Boiler Feedwater Oxygenated Treatment in Power Plants in China

Zhigang Li, Wanqi Huang, Songyan Cao, and Hongbo Zhang

ABSTRACT

This paper presents the development of the oxygenated treatment (OT) technique application in power plants in China. The oxide morphologies of boiler tubes (economizer and water wall) under three different feedwater treatment techniques – all-volatile treatment under reducing conditions (AVT(R)), all-volatile treatment under oxidizing conditions (AVT(O)) and oxygenated treatment (OT) – were analyzed, and it was found that the reddish brown Fe$_2$O$_3$ coating layer formed by oxygen in feedwater only extended as far as the economizer inlet section. This paper also has a detailed discussion about the CrO$_4^{2-}$ release phenomenon and demonstrates that the CrO$_4^{2-}$ detected in the steam cycle comes from sampling tubing and apparently does not originate from the boiler tube material.

INTRODUCTION

The Status Quo of Oxygenated Treatment in China

In the 1980s, the Thermal Power Research Institute (TPRI) realized the value of the oxygenated treatment (OT) technique, which was first proposed and implemented in Germany, and researched the technology both in the laboratory and by field testing. In 1988, TPRI successfully conducted OT field tests for the first time in the Wang Ting power plant subcritical boiler and achieved satisfactory results. Subsequently, the application of OT has become an effective solution to the problem of iron oxide deposition on economizer inlet orifices of 300 MW subcritical units made in China. In the 1990s, as China imported many 300 to 600 MW supercritical units and put them into operation one after another, OT was applied successfully to solve the frequent problems of high boiler heating surface corrosion rates and rapid increases in the boiler pressure differential. In 1995, TPRI first applied the OT technique to the Shanghai Shidongkou Power Plant 2 x 600 MW supercritical boilers, and achieved the desired results [1]. The units have also become the longest OT-operating supercritical units in China at present. In 2002, TPRI formulated a "Once-through Boiler Feedwater Oxygenated Treatment Guideline" to regulate the feedwater oxygenated treatment mode of boilers in domestic power plants [2]. In the 21st century, with a large number of domestic 600 MW supercritical units and 1 000 MW ultra-supercritical units having been put into operation in China, high corrosion rates of boiler heating surfaces, deposits on water wall tube orifices and deposits plugging high-pressure (HP) heater drain control valves have become more prominent (Figures 1 to 4). Corrosion and deposition of downstream equipment caused by flow-accelerated corrosion (FAC) is particularly prominent. These units originally applied the all-volatile treatment under oxidizing conditions (AVT(O)), but to solve the abovementioned problems, OT has been more actively utilized in these supercritical units [3]. At the same time, when the feedwater is in the AVT condition, mixed bed condensate polishing has a heavy operational burden, and many units are forced to operate in ammonium form, which causes severe leakage of chlorine and sodium into the mixed bed effluent. The deposition and corrosion of...
steam turbine blades is also very common (Figures 5 and 6). The advantages and effects of the OT technique for solving these problems are obvious, and therefore have become the driving force for the development of the technology.

As of the end of 2011, there are more than 100 units with OT in China, of which more than 80% are ultra-supercritical or supercritical units. All the 1,000 MW ultra-supercritical units in operation are using OT for feedwater treatment. Statistics of the units with OT and unit capacity are shown in Figure 7.

According to the “Once-through Boiler Feedwater Oxygenated Treatment Guideline,” which was mainly prepared by TPRI, the dissolved oxygen in feedwater is limited within the range of 30 to 150 µg·L⁻¹ for units on OT. In practice, the oxygen content in the feedwater of operating units with OT is in the range of 30 to 80 µg·L⁻¹. The merit of OT is fully reflected in these units, as demonstrated by data showing that the iron content in the economizer inlet and HP heater drain is less than 1.0 µg·L⁻¹ (Figure 8), and the average deposit rate in the tubing of the economizer and water wall after running for six years in this mode is less than 30 g·cm⁻² per year. In addition, the
regeneration cycle for the condensate polishing system has been extended 4 to 5 times compared with AVT operation, and the rate of boiler differential pressure increase is significantly reduced (Figure 9). At the same time, the deposits on the water wall orifice and oxide blockage in the HP heater drain regulating valve have been significantly mitigated.

