Discussion of the Corrosion Mechanism of Drum in a Boiler

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Abstract. Corrosion mechanism of the drum in a boiler was studied by macroscopic observation, hardness and thickness tests, and corrosion products analysis. The damage surface displays a large unsmooth corrosion area with decreased hardness. The materials failed due to dissolved oxygen in feed water and the corrosion process was suggested to be divided into four stages. The formation of the morphologies was also described.

1. Introduction
Boiler, as a special equipment with high tempure and pressure, is largely aggressive and highly corrosive during operating. While the device damaged to a certain extent, stopping behavior would be carried out and economic loss would appear [1-3]. It is expected that the total cost of power plant boiler pipe failures will reach 5 billion dollars a year [4, 5].

Usually, the corrosion behavior in industrial boiler is much more complicated than that in power plant, for the wider coverage and less strict management. 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. The corrosion products could lead to corrosion failure. For example, as the case of caustic corrosion, use of excessive alkaline such as NaOH may lead to corrosion attack. After corrosion, the mechanical properties of the materials deteriorate, indicating the appearance of the corrosion embrittlement [6-8].

Nowadays, for analyzing boiler failure behavior, the failed part was usually removed from the whole device. This would lead to a lot waste of time and cost. In this study, an investigation of the corrosion mechanism in a drum of an industrial boiler is studied. No destructive operating was carried out and no samples was cut and chosen from the matrix. Morphologies observations and properties tests, including macroscopic observation, hardness and thickness tests, are accompanied by internal periodic inspection of the boiler. Corrosive medium and products were taken back for further analysis.

2. Experiments
Morphologies observations and properties tests, including macroscopic observation, microhardness and thickness tests were used and accompanied by internal periodic inspection of the boiler. XRD was used to analyse the corrosive medium. Detailed methods were depicted as follows:

2.1. Hardness
Leeb hardness Meter (MH-100) was used for the examination. Three test area were chosen and polished before operation, and the hardness points show a line with 1cm intervals. On each area, 7 points were
tested, and the highest and lowest values were elected. The average value and error bar were calculated last.

2.2. Thickness
With the hardness measurement, the wall thickness of the drum is also measured using Ultrasonic Thickness Gauge (26MG) simultaneously. As the same of hardness test, 7 points were tested on each area, and the highest and lowest values were elected. The average value and error bar were also acquired.

2.3. Water Quality
While the boiler stopped working, the drum water was immediately taken out from water sampler in accordance with the requirements in GB/T 1576-2018 “Water Quality for industrial boilers” [9]. 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.

2.4. X-ray diffraction
Corrosion products was taken out from the internal surface of the drum, and X-ray diffraction (Rigaku D/MAX-2500PC) with Cu Kα radiation was performed to analysis the phase composition. MDI Jade 5.0 software was used to analyze the obtained XRD patterns.

3. Results

3.1. Macroscope observations

![Figure 1. Corrosive area of the drum internal surface seen from the manhole](image)

(a) low magnification  (b) high magnification

An image of the internal surface of the drum is shown in Fig.1. The macro-morphology of corrosion behavior was observed in reflected light with naked eyes. A large area was unsmooth and covered by corrosion products (Fig. 1a). By magnifying the image, many small pits could be seen (narrowed in Fig.1b) along the corroded region.

3.2. The results of hardness and thickness tests
The Leeb hardness (as seen in Fig. 2) was measured and recorded at three locations of interest: the corroded area, the incorroded matrix and the interface between them. The hardness of these three areas is significantly different. The incorroded matrix hardness is about 377HL, which shows the highest value. However, the hardness on the corroded area is the lowest, with only 325 HL on average.

Compared with the nominal area, the corroded area shows the lowest hardness and the widest error bar. As a result of the two main phases in 20G, ferrite and pearlite, dispersed potential difference could form around the cementite in pearlite, and galvanic corrosion could occur easily. Ferrite is more likely
to corrode than cementite. After ferrite is corroded, cementite would fall off. Finally, the hardness would decrease and fluctuate.

![Corroded Area Interface Incorroded Matrix](image1.png)

**Figure 2.** Leeb hardness of different areas on the drum internal surface

Thickness was also tested with the hardness test. Obviously, the corroded area displays the lowest value, with 5% reduction of original material.

![Corroded Area Interface Incorroded Matrix](image2.png)

**Figure 3.** Thickness of different areas

### 3.3. Water Quality

For the high outlet steam pressure, the water in the drum was carried out to analyze in accordance with the requirements of GB 1576-2018. 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⁺, PO₄³⁻, Cl⁻, conductivity and phenolphthalein alkalinity.

| chemical parameters       | PH (25°C) | PO₄³⁻ (mg/L) | conductivity (25°C) (μs/cm) | phenolphthalein alkalinity (mmol/L) | Cl⁻ (mg/L) |
|---------------------------|-----------|--------------|-----------------------------|-----------------------------------|-----------|
| Actual composition        | 11.9      | 14           | 1220                        | 9.9                               | 49        |
| Requirement in GB 1576    | 10.0~12.0 | ≤4800        | 2.0~12.0                    | No regulations                    |           |
Besides the drum water, the feed water is also checked and listed in Table 2. The harmful ion concentrations (Ca$^{2+}$, Mg$^{2+}$), which were directed as rigidity in Table 2, have no achievement on the dangerous value in the standard for forming scale. The pH and Fe ion are in line with the criterion. Another, the concentration of dissolved oxygen in feed water was nearly twice than that in standard.

