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Research Paper

Failure Evaluation of Cupronickel Alloy Used in the Condenser of the Desalination Unit

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Abstract
This study looks into the various forms of corrosion that affect various elements of the South Pars Gas Company's first refinery's desalination plant, such as water compartments, tubular plates, support tubes, and the self-tube. To investigate the corrosion variables, a thorough analysis of the device's structure and process, as well as the material, was conducted. During repairs, damaged tubes were sampled and subjected to scanning electron microscopy, X-ray diffraction, and X-ray fluorescence testing. Evaluating scanning electron microscopy pictures from the inner surface of the tube reveals deformation and a rise in the tube's inner diameter. The X-ray diffraction patterns and elemental analysis by X-ray fluorescence show that the inner surface is corroded. The external surface of the tube and analysis of the diffraction patterns in this region reveal the formation of copper oxides on the outer surface of the tubes, which, when compared to electron microscopic images, distinguishes pitting corrosion caused by acid condensation collision on the outer surface of the tube. Finally, the major cause of the fracture was pitting corrosion.

Keywords
Desalination, Copper-nickel Alloy, X-ray Diffraction, Electron Microscopy, Pitting Corrosion

1. Introduction

Desalination is employed to address these demands due to a shortage of water resources, particularly water for industrial use and drinking in the Persian Gulf states and Iran. The desalination device may have many cells depending on the demands. Each cell's principal agent is generally a condenser, which transforms steam into distilled water. The condenser is made up of several sections, each of which might be subjected to a different type of corrosion [1-4].

Thousands of copper-nickel alloys (UNS C70600) have been utilized in different engineering structures in recent decades, mostly as pipes for saltwater transport and heat exchangers in a variety of industries such as shipbuilding, electricity, desalination, and so on. This alloy has a high resistance to general and local corrosion in seawater that is oxygenated. Bacterial growth is prohibited on this alloy as a consequence of the release of copper ions and the structure of the oxide layer created during normal corrosion processes, and therefore the alloy becomes resistant to biologic corrosion. In many situations, the resilience of this alloy against erosion and corrosion has led to its application in pipelines [5-7].

On the inner side of the tubes, seawater flows. The sacrificial anodes in this device are mostly responsible for controlling galvanic corrosion across the whole package. The use of stainless steel for copper tubes has decreased galvanic corrosion significantly. Copper-nickel alloys are resistant to chloride pitting and crevice corrosion by nature. As a result, crevice corrosion in this alloy is uncommon. This alloy is not prone to stress cracking or hydrogen embrittlement in chloride or sulfide conditions, and it does not crack in ammonia settings, unlike brass. The presence of ammonia accelerates the corrosion rate of copper-nickel alloy, even though this alloy is more corrosion resistant than other copper-based alloys [8-13].

Galvanic-crevice corrosion is another kind of corrosion that commonly occurs in tubular plates. Corrosion of this sort occurs when the plate surface and self-tubes are covered with defective pits caused by tube expansion. The tubes' expansion generates a small area filled with seawater. When water is covered by base metal, crevice corrosion begins and increases with galvanic corrosion. Corrosion may eventually damage the entire tube plate. Because of the acceleration or lack of experience, corrosion may be undetected in the early phases, when only crevice corrosion develops.

One of the primary challenges in the operation of desalination is sediment accumulation in condenser tubes. Deposition inhibits heat transmission, clogs tubes, and promotes corrosion. The principal product of seawater compounds is sediment, which contains ions of hydrogen carbonate $(HCO3)^-$, calcium Ca^{+2}, and magnesium Mg^{+2}. Thermal breakdown of bicarbonate $(HCO_3)^-$ produces calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$) [14, 15].

Despite the high resistance of the copper-nickel alloy, there were occurrences of tube failure in the desalination condenser of the South Pars Gas Company's first refinery. The current research investigates the causes of this alloy's failure. Different forms of corrosion, including corrosion of the water section and corrosion of the steam, are explored in this study, which affects various sections such as water compartments, tubular plates, tube support, and the self-tube.

2. Material and methods

The tubes used in the desalination device of South Pars Gas Company's first refinery are composed of a 90/10 copper-nickel alloy, the chemical composition of which is shown in Table 1. To evaluate the corrosion of the tubes, several tubes were pulled out for re-tubing, including tubes that had been fractured and filled a long time ago as well as recently corroded tubes (Figure 1). This is a time-consuming process that must be completed with considerable care if decent results are to be obtained. Because some tubes collide with holders while pulling out, causing significant tears and distorting the route to the desired outcomes.

Figure 1. Pulling the tubes out of the apparatus

Table 1 Chemical composition of Cu90/Ni10 used in this study (mass fraction, %).

Material	**Alloying elements**								
	Ni	**Fe**	**Mn**	**Pb**	**P**	**S**	**Zn**	**C**	**Cu**
Cu90/Ni10	10.5	1.5	0.75	<0.020	<0.020	<0.020	<0.50	<0.050	Bal.

Corrosion was noticed at the 6 o'clock position corresponding to the tube cross-section during the initial examination to study the fracture of the tubes. A visual inspection and a scanning electron microscope were used to investigate the tube's internal surface corrosion products, as well as its exterior and interior surfaces (TEScan model). X-ray diffraction (Phillips-XpertPro) and X-ray Spectroscopy (EDS) tests were used to evaluate the chemical analysis of corrosion products and layers generated on the interior and outside of the tubes.

3. Results and discussion

One of the damaged tubes was chosen and cut in length to explore the causes of failure and fracture. This technique was performed multiple times before the best sample was created due to the requirement for a careful operation to minimize failure and fracture effects (Figure 2). The images obtained by the scanning electron microscope from the inner surface of the tube revealed alkaline deposits and pitting corrosion at multiple sites (Figure 3, pits are dark in color and sediments are visible in white spots).

Figure 2. The outer surface of the tube in the fracture area

Images of the external surfaces of tubes subjected to direct steam reveal various modifications. These changes are caused by the collision of water droplets with the steam and liquid droplets on top of the condenser (Figure 4). The change in the appearance of the outer surface suggests the continuance of a process, which is the collision of liquid drops and steam on the surface.

Electron microscope images of the third sample obtained precisely from the cross-section of the tube in the fractured area, reveal corrosion surrounding the tubular thickness and corrosion caused by it (Figure 5). The channel connects the pit to the inner and outer surfaces of the tube, as shown at the bottom and right sides of the figure. When the device is in use, this connection has a defect that causes the conductivity coefficient of the water to exceed the allowable limit. As a result, the device must be decommissioned and fixed.

