DEVOTION Journal of Research and Community Service
Volume 4, Number 7, July 2023
e-ISSN: 2797-6068 and p-ISSN: 2777-0915

BIO-CORROSION PHENOMENON OF TITANIUM GRADE 2 TUBES IN CONDENSER OF A STEAM POWER PLANT

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KEYWORDS
Biocorrosion; titanium corrosion; tube condenser; MIC; power plant

ABSTRACT

Titanium is widely applied for the tube condenser in Indonesia's powerplant especially those that use seawater for the cooling system, because it has excellent properties both mechanical and physical. Leak in titanium in seawater environment occurred, but on the contrary, the leak of titanium tube in the brackish environment frequently occurs. Many defense tasks such as plugging, cleaning, and adjusting operations have taken, but the result remains the same. Until it was decided to perform an overhaul for the condenser and tube mapping using ECT. It was discovered that 80% of the total tube have been wall lost thickness so that total retubing must be conducted. Chemical elements consist of oxygen (O), sulfur (S), and chlor (Cl) were found during DT and NDT. This study aims to analyze the factors causing this severe titanium tube leak in the condenser. This case is like previous research even though it occurred in different equipment and water feed. Sulfur elements came from the excretion of aquatic biota such as mussel. Plentiful mussels grow along the cooling condenser line because biocide injection is difficult to perform. The method used to find the root cause of the problem is performing several tests of titanium tubes samples. The results show titanium tube from the condenser has experienced bio-corrosion. This is supported by the presence of three elements that allow the bio-corrosion reaction to occur by forming titanium sulfide, namely O, S, and Cl.

INTRODUCTION

A steam power plant located in the Bangka-Belitung Islands uses a condenser-type heat exchanger with a titanium grade 2 (TA2) tube and once-through system. That uses brackish water or low salinity for cooling water in the condenser system. In 2018 frequent condenser tube leaks occurred to cause the unit to derate for a long time because it was forced to continue operating to meet electricity demand. After getting a scheduled outage, the condenser was inspected carefully.

A lot of organic materials such as shells and inorganic such as plastic waste in the water box and the inner tube of the condenser were found. At this period, cooling water pre-treatment such as injection of oxidizing biocides using chlorine or debris filter installation has not been performed. It is with the following specifications as shown in Table 1.

Table 1. Condenser Specification

Specifications	Dimension
Cooling area (m2)	2500
Cooling water flow (kg/h)	5840000
Number of path	two
Tube material	titanium tube (TA2)

Specification of tube	
Outer diameter (m)	0.025
Thickness (m)	0.0006
Length (m)	6.569
Quantity of tube (pieces)	4900

Based on a feasibility study, chlorine cannot be used as a biocide agent in this power plant. The reason behind this result is because seawater salinity is too low to produce biocide agents with electrolysis method (NaOCl), while the cost of purchased liquid NaOCl that is needed for daily injection is considerably high. Based on that fact, non-oxidizing type such as ammonium compound is used for antifouling injection two times per week in a brackish cooling system. Ammonium compound will form a slippery film layer that prevents organisms such as mussel sticking on Circulating Water Pump (CWP) pipe and contaminated the cooling water with a chemical they produced. But then, this method was proven ineffective in a once-through type condenser, a plentiful organism such as mussel still found inside CWP pipeline and condenser. The next step for inspection is mapping the tube thickness using Eddy Current Testing (ECT). The result of the ECT stated that more than 90% of total condenser tubes suffering from 80% wall loss thickness which leads to total retubing as a recommendation.

Titanium is lightweight and high-strength metal, it has excellent corrosion resistance in various environments such as saline and high oxidizing condition. Titanium is widely applied for aerospace, seawater services, biomedical implants, and chemical processing. Titanium is highly reactive with oxygen and its corrosion resistance is influenced by the presence of chemical inert, adherent, and oxide films (Dubent & Mazard, 2019; Sereni, 2016).

