Failure analysis of boiler leakage due to caustic corrosion on Cr-Mo steel

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Abstract. In the system of steam generation, condenser and boiler are the most prone to suffer corrosion attack. It usually occurs due to the interaction between the pipe surface that made from steel with the fluid of boiler. One of the dangerous types of failure is pitting corrosion. There are several causes of pitting corrosion, such as; the oxygen content in the fluid, the amount of contaminants that may easily form a deposit on the Cr-Mo steel surface, and the use of improper concentration of inhibitors. The electrochemical process takes place during the occurrence of pitting corrosion. Failure analysis of the boiler water-wall tube is presented in this work. In order to examine the causes of failure, various techniques including visual inspection, optical microscopy, and energy dispersive spectroscopy were carried out. Tube wall thickness measurements were performed on the failed tube. The water-facing side of the tube was observed to have experienced significantly localized wall thinning. The failure mechanism is suggested as oxidation due to caustic corrosion as a result of inappropriate usage of phosphate inhibitors.

1. Introduction
The reliability of the function of equipment and components in fossil-fuelled steam boilers such as boiler tubes, superheaters, heat exchangers, turbines, etc. is very important to ensure a continuous supply of electricity generation. Each component is very important and related to the functioning of the entire system, so that failure of one component can cause a failure of the electricity generation system. One of the main reasons for failure that is often reported in this type of power plant is the failure of the boiler tube [1-3]. The steam boiler is a kind of heat exchanger that turn water into steam by increasing the cold-water temperature using the fuel thermal energy above its saturation point, but usually, this is still wet steam [1]. Superheater is commonly employed to transfer heat from the combustion gases to the wet steam flowing inside to change it into dry steam.

Superheater is the most vulnerable part of failure because this part is exposed to high temperatures from the combustion gases on the outside and high pressure from the dry steam in the inside of the tubes. Cr-Mo steels are among the alloys used for boiler tubes due to its creep resistance at boiler’s working temperature. This creep resistance exists because chromium and molybdenum are strong carbide-forming elements [4,5]. Many studies have been carried out on the analysis of boiler tube failures and the presence of impurities such as sulphur and sodium in boiler feed water is one of the main reasons for failure in these tubes. [6-8]. Ranjbar [6] reported that the presence of impurities especially excessive sodium in the feed water results in pitting, caustic and stress corrosion.
In this study, the material of the superheater tubes is selected using 1Cr–0.5Mo steel (ASTM A213-T12) due to its high temperature and pressure resistance [9]. The failure analysis of this superheater tube was investigated in a steam boiler application.

2. Experimental Procedure
The failure analysis was performed to the failed tube, especially the pitting section of the tube. For examining the outer surface morphology of the tube, visual inspection was carried out. In addition, the chemical composition of the inner and outer surface of the failed tube was analyzed by Spectrophotometry, Atomic Absorption Spectroscopy and Gravimetry.

3. Results and Discussion

3.1. Process Data of Boiler

![Schematic flowchart of boiler process](image)

Table 1. Process Data of Boiler

| Item                          | Shell side | Tube side |
|-------------------------------|------------|-----------|
| Design Pressure, kg/cm²      | 127        | 35.2      |
| Metal Temperature Design, °C | 353        | 495       |
| Operational Temperature Design, °C | 323    | 1000/430 (in/out) |
| Fluid                        | Boiler Feed Water & steam | Process gas |
| Corrosion allowance, mm      | 3          | 1.7       |
| Material                     | 1%Cr, 0.5%Mo |           |
| Tube Material                | 42 mm outer diameter, 4 mm tube thickness, 9200 mm length |