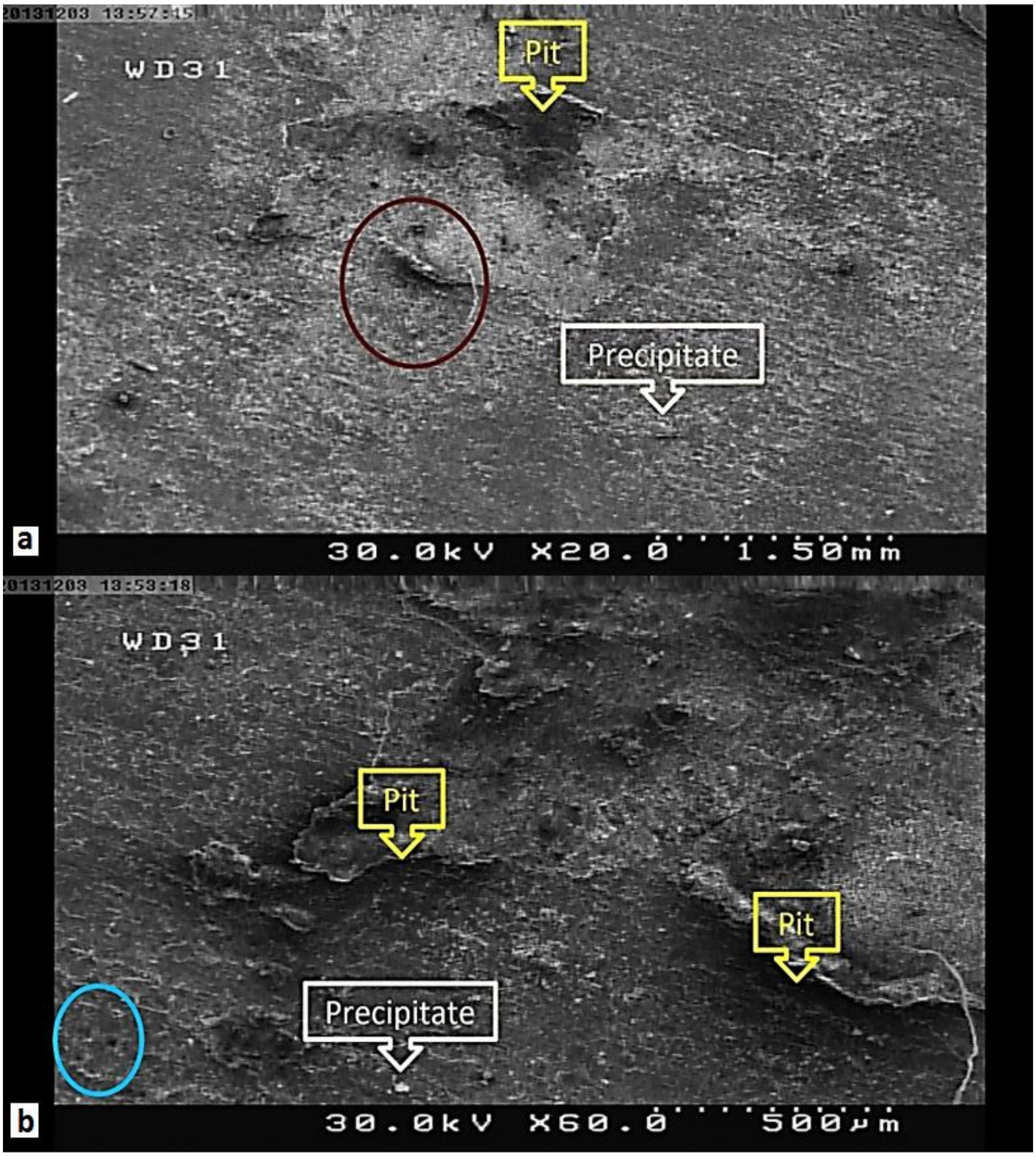

Figure 3. a) Scanning electron microscope image of the inner surface of the tube b) higher magnification on the enclosed area

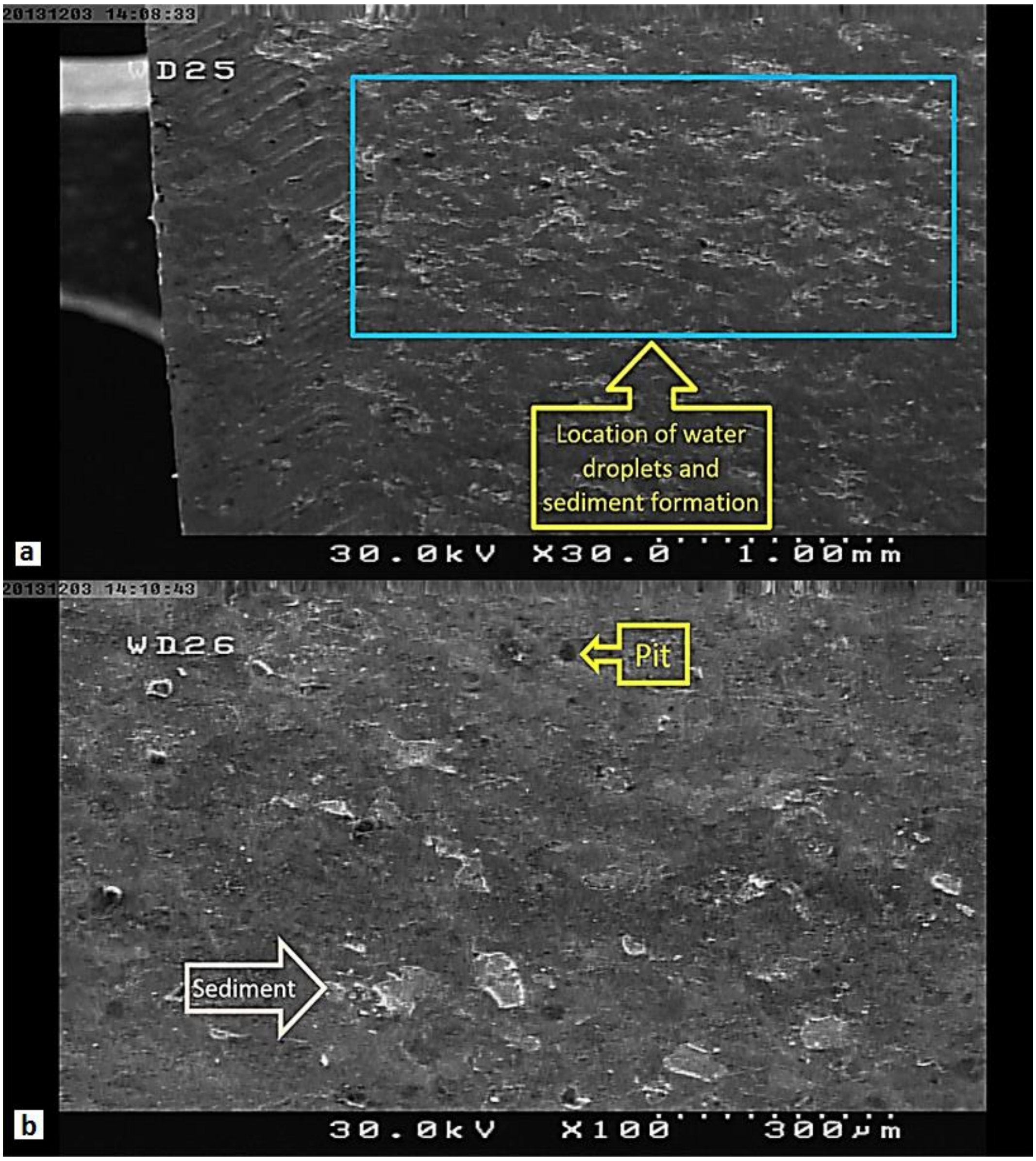

Figure 4. a) Scanning electron microscope image of the outer surface of the tube b) higher magnification on the enclosed area

