Structural Strength Degradation of Oil and Gas Refinery Equipment. Case Study: Heat Exchanger Tubes of Hydrocarbon Vapor

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Structural Strength Degradation of Oil and Gas Refinery Equipment. Case Study: Heat Exchanger Tubes of Hydrocarbon Vapor

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Abstract: Heat exchangers, crucial equipment in oil and gas refinery facilities, play a pivotal role in ensuring reliable energy production. Any structural issues with these heat exchangers can disrupt production and potentially lead to energy supply interruptions. The aim of this research is to investigate the degradation of structural strength in heat exchangers that occurs during their operational lifespan. Several tests, including hardness, metallography, chemical analysis, tensile testing, and SEM analysis, were conducted to assess the condition of the heat exchanger tubes. The results revealed that the tubes had become coated with deposits that reacted with the tube walls, resulting in rust formation. Consequently, the walls of the tubes underwent thinning, ultimately leading to leaks. In conclusion, the structural strength degradation of the heat exchanger tubes was primarily caused by corrosion occurring beneath these deposits.

Keywords: structure; strength; deposit; degradation; failure; heat exchanger.

1. Introduction

In the realm of energy production, the seamless operation of equipment is indispensable. These equipments underpin all processing activities, ensuring the sustained production of energy and guaranteeing reliability is essential for the continued operation of the production system. However, as crucial components or structures within these systems gradually lose their strength during operation, they reach a point where they can no longer support the operational load, resulting in sudden failure. Such failures can lead to the complete shutdown of the entire system[1)]. The resulting potential energy supply shortage can have a profound impact on numerous activities within the country. To mitigate this risk, it is imperative to study structural strength degradation to prevent sudden failures of the structures or components that enable the production system to operate. Several factors can contribute to the degradation of components or structures, particularly in the context of energy production equipment such as [2-5)]:

- **Operational load:** In structural equipment, operational load refers to force or weight, while in processing equipment like pipes, tubes, or tanks, load can be defined as working pressure. Operational load is known to have varying effects on strength degradation, depending on the type of load such as static, dynamic, shear, or impact. Each type of load induces different failure mechanisms and stress levels that can cause failure.
- **Operational temperature:** Elevated operational temperatures provide atoms of materials with sufficient energy to diffuse, leading to microstructure changes such as expansion, grain growth, phase transformations, and other atomic diffusion phenomena. These changes significantly impact the mechanical properties of materials. Conversely, extremely low temperatures or cryogenic conditions can render ductile materials brittle.
- **Operational environment:** Energy production equipment is frequently exposed to various environments, including chemicals, corrosive agents, or mechanically abrasive materials. All of these factors have the potential to degrade the strength of components or structures.

It's important to note that strength degradation in energy production facilities is typically the result of a combination of several factors, with one factor acting as the primary cause and others accelerating the rate of degradation[3-6)]. The novelty of this research lies in the development of an analysis method that combines all potential contributing factors to identify the root cause and degradation rate. This method is then applied through in-depth analysis based on selected evidence strongly indicating the initial failure.

This research focuses on the study of strength degradation in heat exchanger tubes that failed during operation in an Indonesian oil refinery unit. Heat exchangers play a critical role in transferring heat between a source and a working fluid to achieve the desired temperature, serving in both cooling and heating processes. As a result, factors such as pressure, temperature, and environmental considerations like corrosion and oxidation are implicated in strength degradation[7-11]. The investigation found that two heat exchanger tubes had leaked, rendering them inoperative and necessitating the shutdown of the entire system. Historical data indicates that these tubes had been in operation for six years prior to the leakage.

This work presents the identification of the fundamental factors that led to the heat exchanger tube's failure. By doing so, it aims to facilitate the avoidance of similar issues in the future and promote swift decision-making, thereby ensuring the continuous distribution of oil to maintain a sustainable energy supply in Indonesia[12].

2. Materials and methods

The specimens used for examination in this research were extracted from two heat exchanger tubes that had experienced leakage. These specimens were sourced from an oil refinery in Indonesia and were assigned specimen codes E-2-10 and E-2-11. These tubes were located in the lower section of the heat exchanger, as illustrated in Figures 1 and 2.

