. Additionally, this alloy must be used to create tube sheets and channel cladding.

#### REFERENCES

- [1]. API RP 571 (2011) Damage mechanisms affecting fixed equipment in the refining and petrochemical industries, 2nd and. American Petroleum Institute, West Conshohocken, PA, The USA.
- [2]. Groysman A (2014) Corrosion in systems for transportation and storage of petroleum products. Springer, Dordrecht.
- [3]. Heidersbach R (2011) Metallurgy and corrosion control on oil and gas production. Wiley, Hoboken, New Jersey, USA.
- [4]. Garverick L (ed) (1994) Corrosion in the petrochemical industry. ASM International, USA.
- [5]. Esaklul KA (ed) (1992) Handbook of case histories in failure analysis, vol 1, 2. ASM International, USA.
- [6]. Powell GW (1986) Failure analysis and prevention, Metals Handbook, vol 11, 9 and. ASM International, USA.
- [7]. Groysman A et al (2000) Cavitation corrosion in a continuous catalytic reformer unit. Mater Perform 39(6):62–66.
- [8].