Investigation of failure of tubes in a heat exchanger for corrosion of dissolved oxygen

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Abstract. Failure of tubes in a heat exchanger was studied through analysis of Optical microscope, water analysis, X-ray diffraction pattern, and Scanning Electron Microscope. The damage tube displays a large unsmooth corrosion area with decreased hardness. Moreover, two different corrosion layers were found on the waterside of the pipe surface. The tube failed due to dissolved oxygen in feed water. Some recommendations of delaying corrosion was also put forward.

1. Introduction

Boiler failure is a major concern in power plants and other industrial units, and tube corrosion is known to be the main cause [1-2]. Steel alloys such as CrMo steels have been used extensively for construction of tubes and pipes in power plants, such as boilers and super heaters pipes, owing to their excellent corrosion and creep resistance. However, boilers are usually characterized by high temperature and pressure, and critical water shows significantly different corrosion properties compared with liquid water. The high-temperature and high-pressure water is very aggressive for metallic materials, being highly corrosive during the operation of materials [3-5]. In most failure cases, corrosion, such as caustic corrosion, stress corrosion, oxidation, and so on, can be present because of the deposits formed on the boiler pipes. The corrosion products could lead to corrosion failure.

Among these corrosion behaviors, dissolved oxygen corrosion is also very important [6-8]. In liquid phase, dissolved oxygen can be supplied by gas phase (main O2). Dissolved oxygen corrosion usually accompanies stress corrosion, and combined action of the growth stress, tensile stress, and micro cracks nucleate from the pores in the oxide layer. However, ambiguity still exists owing to the complexity of dissolved oxygen mechanism, especially under the condition of complex high temperature and high pressure.

In this study, an investigation of failure of tubes in a heat exchanger for the dissolved oxygen corrosion is studied. The highest operating pressure and temperature of the tube side are 12.6 MPa and 190 °C, respectively. The tube is made of Type 15CrMo steel. This plant was finished in 2013, and corrosion behavior was found on the pipe near the lower right-hand hole. The device was then stopped immediately, and major repairs were started. The failure modeled is studied by the analysis of macro-appearance, micro-appearance, X-ray diffraction (XRD), scanning electron microscope (SEM), and so on.
2. Experimental procedures
Several samples from different parts of the as-received specimen were selected for quant metric, metallographic, electron microscopy, X-ray diffractometry, and hardness examinations. Spectroscopic methods were utilized as follows.

2.1. Optical microstructure
For microstructural examination, specimens from the base metal on the outer surface near the corroded area with no crack were cut. The samples were mounted and polished. After preparation, the samples were etched by nital 2% solution for 15 s. Then, the cross-section was observed by optical microscope (AxiImager.A1m, Zeiss).

2.2. Water Quality
Although corrosion was found, the heat exchanger stopped working, and the drum water was immediately taken out for testing of the water quality in accordance with the requirements in GB12145-2016 “Quality criterion of water and steam for power plant and steam-generating equipment.” In addition, the feed water was also carried for testing the water qualities according to the standard. The experiment methods and parameters are all depicted in this standard.

2.3. X-ray diffraction
For phase analysis of the corrosion products, XRD (Rigaku D/MAX-2500PC) with Cu Kα radiation was performed, and MDI Jade 5.0 software was used to analyze the obtained XRD patterns.

2.4. Scanning Electron Microscope (SEM)
The corrosion morphologies of the specimens from the corrosion area were investigated by SEM (SU-3500, Hitachi) equipped with an energy dispersive X-ray spectrometer (EDS).

3. Results and failure analysis

3.1. Visual inspection

![Figure 1. Corrosive tubes as seen from the hole of blowdown](image)

An image of the outer surface of the failed pipes received from the factory including this corrosive zone is presented in Fig 1. The damaged tubes were observed in reflected light with naked eyes. A large area was unsmooth and covered by corrosion products. By carefully magnifying the image (seen in Fig. 2), the unsmooth zone exhibits a length of 100 mm and a width of 25 mm. Many small pits could be
seen on both sides of the corrosion area (marked by arrows in Fig. 2). A very deep corrosion pit, marked by the oval, is found on the upper left, with a depth of nearly 5 mm, indicating that serious corrosion behavior happened on the exchanger tubes.

Figure 2. High magnification of corrosive area

3.2. Microstructure of the tube material of the heating surface
To test the metallurgical structure of the elbow, failure tubes were cut from the systems, and samples were collected from the base metal on the outer surface near the corroded area with no crack. Fig. 4 displays the optical micrograph images of the microstructure. The matrix displays equiaxed ferrite and pearlite homogenously dispersed at the grain boundary.

Figure 3. Optical micrograph showing the microstructure of tube material (transverse cross section).