Titanium has two elemental crystalline structures, hexagonal close-packed (HCP) α-structure and the body-centered cubic (BCC) β-structure. Pure titanium that has an α-structure with Fe impurities and the addition of alloying elements can produce the desired microstructure [1]. Thin filmed will be formed spontaneously as amorphous or crystalline, depending on the mode and rate of formation when in contact with water and aqueous environments. Mostly crevice corrosion in titanium grade 2 will not occurr at temperature below 70 ^oC (with disregarding pH effect). The initiation of crevice corrosion requires a loss of passivity and the stabilization of active corrosion, which is generally dependent on the film breakdown starting at a temperature of about 70 ^oC.

Previous study for titanium (Ti grade-1) material in a condenser in a nuclear power plant related to uniform wall thinning. The investigation has been carried out by conducting surface deposition analysis using X-Ray Diffraction (XRD), visual inspection, microstructure analysis, and composition analysis using Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS). The analysis result concluded that eccentric contact wear occurred notably near the support plate and severe corrosion between the tube sheet and the first support plate (Chen et al., 2014).

Corrosion is an electrochemical process between a metal and its surrounding that changes the chemical properties of the material and reduces its mass. Corrosion that is affected by micro-organisms is known as bio-corrosion or Microbiologically Influenced Corrosion (MIC). MIC or biocorrosion is an electrochemical process in which the base metal releases electrons which are then captured by metabolic products from micro-organisms (Khan et al., 2019; Papadopoulou & Eliades, 2009).

Commercially pure titanium (grade 1, 2, 3, and 4) is resistant to stress corrosion cracking (SCC) in seawater environments and only needs to be alert if chemicals such as methanol, red fuming nitric acid, nitrogen tetraoxide, and cadmium metal present in the system. Meanwhile, chloride is not a problem for the occurrence of SCC (Mountford Jr, 2002).

Studies on the effect of sulfide on titanium grade-2 have been carried out by conducting simulation experiments in the seawater environment. From this study, it was found that sulfide plays a big role in the formation of passive oxide films as well as contributing to the cathodic hydrogen evolution reaction (Yang et al., 2018).

Titanium passivates in most environments and is virtually inert unless conditions are very reducing. Corrosion in Ti grade 2 occurs due to Sulfate-Reducing Bacteria (SRB). SRB grows well in anaerobic niches and biofilms utilizing organic carbon and reducing sulfate to hydrogen sulfide (H_2S). Elements of Ti, S, and P were obtained during the test using X-ray Photoelectron Spectroscopy (XPS). Based on tests using XPS, elements Ti, S, and P were found indicating corrosion product that formed is a titanium-sulfur compound. In an anaerobic environment, SRB metabolism uses inorganic sulfate as an electron acceptor and produces hydrogen sulfide which causes cathodic hydrogen depolarization, thereby damaging the passivation layer of the material (Li et al., 2010). MIC can cause localized types of corrosion such as pitting, crevice corrosion, under deposit corrosion, cracking, erosion- corrosion, and dealloying (AlAbbas et al., 2013).

Another research studying corrosion on titanium grade 2 stated that initiation of corrosion in the form of destruction of the passive oxide film was influenced by sulfuric acid as medium and electrolyzer operating parameters such as the uniform circulation of electrolytes on the titanium surface [2]. Ti is not completely resistant to MIC, but titanium has more defense than super austenitic Stainless Steel (SS), other steel alloys, and 304 SS (Khan et al., 2019; Zhang et al., 2015).

Based on literature from previous studies, this study aims to profoundly analyze the factors causing this severe titanium tube leak in the condenser. This incident is uniquely considered that titanium is commonly used in several powerplants related to excellent properties such as abrasion resistance, high-temperature resistance, and seawater corrosion resistance. Due to this anomaly, we tried to performed laboratory tests on new and old titanium tube samples so that the differences and material change could be discovered.

RESEARCH METHOD

The method used to find the root cause of the problem is performing several tests of titanium tubes samples on new and old tubes as follows.

Macro-fractography

Two-dimension visual observation performs on metal surfaces with magnifications from 0.5-50x. Based on Fig. 1, the new tube has some spots outside the surface, and there is no corrosion layer either inside or outside the tube. While on the old tube a reddish-brown corrosion layer was found both outside and inside the surface (Fig. 2).