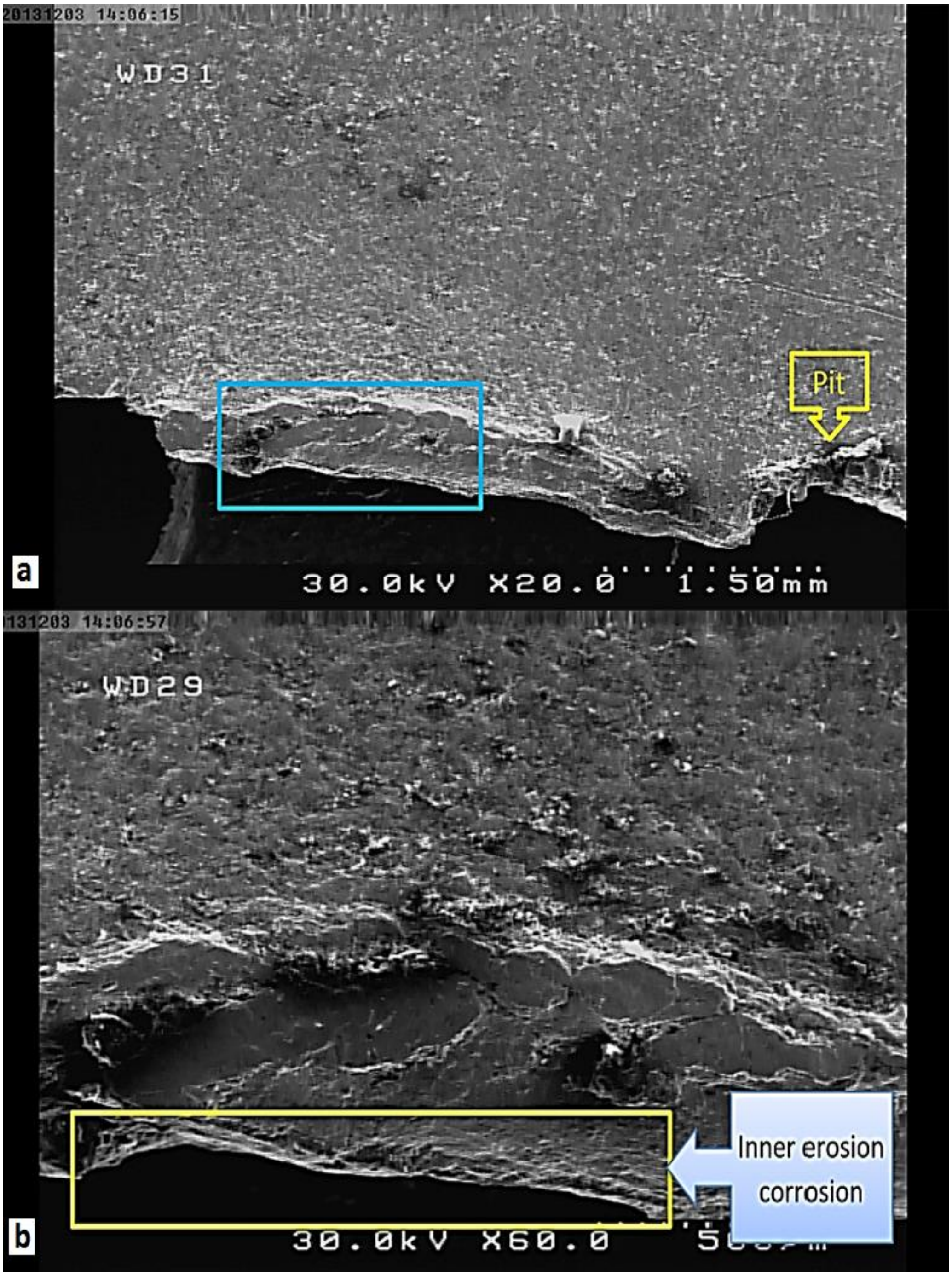

Figure 5. a) Scanning electron microscope image of the tube cross-section and the pits formed b) higher magnification on the enclosed area

The phase composition of the corrosion products was determined using an X-ray diffraction analysis. After removing the passive layer from the inner surface of the tube, this study reveals the presence of ions in water such as calcium, aluminum, carbonate, sulfide, and others. Furthermore, the presence of copper oxide indicates interior deterioration (Figure 6). Figure 7 depicts the diffraction test result for the tube's outside surface. The presence of copper oxides indicates external corrosion, while the presence of carbon dioxide results in the formation of non-condensable gases (NCG) and carbonic acid. The oxygen penetration from the device's gaskets and pores is efficient in exacerbating it. The copper oxides are easily visible on the outer surface of the tubes.

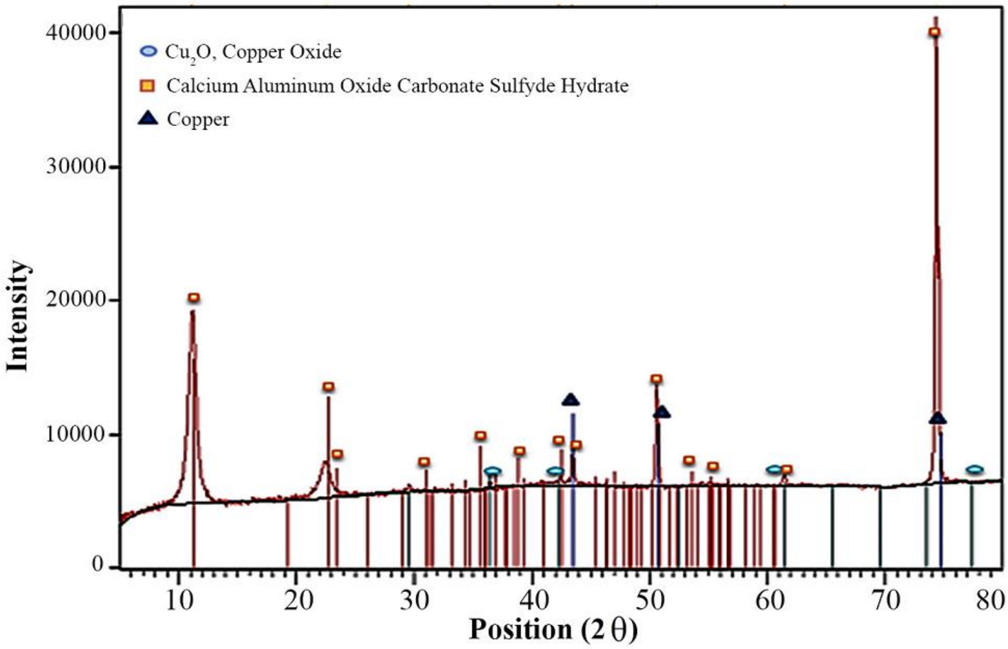

Figure 6. X-ray diffraction pattern of the passive film from the inner tube surface