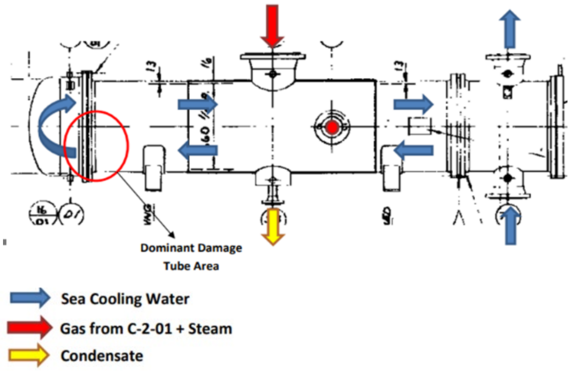

Fig. 1: Schematic figure of gas, condensate and water flow in heat exchanger.

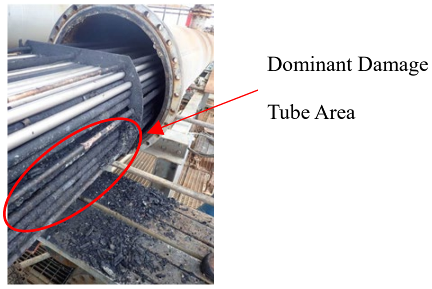

Fig. 2: Location of leaked tubes on bottom part of tube bundle as shown in red circle in Fig.1.

Table 1 contains comprehensive information regarding the material specifications, technical data, and operational parameters of the heat exchanger tubes under investigation. Notably, the table highlights that the heat exchanger operated for a relatively short period at medium operational temperatures and relatively low pressures. In this context, operational pressure and temperature are not expected to be the primary factors contributing to the structural strength degradation of the tubes[1,3,5]. However, it is imperative to validate this under real conditions through thorough examinations and further laboratory testing on the leaked tubes.

Table 1. Technical data and operational parameters

Heat Exchanger Number	**E-2-10**	**E-2-11**
Material specification	ASTM B111	ASTM B111
Outside diameter (mm)	25.4	25.4
Thickness (mm)	2.11	2.11
Tube side service	Sea water	Sea water
Shell side service	Hydrocarbon vapor	Hydrocarbon vapor
Operational temperature of tubes (℃)	In:25.56	In:35.56
	Out:45	Out:45
Operational temperature of shell (℃)	In:150	In:150
	Out:41.6	Out:49
Operational Pressure of (kg/cm²)	Tube:0.43	Tube:1.2
	Shell:2.5	Shell:2.5
Flow rate in tube (m/s)	2.05	1.62
Time of operation (Y)	6	6

The research methodology employed in this study centers around the implementation of root cause analysis. This approach entails the examination of all potential aspects that might have contributed to the degradation of structural strength. Typically, major sources of failure arise from issues such as incorrect design, manufacturing defects, improper operational parameters, and incorrect material specifications[3,13-15]. In this particular study, design and manufacturing aspects were not scrutinized, as the unit's reliability had already been confirmed by the owner before installation, affirming the integrity of these two factors. As a result, the research focused exclusively on operational factors. Once evidence of the most dominant factor was identified, deeper examinations were conducted to uncover additional valuable scientific insights. To execute this method, a series of tests and examinations were performed, including:

- **Visual and Macrographic Examinations:** These were conducted using an optical stereo microscope. Specimens were carefully cut on the fracture surface, especially in areas suspected of containing the initial crack.
- **Metallographic Examinations:** Optical microscopes were utilized to analyze cross-sections and longitudinal planes of the tube, allowing for the monitoring of microstructure changes.
- **Chemical Composition Tests:** These tests were carried

out on the tube's base metal using Optical Emission Spectroscopy to validate its compliance with ASTM B111 material specifications.

- **Hardness Tests:** The Vickers method was employed to assess the current mechanical properties of the material.
- **Tensile Tests:** Universal testing machines were used to evaluate the current strength properties of the material.
- **Scanning Electron Microscopic (SEM) Analysis:** This analysis, coupled with Energy Dispersive X-ray Analysis (EDX), delved into a deeper exploration of fracture surfaces.

All the results obtained from these examinations and tests were subsequently subjected to rigorous analysis to identify the most dominant factor responsible for the initial crack or leak, as well as any contributing factors that accelerated the further degradation of the two tubes.