The boiler tube is made from 1wt%Cr-0.5wt%Mo steel. The dimension of the tubes is 42 mm of outer diameter, 4 mm of tube thickness, and 9200 mm in length. The flue gas enters the tube boiler at high temperature and pressure; 1000°C and 127 bar, respectively. From a different direction, boiler feed water enters the boiler at 35 bar. Prior to entering the boiler, phosphate as chemical treatment was injected into the water at a concentration of 4,000 ppm TSP and 1,000 ppm in 0.1% of volume. The result of boiling the water is superheated steam and waste heat of 430°C. Comparing the temperature at
the entry and exit point of the boiler, 1000 and 430°C, respectively, there is a loss of energy of 670°C that was used to heat up the water and changed its phase to superheated steam. In general, the boiler was operated in accordance with design requirements. However, repeated corrosion and leakage occurred on the boiler. Actions had been taken to prevent the failure but brought little effect. Therefore, comprehensive investigation and analysis of the failed economizer tubes were conducted and reported in this paper. Root cause of the corrosion was found, and effective countermeasures were put forward as well.

Figure 2. Schematic layout of boiler. a. Cross-section of boiler and the location of tube leakage, b. Surface of boiler.

Figure 2 shows the schematic layout of the boiler. Fig. 2a indicates the cross-section of the boiler and the location of tube leakage. These 4 tubes were located in quadrant II, III, and IV where the water phase was flooding in the boiler. The first hypothesis about the root cause of tube leakage came from the water composition.

Table 2. The quality of boiler feed water

| Content       | Amount          |
|---------------|-----------------|
| Conductivity  | 0.2 micro S/cm max. |
| Dissolve O₂   | 0.02 ppm        |
| Na + K        | 0.01 ppm        |
| Chlorine      | 0.02 ppm        |
| Cu            | 0.003 ppm       |
| Fe            | 0.02 ppm        |
| SiO₂          | 0.02 ppm        |
| pH (25°C)     | 8.5 – 9.5       |
Table 2 shows the quality of boiler feed water. All-important parameters such as conductivity, the content of dissolve oxygen, sodium, potassium, chlorine, metal impurities (copper and iron), silica and the pH were measured. They are all at acceptable range and can be used as BFW. One purpose of phosphate injection was to maintain silica to keep soluble in fluid flow, not deposited on the tube surface nor on the wall of boiler.

3.2. Chemical Composition of Materials
Chemical composition of the tube is listed in Table 3. The tube was proved to be in accordance with the ASTM A213-T12 steel which was a kind of low-cost carbon steel for high-temperature service [9].

| Material         | Element (Wt%) |
|------------------|---------------|
|                  | C  | Si | Mn | P  | S  | Cr | Mo |
| ASTM A213-T12    | 0.08–0.18 | < 0.35 | 0.4–1.0 | 0.03 | 0.025 | 1  | 0.5 |
| Boiler Tube      | 0.13 | 0.25 | 0.56 | 0.02 | 0.009 | 0.86 | 0.5 |

Visual Inspection of the Failed Tube

Visual examination of the outer surface of failed tube revealed single pit and equiaxial shape. The pit is deep, went through to the inner surface of the tube, as thick as 4 mm. On the outer surface of tube, the pit has a dimension of 8 mm in diameter, and getting smaller in the inner surface of the tube, around 4 mm in diameter. It was also found a deposit on the outer tube 2 m along of inlet side which is thicker than the rest of tube. Probably the phosphate injection was not working properly to keep the impurities remain flow with the fluid, not deposited on the tube. The working temperature around this length is between 800-1000°C. Considering the difference in shape and dimension of the outer and inner surface of the failed tube, it is suggested that the pit occurred initially at the outer surface and then the pit grew become deeper until a hole is formed. This analysis strengthened the first hypothesis about the root cause of the leakage; that it might be due to the boiler feed water composition.