**Table 2.** Water quality of the feed water

| chemical parameters | dissolved oxygen (mg/L) | pH (μg/L) | Rigidity (Ca, Mg ion) (mmol/L) | Fe ion (mg/L) |
|---------------------|-------------------------|-----------|-------------------------------|---------------|
| Actual composition  | 0.09                    | 8.6       | 0.01                          | 0.08          |
| Requirement in GB 1576 | ≤0.05                   | ≤7.0~9.0  | ≤0.03                         | ≤0.30         |

3.4. XRD patterns of the corrosion product

Fig. 4 shows the XRD patterns of the phase types of the corrosion products. Besides of α-Fe, peaks of Fe$_2$O$_3$, Fe$_3$O$_4$, Na$_3$PO$_4$ and NaCl could be seen in the patterns.

4. Discussion about the corrosion mechanism

Previous study shows that the oxygen corrosion plays an important role in the failure process of boiler. In this service environment, all the chemical parameters are in line with the criterions except the concentration of dissolved oxygen. According to the water quality analyse and XRD patterns, for oxide and chloride is the most corrosion product, it could be inferred that the dissolved oxygen corrosion may be the main reason which lead to the surface corrosion morphology. The corrosion processed is suggested as Fig.5

4.1. Stage I (the effect of Cl$^-$)

While the drum was fed into water, a protective film forms on the waterside of the drum and pipes with the passage of time. At Stage I, the protective film would be affected by the attacking of Cl$^-$ continuously because the interior products adjacent to the matrix show higher content of Cl$^-$ and with the increase of Cl$^-$. Similar phenomenon was also found in other corrosion processes [10]. Some micro-hole would appear at a certain time.

At the same time, PO$_3^{3-}$ and Na$^-$ existing in the solutions would start to deposit on the surface with the progressively increasing ion content, which makes the exterior corrosion products have higher Na and P.
4.2. **Stage II (the beginning of anode and cathode reactions)**

After micro-holes appear, the fresh metal surface would be exposed. At that time, PO\textsuperscript{3−} would undergo hydrolysis to form OH\textsuperscript{−}. Under this alkaline condition, the fresh Fe begins to erode and generate Fe(OH)\textsubscript{2}. If the O\textsubscript{2} concentration is too high in the water, the dissolved oxygen would enrich and attach to the fresh surface. At last, the pit will begin to finally form.

4.3. **Stage III (the continuous corrosion of matrix)**

With the corrosion reaction proceeding further, the amount of corrosion products increased and covered some of the pitheads. As a result, the dissolved oxygen found difficulty in diffusing into the pit. Then, more Fe\textsuperscript{2+} was generated inside the pit. However, because of the hindering effect, OH\textsuperscript{−} ions had difficulty penetrating. As a result, Fe\textsuperscript{2+} would hydrolyze as the following equation:

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{H}^+
\]

Increasingly more H\textsuperscript{+} would appear during the process, and the local PH would decrease. It would treat the materials of the pipe as an activation state and accelerate the dissolution. Finally, the pit extended.

On the other hand, two phases, namely, cementite and ferrite, existed in this 20G (the drum materials). Severe micro-galvanic corrosion occurred at this stage because of the potential difference between them. For low potential, cementite plays the role of cathode and O\textsubscript{2} would be reduced around the cementite.

![Figure 5. Process of the formation of surface corrosion morphology](image)

4.4. **Stage IV (the falling off of cementite)**

With the progress of corrosion, the anode (ferrite) would continually be active and become increasingly less. On the contrary, the cementite is the zone of cathode reaction, which is protected. When the anode around the cathode was all corroded, the cathode would fall off. Then, the hardness of the materials would decline.

In summary, it can be concluded that dissolved oxygen in feed water makes the ferrite, leading to the appearance of potholes on the surface and reduced local hardness.
5. Conclusion
The corrosion mechanism of drum in an industrial boiler is discussed in this paper. The following are the inferences obtained from this study:

1. The damage surface displays a large unsmooth corrosion area, with the decrease of hardness and thickness.
2. The dissolved oxygen in feed water was higher than that in standard, which is suggested to the cause of the corrosion behavior.
3. The corrosion process is divided into four stages: the effect of Cl⁻, the beginning of anode and cathode reactions, the continuous corrosion of matrix, and the falling of cementite.

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