3. Results and discussion

After conducting a series of tests and examinations, a wealth of scientific data was acquired, providing accurate evidence for the analysis of the root cause behind the leakage in the heat exchanger tubes. The results of the chemical composition tests indicated that both tubes, E-2-10 and E-2-11, conformed to the specifications of ASTM B111 Copper Alloy UNS number C70600[7)]. The composition details are presented in Table 2. No suspicious elements that might have contributed to the initial leakage were found. These results confirm that the failure was not caused by incorrect material specifications, as ASTM B111 Copper Alloy UNS Number C70600 is commonly used for heat exchanger tubes[16-20)].

Table 2. Chemical composition test result of both tubes.

Elements	ASTM B111 Specification	Tube E-2-10	Tube E-2-11
Mn (wt%)	1 max	0.73	0.70
Fe (wt%)	1-1.8	1.4	1.21
Pb (wt%)	0.05 max	0.02	0.02
Zn (wt%)	1 max	0.02	0.02
Ni+Co (wt%)	9-11	9.23	9.23
Cu (wt%)	Remainder	Remainder	Remainder

The results of the hardness tests showed that tube E-2-10 exhibited an average hardness within the range of 83.8 - 122.8 HV, while tube E-2-11 had an average hardness ranging from 85.8 – 91.3 HV. Both hardness values fell within the specifications outlined by ASTM B111, which is typically around 85 to 140 HV[7)]. However, the tensile test results revealed differences between the two tubes. Tube E-2-10 had an average tensile strength of 354 MPa, whereas tube E-2-11 exhibited a tensile strength of 239 MPa. The tensile strength specification for this material typically falls between 340-380 MPa. This discrepancy indicates that the strength of tube E-2-11 was lower than the ASTM B111 specification, suggesting the occurrence of strength degradation.

Visual and macrographic examinations yielded valuable insights. Tube E-2-10 displayed holes and wall thinning (Fig.3), with the initiation of wall thinning identified on the inner surface of the tube, propagating outward to eventually cause leakage (Fig.4). Additionally, black and green deposits were found around the hole area.

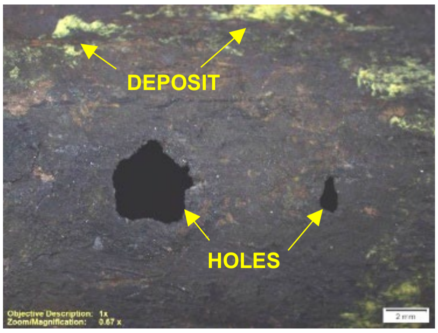

Fig. 3: Holes that were found on the leakage area of tube E-2-10. This area was covered by black and green deposits.

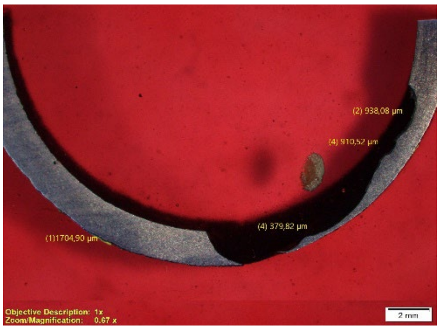

Fig. 4: Cross section of holes area showing wall thinning which initiated from the inner surface of the tube.

Tube E-2-11 exhibited similar deposit-related issues, with black and green deposits covering a larger area and more severe wall thinning compared to E-2-10 (Fig.5).

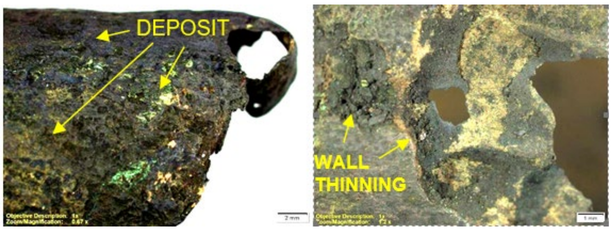

Fig. 5: The failure area of tube E-2-11 was covered by black and green deposits, while wall thinning was also found in this area.