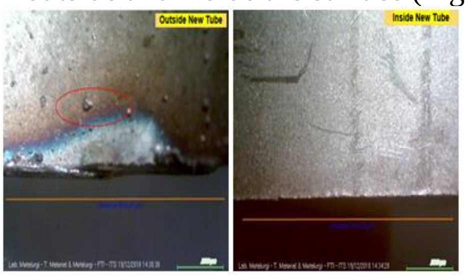

Figure 1. Macro-fractography test, inside-outside surface of the new tube.

Figure 2. Macro-fractography test, inside-outside surface of the old tube

Penentrant test

The test was carried out using a special liquid that penetrates within the surface defect and is visually projected to its surface. Based on Fig. 3, the new tube showed zero-defect but on the contrary, the old tube showed red spots which indicate a leak which is indicated as pitting corrosion.

Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX)

Testing on SEM-EDX was performed inside and outside old tube samples to discover the dominant chemical composition on the surface along with its percentage using the SEM FEI Inspect S50-EDAX Ametex tool. As shown in Fig. 4-7, an uneven surface was found outside the tube. Inside the tube, a dark spot covered the surface. Both of those found were identified as corrosion products. In this corrosion product, a high level of oxygen element has been found, which indicated the oxide compound of corrosion products. Other than oxygen (O), corrosion agent chlor (Cl), and sulfur (S) were also found.

Figure 3. Penetrant test, surface of the new and old tube.

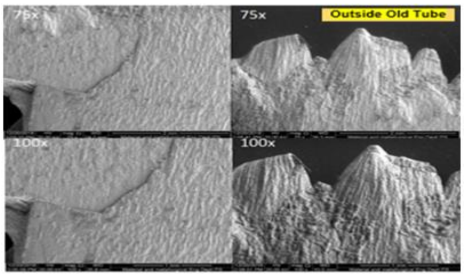

Figure 4. SEM test, outside surface of the old tube.

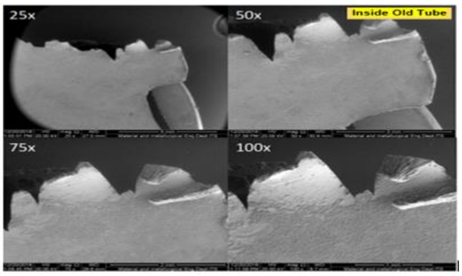

Figure 5. SEM test, inside surface of the old tube

X-Ray Diffraction (XRD)

Samples of the inner scale of both old and new tubes were tested using the XRD Terra Olympus tool. As the result in the new tube TiO_3 as a passivation layer has been found (Fig. 7), but not found in the old tube (Fig. 8). Instead of TiO_3, iron oxide as a corrosion product was found in the old tube. To summarize passivation layer has been removed from the old tube and iron oxide has been found in terms of corrosion product.

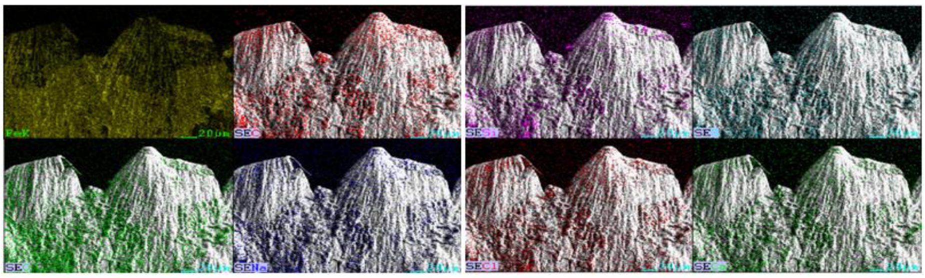

Figure 6. SEM-EDX test.