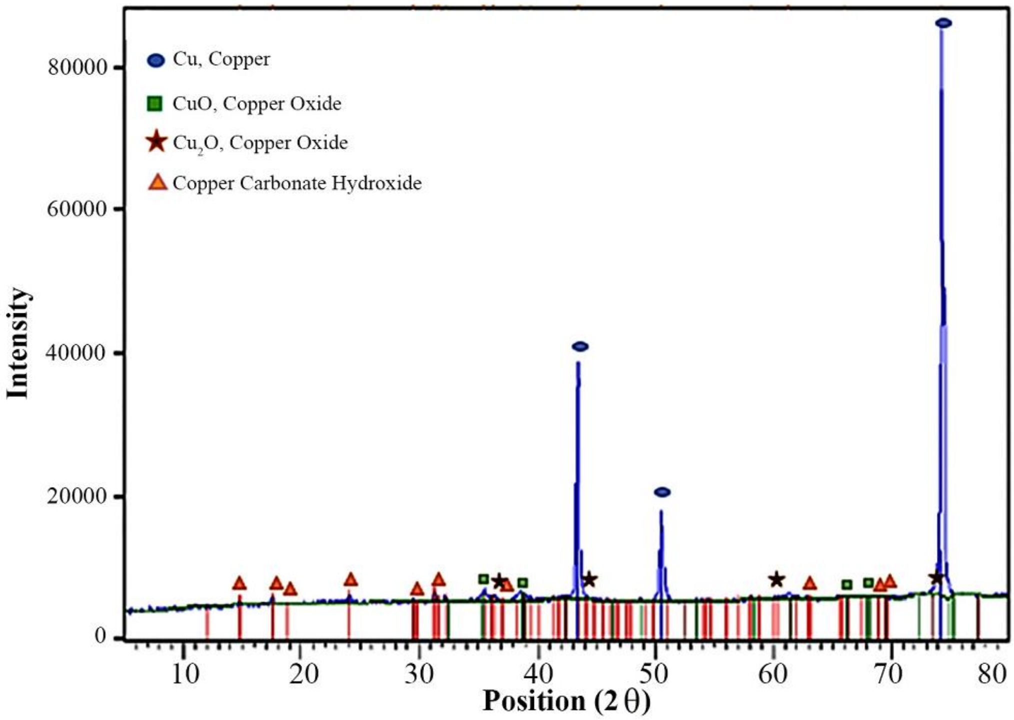

Figure 7. X-ray diffraction pattern of corrosion product on the outer surface of the tube

Figure 8 depicts the outcome of the corrosion product analysis. The results show that copper oxide is created by corrosion, copper chloride hydroxide is formed by chlorine injection in a reservoir unit, calcium, aluminum, and other minerals in salt water, and copper carbonate hydroxide is produced as a result of aquatic corruption. Copper oxides (CuO, Cu_2O) and copper hydroxide carbonate ($Cu_2CO_3(OH)_2$) are present on the surface of the tubes. The first example is caused by copper oxidation in the presence of oxygen. Oxygen entry pathways should be studied in this case. Seawater contains oxygen, and oxygen can also be delivered by gasket leakage. Oxygen, in any form, is harmful and should be avoided as much as possible. The second example is made by breaking down the carbonate of saltwater at the package temperature and settling down on the tube surface, and CO_2 gas is produced as a byproduct of carbonate breakdown. This gas forms corrosive condensates in a condenser and causes corrosion by producing corrosive carbonic acid [16].

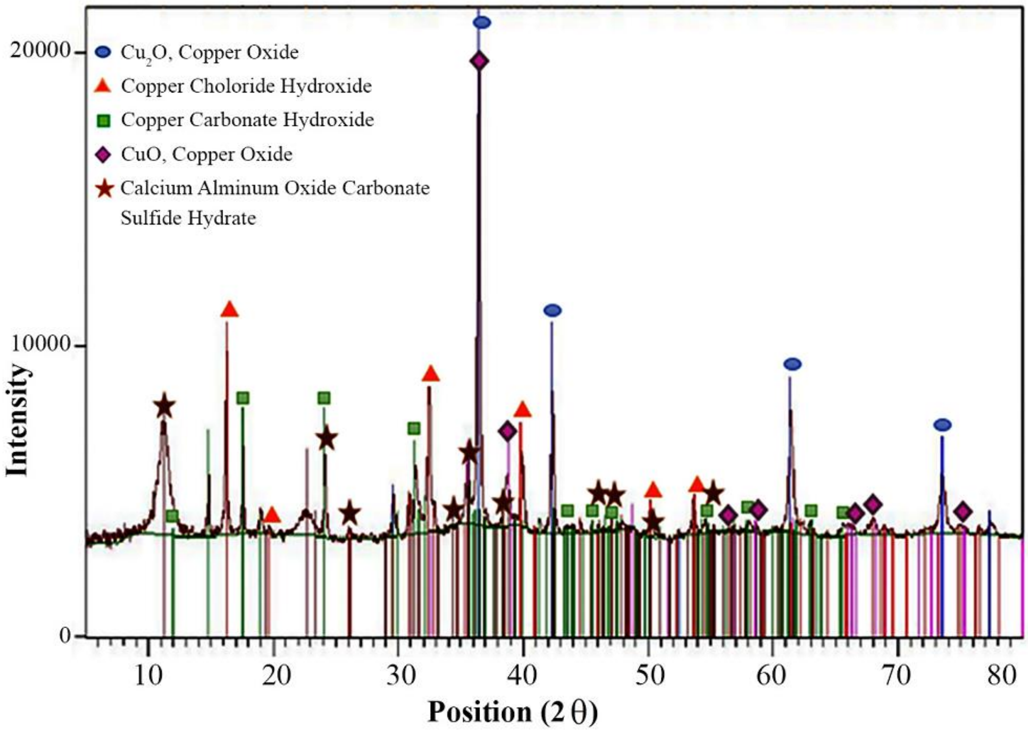

Figure 8. X-ray diffraction pattern of the corrosion products

Following visual examinations of the desalination system, we discovered that the majority of the corrosive tubes of the condensers are in the final effects, particularly in the main condenser. Meanwhile, the position of a fracture in a certain condenser is typically fixed. This position is at the lower part of the condenser tubes, at the bottom of the first pass. One of the indicators of tube failure is an increase in the electrical conductivity of distilled water, and to locate and fix the failure, the package is taken out of operation and a hydro-test is performed. The damaged tubes have become blocked (plugged). After the package has been restarted, newly damaged tubes are generally discovered near the same damaged tubes (Figure 9).

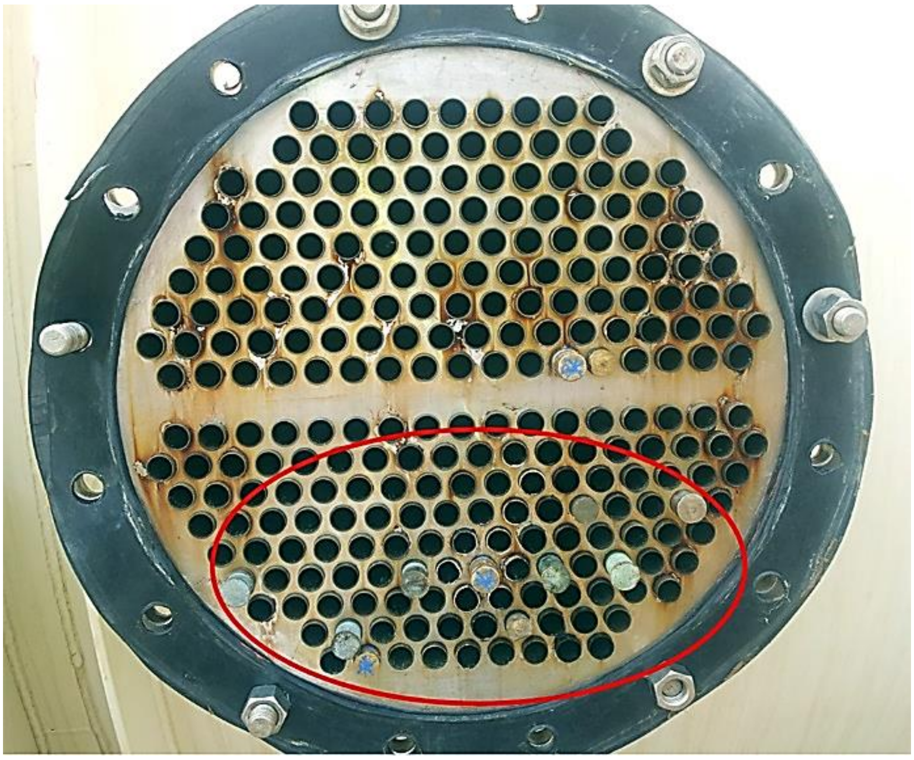

Figure 9. Location of tube failure

According to the explanation and measurements, the loss of the wall thickness of the tubes in the various passages of the condensers is due to abrasion induced by the sea entrance, as is the reduction of the outer diameter of the tubes in sections exposed to lower temperature steam. However, the outer diameter of the extruded tubes is not reduced to the same extent because the internal diameter of the tube is not raised to the same extent, and it is greater in deflection areas beyond the range covered by the tube holder.