The deposits covered almost the whole outside surface of tubes, especially on the bottom part of the heat exchanger with different quantities as seen in Fig.2. Energy Dispersive Spectroscopy (EDS) analysis confirmed that the deposits were primarily composed of corrosion products of Cu-Ni alloy elements, including carbon, oxygen, and sulphur[2,21-26)]. The detailed results are presented in Fig. 6-7 and Table 3.

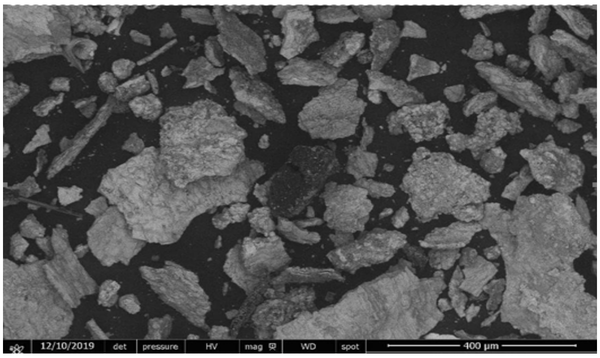

Fig. 6: SEM analysis result on flakes of outside tube deposit.

Table 3. Chemical test result on deposits by EDS

Element (wt %)							
Cu	Ni	Fe	C	O	S	N	Cl
43.0	9.6	3.6	19.4	13.4	11.0	0.1	0.3

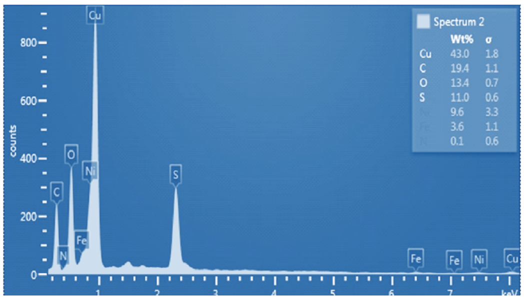

Fig. 7: Spectrum of EDS on flakes of outside tube deposit

Metallographic examination results indicated that both tubes exhibited a Cu single-phase α microstructure, typical of Cu-Ni alloys[7,11,15)]. No indications of microcracks or other manufacturing defects were found in the microstructure, ruling out these factors as contributors to the initial leakage. However, material degradation was evident, as indicated by the presence of deposits on either the inner or outer surface of the base metal. These deposits cut trans-granularly across the grain of the microstructure, separating from the base metal and causing wall thinning (Fig.8). The presence of deposits on the surface resulted from a continuous reaction between the base metal and the surrounding atmosphere or media which made direct contact with the surface of metal[27-29)]. This reaction produced deposits as it progressed during operation[19-21)].

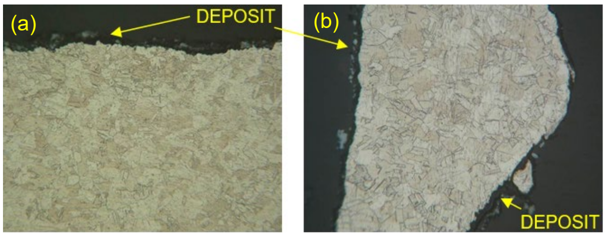

Fig. 8: (a) Microstructure of tube consist of Cu single phase α, (b) deposit on the inner and outer surface.

The main cause of leakage in both tubes, E-2-10 and E-2-11, was found to be similar: it initiated with the formation of deposits and was followed by wall thinning and eventual leakage. The rate of wall thinning was dependent on the reactivity of the element connected with the base metal in a specific area and the thickness of deposits. This rate of wall thinning aligned with the likelihood of leakage[27-29)]. Copper-based alloys typically form a passive layer, Cu_2O, in brown color on the surface. When this passive layer is removed, the metal surface makes direct contact with corrosive elements, leading to corrosion and the formation of corrosion products referred to as patina. Patina is characterized by various colors, with a typical patina being greenish-blue (tosca)[21,22)]. The transformation process from passive layer Cu_2O to patina was visually evident by the change in color on the surface of the tubes, ranging from light red to pink, orange, blue, green, and purple, with permanent patina typically appearing greenish-blue (tosca), as observed in Fig. 9. The reaction of Cu base alloy with reactive elements like oxygen, carbon and sulphur can be accelerated with the presence of chlorine (Cl) to form a patina. In this research, chlorine was introduced through contact with seawater[12,21)]. Chlorine reacted with copper base alloy to form atacamite ($Cu_2(OH)_3Cl$), which is a form of green-colored patina called hydroxychloride. Additionally, high humidity in the heat exchanger, caused by the presence of seawater inside the tube and hydrocarbon vapor outside, accelerated the corrosion rate of the tubes.