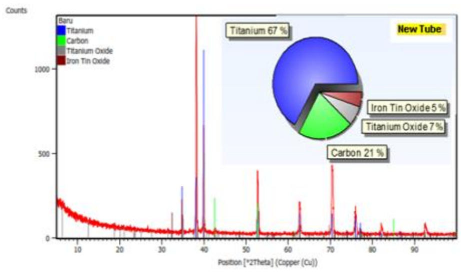

Figure 7. XRD test, surface of the new tube

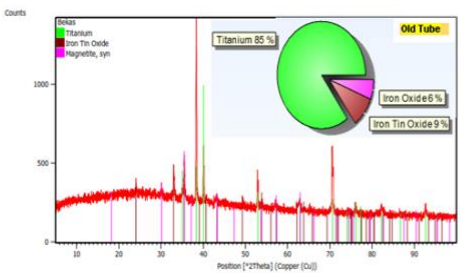

Figure 8. XRD test, surface of the old tube

Hardness mechanical testing

Hardness test was performed using Wilson Hardness 402 MVD tool. As shown in Table II, the hardness number of old tubes is lower compared to new ones. Lower hardness in the old tube is probably caused by the porosity that occurs due to corrosion.

Table 2. Hardness Test Results

No.	New Tube (VHN)	Old Tube (VHN)
1	195.2	186.9
2	194.9	186.4
3	190.0	185.7
Average	193.4	186.33

Micro-spectrograph

Micro-spectrograph of tube surface was performed with the Olympus U-TV0.5XC-3 tool. Based as shown in Fig. 10, the old tube has a rougher surface compared to a new tube which indicated a corroded surface.

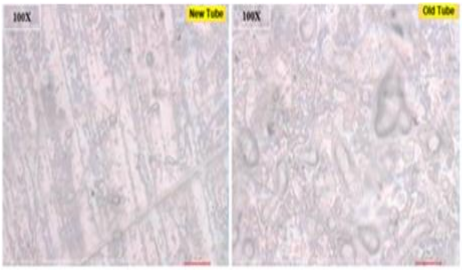

Figure 9. Micro spectrograph test, surface of the new and old tube

RESULTS AND DISCUSSION

Several tests have been done on both new and old titanium tube condenser specimens so that profound analysis can be carried out. All the results indicated titanium tube leakage was caused by corrosion. Corrosion in titanium tube induced by three dominant elements which are oxygen (O), chlor (Cl), and sulfur (S) there was confirmed by performing SEM-EDX test. Oxygen coming from atmospheric air along with the line cooling condenser and is generally known as aerobic.

The steps of testing to identify failures experienced by titanium tubes in the form of corrosion are as follows: (i) XRD results which indicated that there was peeling of the titanium oxide layer which was analyzed from the comparison between new and old tubes. The oxide layer plays a role as a protector of the titanium surface from chemical corrosion attacks; (ii) SEM-EDX results state that there is a corrosion area covering the titanium surface. There are three corrosive elements (O, S, and Cl) with a fairly large percentage that was found; (iii) the results of the macro-fractography and micro-spectrograph show the presence of a corrosion layer on the inside surface of the old tube; (iv) the results of the penetrant test indicate the presence of pitting corrosion; (v) the results of hardness testing show lower hardness number of the old tube compared to the new tube, thus confirming that the titanium tube has decreased its mechanical properties in the form of widening of the porosity caused by corrosion.

The oxidation film damage on the titanium surface is preceded by aerobic corrosion because oxygen acts as an electron acceptor forming hydroxides which corroded the oxidation film layer and then an increase in pitting corrosion (Pillay & Lin, 2013). Sulfur (S) comes from the excretory activity of aquatic organisms such as mussels that exist along the CWP pipe (Moura et al., 2013). Ideally, an organism such as mussel should not breed and multiply along the cooling condenser pipeline, so that biocide injection is required to prevent that case. Chlorine injection was proven to be highly efficient in lessening the proliferation of aquatic organisms in the condenser. Based on historical data in powerplant using chlorine injection, a leak in titanium tubes rarely occurred. On the contrary, a severe tube leak was found in this case study.