3.1 The reasons for fracture

There is a possibility of greater galvanic corrosion, erosion-corrosion, crevice corrosion, and pitting corrosion based on the findings of the tests, prior research, and objective observations. The corrosion mechanisms described above may be separated into two types: corrosion on the waterside (within the tubes) and corrosion on the steam side (outside the tubes). We will go over them in detail below.

- Inside the tubes

Brown-colored corrosion products of iron oxide form between the tubes and tabular plates during galvanic corrosion. Figure 10 depicts this type of corrosion in the first refinery's desalination unit [6, 17, 18].

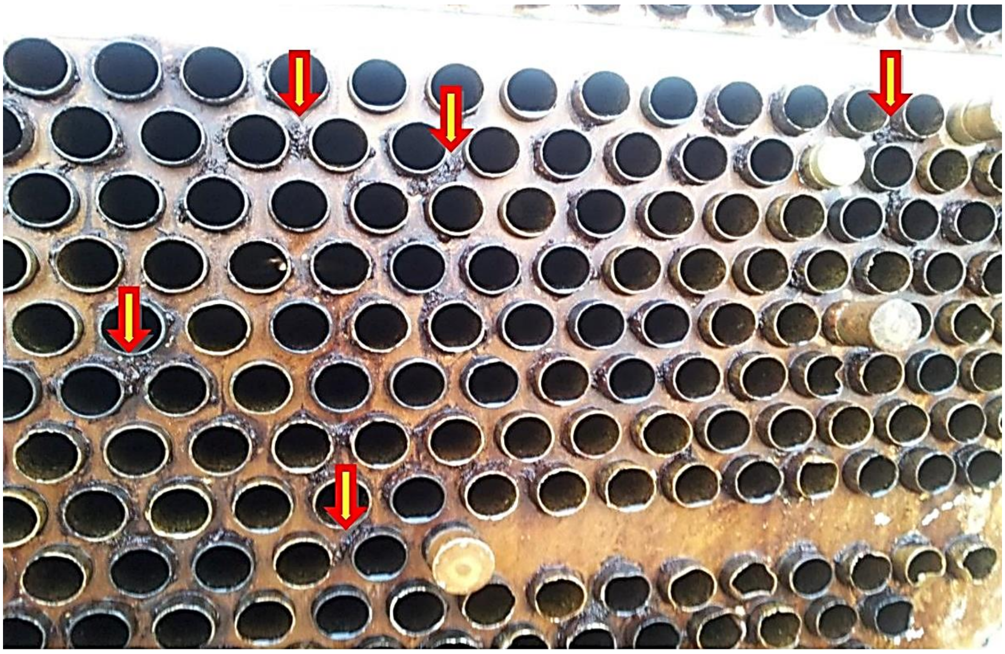

Figure 10. Galvanic-Crevice corrosion in tube plates

According to information on the alloy used in the first refinery's condenser tubes of desalination, the flow rate can reach up to 2.5 m/s and as high as 3 m/s. Higher velocities and suspended particles in the water caused by a lack of filtration and proper sedimentation in the reservoir, at the entrance to the tubes, before the developed hydrodynamic region with flow separation from the reverse pressure gradient, can cause multiple strikes to the tube wall, causing internal wear in this area in the long run. Figure 11 demonstrates this. Most failures have occurred in the region with the worst turbulence. Erosion corrosion affects the thickness of the tube body from the inside and increases the likelihood of tube breakage [5,17].

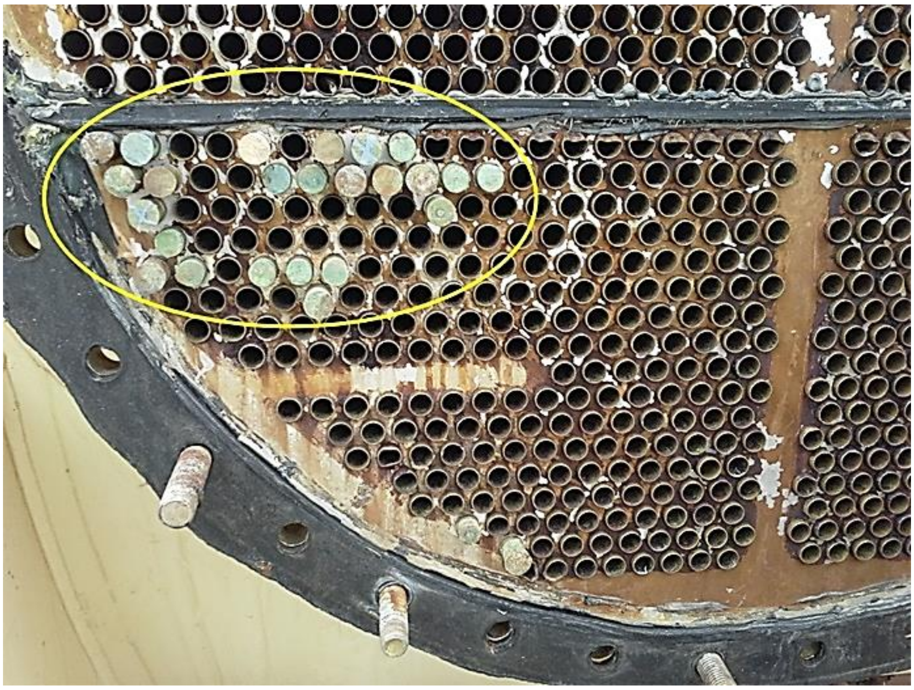

Figure 11. The turbulent area in heat exchangers exposed to abrasion

Green deposits are formed in the condenser tubes as a result of the interaction of chlorine with copper and the creation of copper chloride ($CuCl_2$) deposition, and corrosions are noticed after cleaning the deposits below them. This issue is caused by a lack of control over free chlorine content by sodium bisulfate injection for chlorination at the desalination device's entry. Also, due to the absence of circulations in this condenser with ordinary or distilled water in the first two passes, this green deposit is noticed in the rear cover of the sediment in the main condenser tubes of package C of the first refiner (Figure 12). It is worth noting that owing to the continual monitoring of free chlorine injection and sodium bisulfate, this sort of corrosion in the first refinery's desalination equipment is quite low. The absence of drainage and stagnation of water when the device is out of service, the failure to wash the path with proper water, the failure to dry the device after washing, the absence of harmful gases, and the failure to compress the compartment of the device with nitrogen gas to prevent the introduction of moisture and corrosion are the causes of this corrosion [19, 20].