4. Results and Discussions

4.1. Chemical Analysis of Corrosion Products
Table 4 indicates the chemical analysis of corrosion products. The presence of magnetite iron oxide (Fe₃O₄) dominated the corrosion products because it is a natural product of iron and oxygen reaction at high temperature. The temperature of magnetite formation around 800°C and it is in good agreement
with a working temperature of the boiler; between 430 and 1000°C. Other compounds were also detected in the scale. A significant amount was contributed by calcium oxide (CaO), insoluble and soluble silica (SiO₂). It seemed the phosphate inhibitor that injected into the water flow line, was not able to control the insoluble silica to be remained in the fluid, so that the silica could not form a deposit on the tube. The next mechanism to reduce the amount of silica is by blowdown.

Table 4. Chemical Analysis of Corrosion Products

| No | Oxide     | % wt | ppm    | Method                  |
|----|-----------|------|--------|-------------------------|
| 1  | Fe₂O₃     | 2.14 | 21,400 | Spectrophotometry       |
| 2  | Fe₃O₄     | 75.83| 758,300| Spectrophotometry       |
| 3  | PO₄        | 4.18 | 41,800 | Spectrophotometry       |
| 4  | Na₂O      | 0.31 | 3,100  | Atomic absorption spectroscopy (AAS) |
| 5  | Al₂O₃     | Trace| Trace  | AAS                     |
| 6  | CaO       | 2.3  | 13,000 | AAS                     |
| 7  | MnO       | 0.54 | 5,400  | AAS                     |
| 8  | CuO       | 0.09 | 900    | AAS                     |
| 9  | ZnO       | 0.54 | 5,400  | AAS                     |
| 10 | NiO       | 0.17 | 1,700  | AAS                     |
| 11 | MgO       | 0.02 | 200    | AAS                     |
| 12 | Cr₂O₃     | 0.06 | 600    | AAS                     |
| 13 | SO₄       | Trace| Trace  | Spectrophotometry       |
| 14 | Insoluble SiO₂ | 2.12 | 21,200 | Gravimetry              |
| 15 | Soluble SiO₂ | 5.01 | 50,100 | Spectrophotometry       |

4.2. Mechanism Corrosion of Caustic Corrosion

Trisodium Phosphate (TSP) is precipitation inhibitor that reacts with metal and forms Fe₃(PO₄)₂ precipitate. The details of reactions are explained below;

\[
\begin{align*}
\text{Na₃PO₄} + 3\text{H₂O} & \rightarrow 3\text{Na}^+ + 3\text{OH}^- + \text{H₃PO₄} \quad (1) \\
\text{H₃PO₄} + \text{H₂O} & \leftrightarrow \text{H}_4\text{O}^+ + \text{H}_₂\text{PO}_₄^- \quad (2) \\
\text{H}_₂\text{PO}_₄^- + \text{H₂O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{HPO}_₄^{2-} \quad (3) \\
\text{HPO}_₄^{2-} + \text{H₂O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{PO}_₄^{3-} \quad (4)
\end{align*}
\]

In boiler feed water, the product of reaction (1) works to increase the pH and forms hydroxide ion, as shown in the following reactions;

\[
\text{Fe(OH)}_₂ \rightarrow \text{Fe}^{2+} + 2\text{OH}^- \quad (5)
\]
The reactions that occur between reaction products (4) and (5) are written as follows:

$$\text{Fe}^{+2} + PO_4^{-3} \rightarrow Fe_3(PO_4)_{2}$$  \hspace{1cm} (6)

$Fe_3(PO_4)_{2}$ is a protective layer on the surface of metal. The amount of $Fe_3(PO_4)_{2}$ formation depends upon the amount of hydroxide ions in the water. If its amount is not sufficient, the formation of $Fe_3(PO_4)_{2}$ will be retarded.

5. Conclusions

Failure analysis of high temperature and pressure boiler tubes made of Cr-Mo steel was investigated. Based on the observations and results, the following conclusions can be drawn:

1. Pitting is caused by excessive NaOH that leading to caustic corrosion
2. Temperature and concentration of inhibitor has a large effect to deposit formation and leading to pitting formation.

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