3.3. Water quality results
After the leakage of tubes, because of the high outlet steam pressure, the water in the drum was chosen to carry out water quality analysis in accordance with the requirements of GB 12145-2016 [9], quality criterion of water and steam for power plant and steam-generating equipment, in China. Table 2 shows the water quality of the drum water. Careful analysis shows that the test results are in line with the criterion. All ion and dissolved salt concentrations are limited, including $H^+$, $PO_4^{3-}$, $Cl^-$, $SiO_2$, and conductivity.

| chemical parameters | PH (25°C) | $PO_4^{3-}$ (mg/L) | $Cl^-$ (mg/L) | conductivity (25°C) (μs/cm) | $SiO_2$ (mg/L) |
|---------------------|-----------|--------------------|---------------|-----------------------------|---------------|
| Actual composition | 9.1       | 0.4                | 1.1           | 18                          | 0.08          |
| Requirement in GB 12145 | 9.0–9.7  | $\leq$3           | $\leq$1.5     | $<20$                       | $\leq$0.45    |

Table 1. Water quality of the drum water
3.4. Morphology and phase compositions of the corrosion area

To study the corrosion behavior further, the morphologies of the corrosion area were observed by SEM. Fig. 4a displays the surface morphology of the corrosive tubes. The surface was covered with some particles as well as many deep holes. For high magnification in Fig. 4b, no micro crack was observed on the surface in different areas, only some river-like patterns appeared.

![Figure 4. Surface morphologies the corrosion area](image)

(a) Low magnification; (b) high magnification

EDS was utilized to identify the corrosion products, as shown by narrow red lines in Fig. 4b. Weight percentage of some elements such as O, Na, P, and Cl could be indexed and could be attributed to their presence during water treatment by using ion exchange resin. In this deposit, the atomic ratio of O reaches 34.13, whereas P is lower than 2, implying that the oxide of Fe predominates in the corrosion products.

![Figure 5. Corrosion morphology of the cross-section](image)

To study morphology of the oxide layer and corrosion products further, the cross-section of a typical etch pit was researched and displayed in Fig. 7. The deposits on the surface of the base alloy consisted
of two different layers and show a total thickness of nearly 70 mm. The relatively thick layer adjacent to the base metal contained a large size of the bulk products, whereas another thin uniform layer including fine products covered the surface. Compared with the interior products, EDS results show the exterior has higher content of Na and P but lower O and Cl, possibly implying that the oxide of Fe was covered by phosphate.

![Figure 6. XRD patterns of the corrosion area of the pipe](image)

Phase types of the corrosion products were studied by XRD and depicted in Fig. 8. Besides $\alpha$-Fe, peaks of Fe$_3$O$_4$, Na$_3$PO$_4$ and NaCl were found in the patterns. However, no peaks of Fe$_2$O$_3$ were indexed.

4. Discussions

Nearly all the chemical parameters are in line with the criterions except the concentration of dissolved oxygen in feed water. The main reasons which cause the corrosion behavior could be the overly high concentration of dissolved oxygen.

Similar to other two-phase alloys, both the chemical corrosion and electrical chemical corrosion could happen in this 15CrMo alloys. Electrical chemical corrosion could be more easily found in electrolyte solutions. In drum water, Cl$^-$, Na$^+$, PO$_4^{3-}$, and some other ions existed, so ferrite and cementite could play roles as anode and cathode, respectively, to form electrical chemical corrosion.

Under this condition, in accordance with the corrosion mechanism proposed by most previous studies [10, 11], the anode and the cathode reactions are given by Eqs. (1) and (2), respectively:

$$\text{Fe-2e}=\text{Fe}^{2+}$$

$$\text{O}_2+2\text{H}_2\text{O}+4\text{e}=4\text{OH}^-$$

Next, the secondary reactions could happen as shown in the following equation:

$$\text{Fe}^{2+}+2\text{OH}^-=\text{Fe(OH)}_2$$

The peaks of Fe$_3$O$_4$ which appeared in XRD patterns are evidence of these reactions.

On the other hand, the drum water also presents alkaline because of the hydrolysis of PO$_4^{3-}$. This would be a catalyst of the ionization process of Fe$^+$, accelerating the corrosion process.

However, the corrosion state happened near the hand-hole of the drum. The materials near the hand-hole generally show local stress concentration and aggregation of the corrosion product. Then, the local concentration of the drum water would increase, with the elevated concentration of PO$_4^{3-}$, OH$^-$, and
other ions involved in corrosion reactions. Finally, the drum water near the handhole exhibits higher ion concentration and shows more serious corrosivity compared with other areas.

During the operation of the heat exchanger, the drum water shows high temperature and pressure. When the saturation vapor pressure of water reaches 12.6 MPa, the water temperature approaches 190°C. With the increase of temperature and pressure under alkaline environment, the corrosion behavior shows more deterioration [12].

In this case, the main reason of the corrosion phenomenon is the overproof of dissolved oxygen. The media with high temperature and pressure is the catalyst of the corrosion process and provides the reaction environment.

5. Conclusions and recommendations

The failure analysis of tubes in a heat exchanger for the dissolved oxygen corrosion is discussed in this paper. The following are the inferences obtained from this study:

The corrosion behaviour happened in a heat exchanger used for three years. The damage tube shows a large unsmooth corrosion areas. We conclude that the tube failed because of the dissolved oxygen in feed water. The corrosion process makes the ferrite in pipe corrode, leading the appearance of potholes on the surface and reduced local hardness.

To prevent this problem, following suggestions are presented:

1. The control of water treatment should be strengthened and monitored effectively. Checking of quality of water regularly is required to maintain its pH and oxygen content at specified levels.

2. The device must be prevented from having over-temperature and overpressure. Regular inspection of the tube is also necessary to detect any problems.

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