Figure 12. Partial selective corrosion in desalination tubes

- Out of the tubes

This section will look into corrosion on the exterior of the tubes (steam). There are oxygen, carbon dioxide, nitrogen, and other gases in the steam section. Figure 13 depicts a tube failure induced by an environmental attack at the tube connection point to the tube holder, which is produced by crevice corrosion. The areas under the tube holder did not change in diameter, as indicated in the figure, however, the portions near the outside edge of the tube decreased in diameter owing to crevice corrosion and were cracked due to pitting corrosion. Each desalination equipment offers a unique set of effects. Each desalination device effect is composed of three major components: a condenser, an evaporator, and a flash chamber (Figure 14).

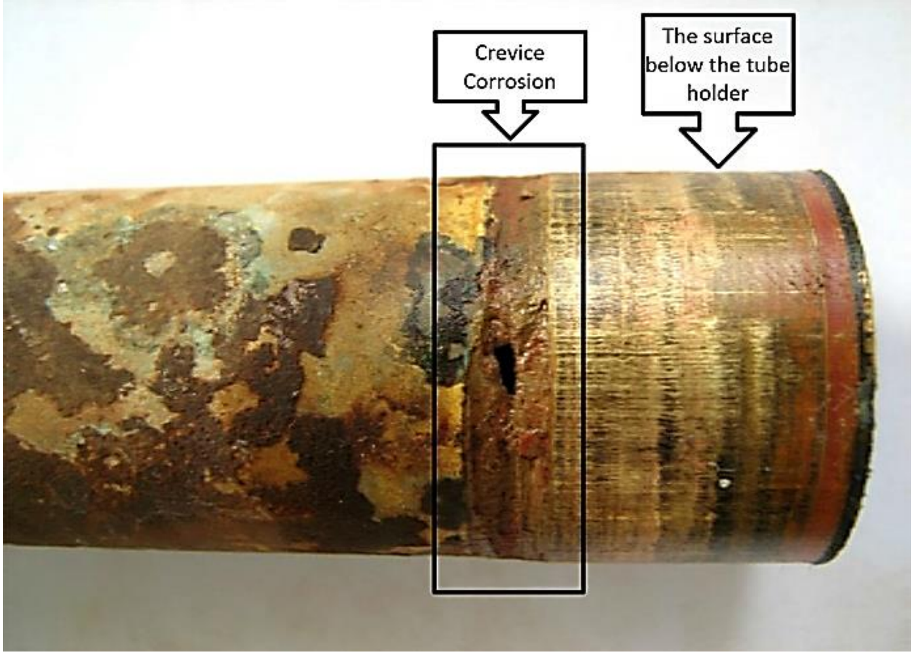

Figure 13. Crevice corrosion in desalination tubes

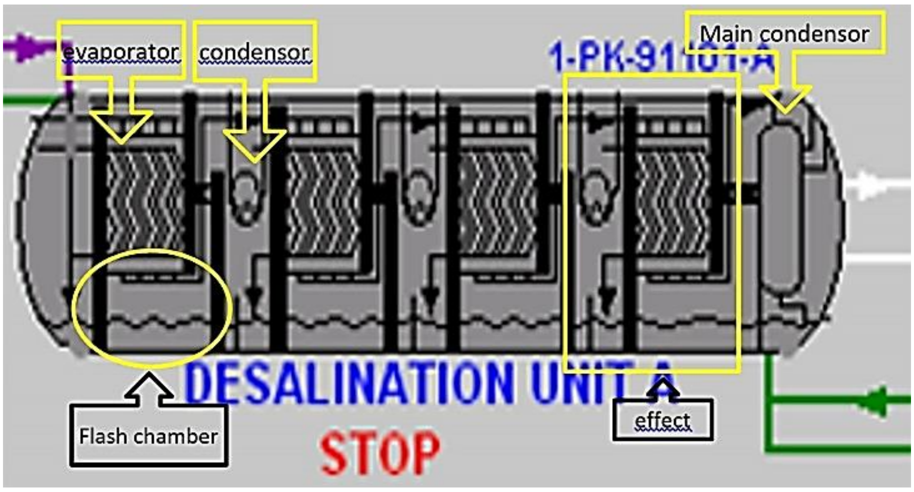

Figure 14. Schematic image of different parts of desalination unit

The effect's entrance is made up of seawater and steam. The steam is heated by the saltwater in the evaporator and becomes distilled water in the first effect. It then flows into the enclosure through the channel embedded in it and based on the pressure difference in the package, it moves to the last effect, which eventually delivers the device's product. In all impacts, this cycle is repeated. Each effect has its seawater input, although the second effect flushes steam from the flash unit's concentrated saline water. Non-condensable gases such as CO_2, N_2, O_2, and others can be found in saltwater. When polluted with water, hydrogen sulfur (H_2S) and ammonia (NH3) might be present, causing severe corrosion. To control them, chlorine is pumped into saltwater. As illustrated in Figure 15, gases in seawater, including CO_2, are released from the saltwater in the flash chamber [21]. Carbonic acid is formed when carbon dioxide reacts with existing water (Eq. 1).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (1)$$

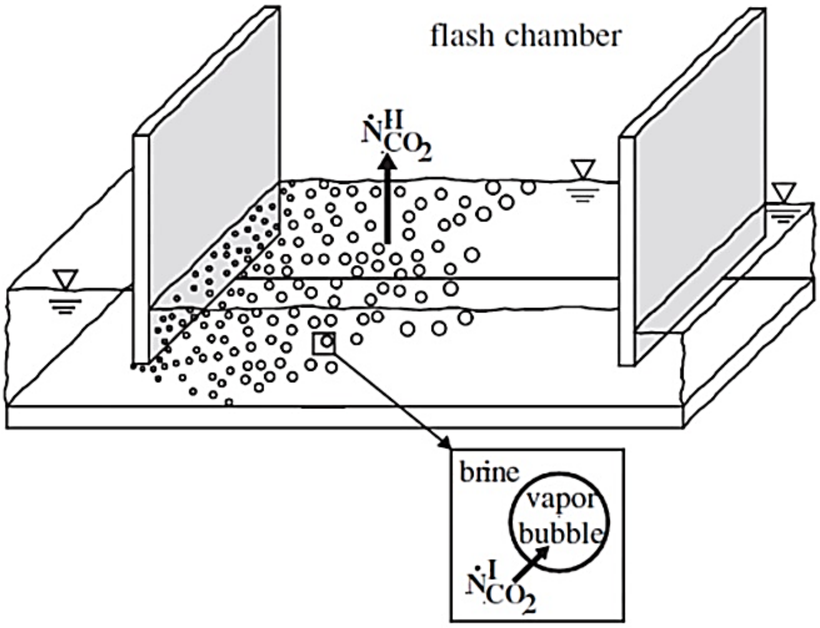

Figure 15. Condensate flow in desalination flash chamber

The heat source (steam) for the following phase is generated by the steam trapped in the flash unit with corrosive gases. Of course, before proceeding to the next stage, they must pass through a condenser, which produces distilled water by condensation and separates non-condensable gases. There is also an outgoing channel for non-condensable gases that do not condense into the main condenser and transforms it into a condenser under the same circumstances at a certain temperature. Finally, non-condensable gases that have not been converted to liquid in either of these zones are separated by the system's two-stage output. Existing condensers have compartments with a gas trap, and the fluid remains in them (Figure 16).