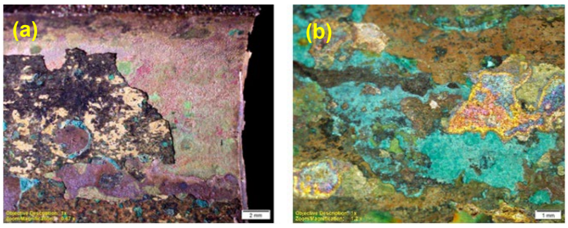

Fig. 9: (a) Transformation of a passive layer to different levels of patina, (b) permanent patina is formed and identified with tosca color.

Detailed reactions of patina formation and the color changes can be explained by reactions[2,8,15)]:

$$\text{Cathodic: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

$$\text{Anodic: } Cu + 2OH^- \rightarrow Cu(OH)_2 + 2e^- \tag{2}$$

$$2Cu(OH)_2 + 2e^- \rightarrow Cu_2O + 2OH^- + H_2O \tag{3}$$

All of the above reactions can be combined as:

$$3Cu + H_2O + O_2 \rightarrow Cu_2O + Cu(OH)_2 \tag{4}$$

Cu_2O: Cuprous Oxide/Cuprite, color: red – pink

$Cu(OH)_2$: Copper Hydroxide

Patina also forms when SO_2 is available in the atmosphere or environment, and the humidity on the metal's surface is high. The patina formation reaction continues from reaction no (4) as:

$$2Cu_2O + O_2 \rightarrow 4CuO \quad (5)$$

The result of the reaction is Cupric Oxide, color: light black

$$Cu + S \rightarrow CuS \quad (6)$$

$$2CuO + CO_2 + H_2O \rightarrow Cu_2(OH)_2CO_3 \quad (7)$$

The result of the reaction is Malachite, color: green

$$3CuO + 2CO_2 + H_2O \rightarrow Cu_2(OH)_2CO_2 \quad (8)$$

The result of the reaction is Azurite, color: light blue/tosca

$$4CuO + SO_3 + 3H_2O \rightarrow Cu_4(OH)_6SO_4 \quad (9)$$

The result of the reaction is Brochantite, color: light blue/tosca.

When sulphur is present in the form of H_2S from polluted seawater and hydrocarbon vapor, it reacts with Cu^+ ions to form cuprous sulfide (CuS), which appears black in color. This corrosion deposit is brittle and easily peeled off. The maximum threshold for the passive Cu_2O layer to protect the base metal against H_2S attack is 0.5 ppm H_2S[2,8)].

From this analysis, it becomes evident that the primary cause of leakage is the presence of sulphur (S) from seawater and carbon from hydrocarbon vapor. This combination leads to deposit formation, followed by corrosion reactions and subsequent wall thinning. Notably, the typical hole shape of the leakage provides no indication or evidence that it is caused by operational pressure or temperature.

3. Conclusion

Based on the results of numerous examinations, tests, and discussions, it can be concluded that the primary cause of structural strength degradation in heat exchanger tubes E-2-10 and E-2-11 is wall thinning. Wall thinning occurred on both the inside and outside surfaces of the tubes. The principal factor leading to wall thinning is a corrosion reaction, wherein the passive layer of the copper-based alloy is eroded due to the presence of high quantities of sulphur, oxygen, and carbon. These corrosive elements originate from polluted seawater or hydrocarbon vapor, resulting in the formation of deposits. Unfortunately, these deposits were not regularly cleaned or removed, allowing the corrosion reaction beneath the deposits to persist and cause progressive wall thinning until the tubes developed leaks. Consequently, the structural strength degradation of this energy production equipment is primarily attributed to the corrosion factor.

To mitigate the effects of wall thinning, it is strongly recommended that maintenance of the heat exchanger be performed routinely in accordance with established standard operational procedures. Additionally, if feasible, the use of chemical inhibitors for corrosion prevention should be considered.

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