Titanium is supposed to have good resistance in acidic environments except for drastically lower pH conditions and is also resistant to oxidizing media. While the corrosion resistance will lessen in the presence of fluoride ions and very reducing media (i.e., concentrated sulfuric) (Dubent & Mazard, 2019). According to AlAbbas (2013), titanium as a material with excellent corrosion resistance also has a weakness. Titanium is vulnerable to bio-corrosion which is mainly caused by elemental sulfur (S). The stages of the corrosion mechanism of titanium are as follows: (i) titanium oxide film, namely TiO_2 under anaerobic conditions, is broken down into Ti_4^+; (ii) metabolism of microorganisms reduce sulfate to sulfide and reacts to produce H_2S which is a reducing agent. The corrosion mechanism is shown by the following reaction:

$$SO_4^{-2} + 8H^+ + 8e \longrightarrow HS^- + OH^- + 3H_2O \qquad (1)$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \qquad (2)$$

$$HS^- + H^+ \longrightarrow H_2S \qquad (3)$$

The oxide film is susceptible to H_2S; (iii) a bonding reaction with titanium occurs according to the reaction:

$$Ti_4^+ + 2S^{-2} \longrightarrow TiS_2 \qquad (4)$$

The final product of the reaction which is TiS_2 (titanium sulfide) is the reason behind pitting corrosion that occurred in titanium (AlAbbas et al., 2013; Prithiraj et al., 2019; Rao et al., 2005). Chlor (Cl) which originated from seawater is a salinity compound of brackish water. This compound will accelerate the corrosion rate when pitting corrosion caused by oxygen and sulfur start to occur. When chlor (Cl) is trapped near the pitting corrosion, it will react with H_2O to form HCl compounds based on this reaction:

$$Cl^- + H_2O \longrightarrow HCl + OH^- \qquad (5)$$

HCl compound that formed between chlorine and H_2O is a strong acid (low pH) so that its condition will able to accelerate pitting corrosion on titanium that initially caused by sulfur.

Corrosion in material or metal caused by aquatic life is known as bio-corrosion or MIC. This phenomenon is rarely found and tends to unidentified during the Root Cause Failure Analysis (RCFA) process because generally the failure mode of condenser tube leakage, especially titanium material, is predictable. This failure mode generally due to degradation mechanical properties or how the operator setting the parameter. Meanwhile, there are several aspects from a chemical point of view that are often overlooked for analysis such as: (i) biocide injection; (ii) film coating chemical on the surface of the condenser tube; (iii) anti-scale injection.

The role of chemicals as a pre-treatment cooling condenser line is vital and an evaluation must be carried out so that the failure of the condenser tube caused by aquatic biota can be minimized. Aquatic biota such as shellfish and mussel in this research are found in abundance along the cooling condenser path. When overhauling and opening the access to the CWP pipe, many shells were found sticking to the pipe surface with a very strong smell of excretion. Dead mussels leave their shells and gather them in the water box and tube condenser.

This data supports the prognosis that the titanium tube condenser leak is caused by bio-corrosion. The bio-corrosion process being preceded by the presence of oxygen (O) as a destroyer of the titanium oxide layer then element sulphur (S) reacts with titanium to form titanium sulfide (TiS_2) and element chlor (Cl) forms hydrochloric acid (HCl) which worsens the environmental conditions where corrosion occurs.

CONCLUSION

Based on the results of this study and literature with similar incidents, it was concluded that the titanium tube from the condenser has experienced bio-corrosion. This is supported by the presence of three elements that allow the bio-corrosion reaction to occur by forming titanium sulfide, namely O, S, and Cl. The stages of bio-corrosion in titanium are: (i) element O acts as an electron acceptor to form hydroxides, which then oxidizes titanium to produce aerobic corrosion and damages the oxide film of titanium to form pitting corrosion; (ii) element S reacts to form hydrogen sulfide which is a reducing agent that damages the oxide film layer and then binds to titanium to form titanium sulfide and caused pitting corrosion; (iii) elemental Cl reacts with water to form hydrochloric acid which is a strong acid low pH and these conditions assist titanium sulfide to form pitting corrosion.