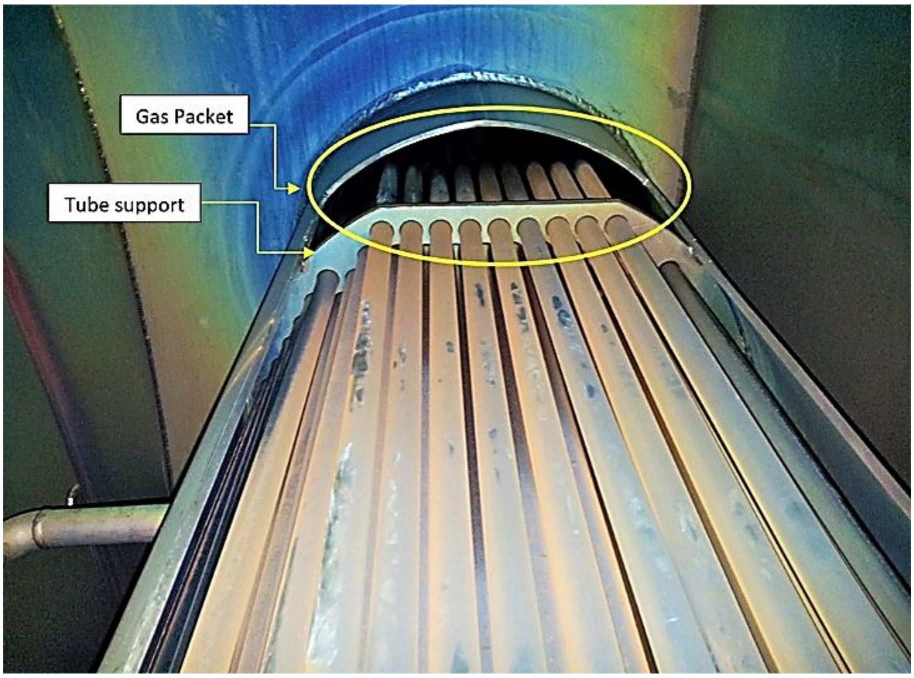

Figure 16. Heat exchanger interior

Gas traps typically form between the support tubes and the tubular plate on the device's side. Corrosion conditions are comfortable due to the corrosive gas environment and the ideal time in this location. As seen in Figure 17, there is substantial corrosion in this area.

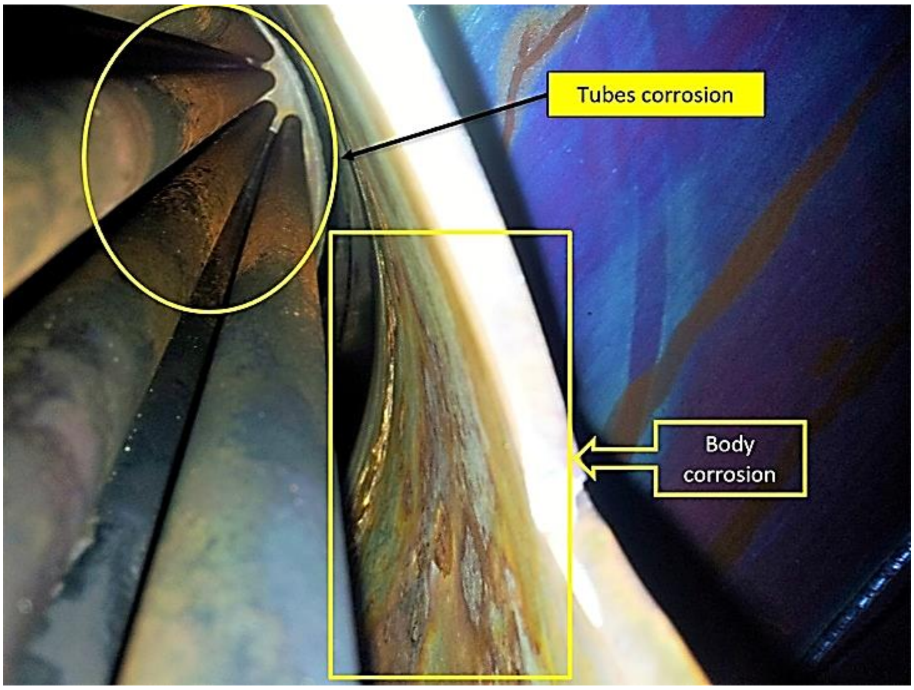

Figure 17. Another view of the heat exchanger interior

The tubes in the condenser are arranged horizontally. Because of the lower temperature of the condenser relative to the surrounding environment, steam and non-condensable gases are converted to liquid in the atmosphere and forced out of the condenser's low output. During steam distillation, water droplets from the higher tubes collide with the outer surface of the lower tubes, as seen in Figure 18. Therefore, we will have general corrosion on the surface of the tubes [21-23].

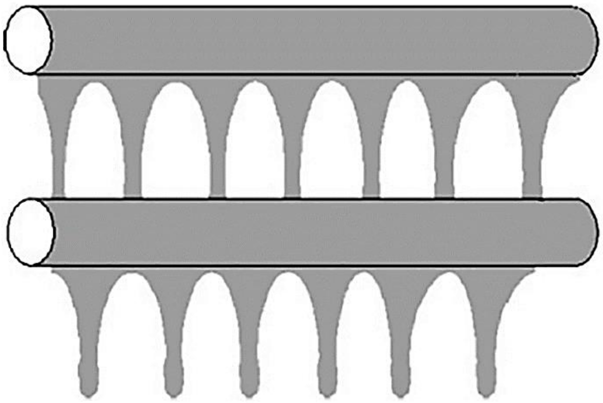

Figure 18. Condensate flow in desalination flash chamber

The tubes are not perfectly aligned, and their inclination is toward the gas trap chamber placed on the device's sidewalls, according to the findings. As a result, additional droplets gather in these places, and their severity diminishes after colliding with the supporting tube surface and tubular plate. Drops that fall from the top tubes induce corrosion in the lower tubes. We notice the maximum corrosion rate in this location due to the nature of the droplets and the corrosive acidic environment. The corrosion process proceeds in such a way that, in an anodic reaction, the ionization of each copper atom results in the release of two electrons and the production of the copper ion at the surface (Eq. 2).

$$2\mathrm{Cu} = 2\mathrm{Cu}^{2+} + 4\mathrm{e}^- \qquad (2)$$

In the cathode reaction, free electrons are also collected and reactivated with oxygen and form a hydroxide ion (Eq. 3).

$$\mathrm{O}_2 = 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^- = 4\mathrm{OH}^- \qquad (3)$$

In the oxidation step, Cu^{2+} and OH^- are put together and create copper oxide (Eq. 4).

$$2\mathrm{Cu}^{2+} + 4\mathrm{OH}^- = 2\mathrm{CuO} + 2\mathrm{H}_2\mathrm{O} \qquad (4)$$

The resulting oxide reacts rapidly with carbon dioxide in the water and causes the Cu^{2+} ion to be separated (Eq. 5).

$$2\mathrm{CuO} + 2\mathrm{H}_2\mathrm{CO}_3 = 2\mathrm{Cu}^{2+} + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{HCO}_3^- \quad (5)$$

This corrosion, which is a pit, has been observed in many of the desalination condenser tubes in the first refinery. In Figure 19, the formation of copper oxide (CuO), a black substance, and copper oxide (Cu_2O), which is a red substance, is evident.