The bio-corrosion agent's main source is coming from the excretion of an organism such as mussel so that biocide injection has a significant role in maintaining the cooling condenser line. The non-oxidizing ammonium compound system proved to be less effective in once-through condensers and CWP pipe that has a rubber lining. That is because the slippery amine film (one of the non-oxidizing biocide compositions) cannot adhere perfectly even though the function was supposed to form a barrier that prevents attachment of aquatic organisms that carried within the condenser.

A feasibility study using liquid or gas chlorine and copper-ion for biocide injection is recommended to perform for the condenser in low-salinity seawater (brackish) with the main goal to prevent aquatic biota growth along the cooling condenser line. Organism proliferation inside brackish water cooling system will lead to bio-corrosion in titanium tubes and became the unanticipated silent threat.

REFERENCES

AlAbbas, F. M., Williamson, C., Bhola, S. M., Spear, J. R., Olson, D. L., Mishra, B., & Kakpovbia, A. E. (2013). Influence of sulfate reducing bacterial biofilm on corrosion behavior of low-alloy, high-strength steel (API-5L X80). *International Biodeterioration & Biodegradation*, *78*, 34–42.

Chen, F.-J., Yao, C., & Yang, Z.-G. (2014). Failure analysis on abnormal wall thinning of heat-transfer titanium tubes of condensers in nuclear power plant Part II: Erosion and cavitation corrosion. *Engineering Failure Analysis*, *37*, 42–52.

Dubent, S., & Mazard, A. (2019). Characterization and corrosion behaviour of grade 2 titanium used in electrolyzers for hydrogen production. *International Journal of Hydrogen Energy*, *44*(29), 15622–15633.

Khan, M. S., Li, Z., Yang, K., Xu, D., Yang, C., Liu, D., Lekbach, Y., Zhou, E., & Kalnaowakul, P. (2019). Microbiologically influenced corrosion of titanium caused by aerobic marine bacterium Pseudomonas aeruginosa. *Journal of Materials Science & Technology*, *35*(1), 216–222.

Li, J., Li, J., Yuan, W., & Du, Y. (2010). Biocorrosion characteristics of the copper alloys BFe30-1-1 and HSn70-1AB by SRB using Atomic Force Microscopy and Scanning Electron Microscopy. *International Biodeterioration & Biodegradation*, *64*(5), 363–370.

Mountford Jr, J. A. (2002). Titanium-properties, advantages and applications solving the corrosion problems in marine service. *NACE CORROSION*, NACE-02170.

Moura, M. C., Pontual, E. V, Paiva, P. M. G., & Coelho, L. (2013). An outline to corrosive bacteria. *Methods*, *18*(January 2013), 19.

Papadopoulou, K., & Eliades, T. (2009). Microbiologically-influenced corrosion of orthodontic alloys: a review of proposed mechanisms and effects. *Aust Orthod J*, *25*(63), 19634466.

Pillay, C., & Lin, J. (2013). Metal corrosion by aerobic bacteria isolated from stimulated corrosion systems: effects of additional nitrate sources. *International Biodeterioration & Biodegradation*, *83*, 158–165.

Prithiraj, A., Otunniyi, I. O., Osifo, P., & van Der Merwe, J. (2019). Corrosion behaviour of stainless and carbon steels exposed to sulphate–reducing bacteria from industrial heat exchangers. *Engineering Failure Analysis*, *104*, 977–986.

Rao, T. S., Kora, A. J., Anupkumar, B., Narasimhan, S. V, & Feser, R. (2005). Pitting corrosion of titanium by a freshwater strain of sulphate reducing bacteria (Desulfovibrio vulgaris). *Corrosion Science*, *47*(5), 1071–1084.

Sereni, J. G. R. (2016). *Reference module in materials science and materials engineering*.

Yang, X., Du, C., Wan, H., Liu, Z., & Li, X. (2018). Influence of sulfides on the passivation behavior of titanium alloy TA2 in simulated seawater environments. *Applied Surface Science*, *458*, 198–209.

Zhang, D., Zhou, F., Xiao, K., Cui, T., Qian, H., & Li, X. (2015). Microbially influenced corrosion of 304 stainless steel and titanium by P. variotii and A. niger in humid atmosphere. *Journal of Materials Engineering and Performance*, *24*, 2688–2698.