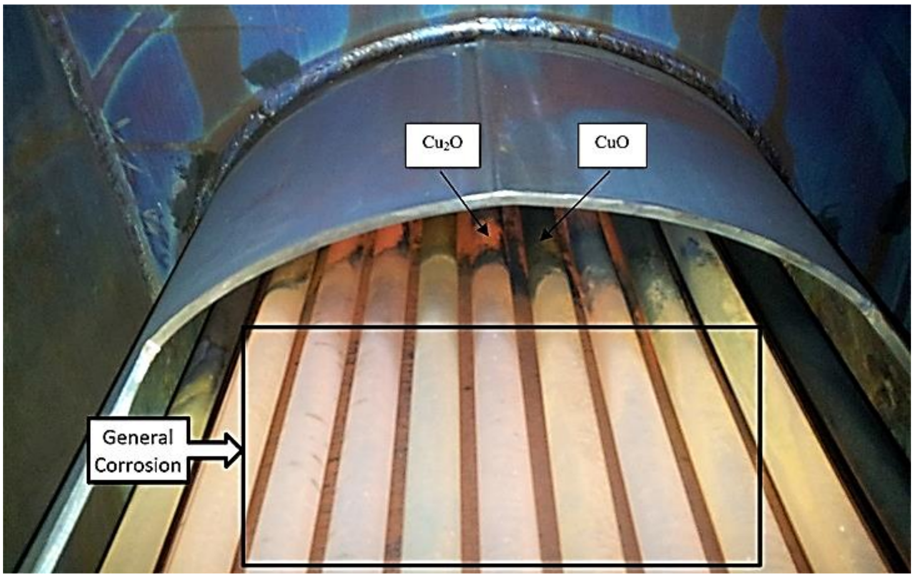

Figure 19. Copper oxides and general corrosion

4. Conclusions

The many forms of corrosion that affect different elements of the desalination plant of the South Pars Gas Company's first refinery, such as water compartments, tubular plates, support tubes, and the self-tube, were investigated in this study, and the following results were obtained:

1. 1. The deformation and expansion of the internal diameter are presumed by studying the SEM pictures from the inner surface of the tube. XRD and XRF material analyses reveal abrasive corrosion at the interior surface.
2. A very minor amount of selective separation was discovered, which cannot be regarded as the primary failure reason.
3. Galvanic and crevice corrosions were discovered, with the greatest concentrations on the tubes' and tabular plate's exterior edges.
4. Crevice corrosion was noticed at the contact surface of the tube with the support tubes and tabular plate by inspecting the external surface of the tube and the XRD data. One of the most common causes of tube failure is crevice corrosion.
5. The existence of pitting corrosion is assumed based on the aforementioned reasons and their proofs with XRD results indicating the presence of copper oxides on the external surface, and its adaptation to SEM images indicating the pitting corrosion caused by the collision of acid condensate with the outer surface of the tube.
6. To summarize, the primary reasons for the failure of the desalination tubes of the South Pars Gas Company's first refinery are pitting corrosion, crevice corrosion, and erosion-corrosion, in that order.

5. References

[1] El-Dahshan, M.E. 2001. Corrosion and scaling problems present in some desalination plants in abu dhabi. Desalin. 138: 371-377.
[2] Hassan, A.M. and Malik, A.U. 1989. Corrosion resistant materials for seawater ro plants. Desalin. 74: 157-170.
[3] Zhang, Y., Wang, L. and Presser, V. 2021. Electrocatalytic fuel cell desalination for continuous energy and freshwater generation. Cell Reports Physical Science. 2(5): 1-9.
[4] Zapata-Sierra, A., Cascajares, M., Alcayde, A. and Manzano-Agugliaro, F. 2021. Worldwide research trends on desalination. Desalin. 519: 1-16.
[5] Hodgkiess, T. and Vassiliou, G. 2005. Complexities in the erosion corrosion of copper-nickel alloys in saline water. Desalin. 183(1-3): 235-247.
[6] Elragei, O., Elshawesh, F. and Ezuber, H.M. 2010. Corrosion failure 90/10 cupronickel tubes in a desalination plant. Desalin. Water Treat. 21(1-3): 17-22.
[7] Liu, Y., Alfantazi, A., Schaller, R.F. and Asselin, E. 2020. Localised instability of titanium during its erosion-corrosion in simulated acidic hydrometallurgical slurries. Corros. Sci. 174: 1-12.
[8] Pimputkar, S., Malkowski, T.F., Griffiths, S., Espenlaub, A., Suihkonen, S., Speck, J.S. and Nakamura, S. 2016. Stability of materials in supercritical ammonia solutions. The Journal of Supercritical Fluids. 110: 193-229.
[9] Abouswa, K., Elshawesh, F., Elragei, O. and Elhood, A. 2007. Corrosion investigation of cu–ni tube desalination plant. Desalin. 205(1-3): 140-146.
[10] Mantzavinos, D., Hodgkiess, T. and Lai, S.L.C. 2001. Corrosion of condenser tube materials in distilled water. Desalin. 138(1): 365-370.
[11] Ma, A.L., Jiang, S.L., Zheng, Y.G. and Ke, W. 2015. Corrosion product film formed on the 90/10 copper–nickel tube in natural seawater: Composition/structure and formation mechanism. Corros. Sci. 91: 245-261.
[12] Al-Odwani, A., El-Sayed, E.E.F., Al-Tabtabaei, M. and Safar, M. 2006. Corrosion resistance and performance of copper–nickel and titanium alloys in msf distillation plants. Desalin. 201(1-3): 46-57.
[13] Kear, G., Barker, B.D., Stokes, K.R. and Walsh, F.C. 2007. Electrochemistry of non-aged 90–10 copper–nickel alloy (uns c70610) as a function of fluid flow. Electrochim. Acta. 52(7): 2343-2351.
[14] Liu, M. and Gadikota, G. 2020. Single-step, low temperature and integrated co2 capture and conversion using sodium glycinate to produce calcium carbonate. Fuel. 275: 1-10.
[15] Anonymous. 1999. Studies in Physical and Theoretical Chemistry. Chapter 12 decomposition of carbonates.
[16] Nair, M. and Kumar, D. 2013. Water desalination and challenges: The middle east perspective: A review. Desalin. Water Treat. 51(10-12): 2030-2040.
[17] Parvizi, M.S., Aladjem, A. and Castle, J.E. 2013. Behaviour of 90–10 cupronickel in sea water. Int. Mater. Rev. 33(1): 169-200.
[18] Karthick, S., Muralidharan, S. and Saraswathy, V. 2020. Corrosion performance of mild steel and galvanized iron in clay soil environment. Arabian Journal of Chemistry. 13(1): 3301-3318.

[19] Alfantazi, A.M., Ahmed, T.M. and Tromans, D. 2009. Corrosion behavior of copper alloys in chloride media. Mater. Des. 30(7): 2425-2430.

[20] Wilhelm Schleich, K.M. and Powell, C. 2007. CuNi 90/10: How to avoid typical failures of seawater tubing systems and marine biofouling on structures A2 - Féron, D. In: Corrosion Behaviour and Protection of Copper and Aluminium Alloys in Seawater. New york: Woodhead Publishing.

[21] Glade, H., Meyer, J.-H. and Will, S. 2005. The release of co2 in msf and me distillers and its use for the recarbonation of the distillate: A comparison. Desalin. 182(1-3): 99-110.

[22] Tian, J., Wang, L., Sun, W., Yang, Y., Liu, Z., Wang, G., Zhao, L., Zhou, Y. and Liu, G. 2019. Failure analysis of steam jet pump at top of crude oil vacuum distillation tower. Engineering Failure Analysis. 103: 9-19.

[23] Al-Moubaraki, A.H. and Obot, I.B. 2021. Corrosion challenges in petroleum refinery operations: Sources, mechanisms, mitigation, and future outlook. Journal of Saudi Chemical Society. 25(12): 1-28.