However, the use of OT is still limited in many generating units in China due to the concern about high-temperature steam oxidation. To reduce the possible risk of introducing increased oxygen concentration into the steam system, hypoxia (low-oxygen) treatment in feedwater, also called weak oxygenated treatment (WOT), has been adopted in some units, and the dissolved oxygen content in the economizer inlet is generally controlled at 5 to 20 µg·L⁻¹. It is evident that hypoxia treatment cannot protect the HP heater drain system. High iron content in the drains caused by two-phase flow-accelerated corrosion (FAC) and drain valve blockage still cannot be avoided with low-oxygen treatment. In addition, the frequent regeneration of the condensate polishing mixed beds is a difficult problem for power plant chemistry workers.

Oxygen injection to feedwater systems often uses the auto-adjustment mode. An automatic oxygen feed device developed by TPRI for units with OT is popular in China. Normally, the dissolved oxygen content in the feedwater...
can be controlled within the setting range \( \pm 20 \mu g \cdot L^{-1} \)
even in the case of unit load fluctuations, because this
unique oxygen feed device is equipped with a trace gas
regulatory agent and a differential pressure stabilization
adjusting device, as shown in Figure 10.

**THE INVESTIGATIONS**

**Change in the Metal Oxide Film in the Low-Tempera-
ture Zone of the Boiler Heating Surface**

At the water temperature of the condensate low-pressure
heaters and the first high-pressure heater, the magnetite
film has higher solubility and it is in an active state.
Magnetcite solubility reaches the highest point at about
150 °C. When the local flow conditions deteriorate, disso-
lution of the oxide film can cause FAC at local metal
surfaces in the feedwater system under reducing condi-
tions, and that is why the iron content is higher (average 8
to 10 \( \mu g \cdot L^{-1} \)) in the feedwater systems of boilers treated
with AVT(R) (all-volatile treatment, reducing conditions).
When the feedwater treatment was changed from AVT(R)
to AVT(O) (all-volatile treatment, oxidizing conditions), the
FAC was only partly mitigated, and the iron content of the
feedwater was only lowered to an average of 4 to 6 \( \mu g \cdot L^{-1} \)
due to less dissolved oxygen in the feedwater. The corro-
sion products deposit at various locations in the system,
as previously mentioned, and this deposition is a widespread problem in supercritical boilers in China.

**Metal Oxide Film Forming Mechanism**

According to the oxide film formation mechanism, the metal oxide film in pure water without oxygen below 300 °C consists of a compact Fe₃O₄ topotactic layer and a porous Fe₃O₄ epitactic layer due to the insufficient oxidizing effect of water. Oxide film forming reactions can be divided into the following steps [4]: carbon steel is dissolved to form ferrous hydroxide and the magnetite and hydrogen is released. The third step is the slowest.

\[
\begin{align*}
\text{Fe} + 2\text{H}_2\text{O} & = \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2 \uparrow \\
\text{Fe}^{2+} + 2\text{OH}^- & = \text{Fe(OH)}_2 \\
3\text{Fe(OH)}_2 & = \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \uparrow
\end{align*}
\]

As the water temperature increases above 200 °C, the third step of the Fe₃O₄ oxide film formation mechanism is accelerated, but the presence of ferrous hydroxide is still an intermediate link in the corrosion cell reaction. As Fe(OH)₂ has high solubility, suppression of Fe²⁺ will occur if the pH of the water is elevated.

When oxygen is added to the water, the oxygen molecules accept electrons to form OH⁻ in the corrosion cell cathode. While water as an oxidizer has insufficient oxidizing strength to transform Fe²⁺ to Fe³⁺, oxygen molecules support the reduction reaction at the cathode and provide the required energy for Fe²⁺ to convert to Fe³⁺. This increases the phase interface reaction speed, and eventually accelerates the conversion of ferrous hydroxide to ferric oxide.

\[
2\text{Fe(OH)}_2 + \frac{1}{2}\text{O}_2 = \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}
\]

Because oxygen is continuously added to the feedwater, the Fe²⁺ diffused through the Fe₃O₄ topotactic layer is oxidized to form FeOOH or Fe₂O₃, as shown in Eq. (4), which then is deposited in holes and surface pores in the Fe₃O₄ epitactic layer. The Fe₂O₃ seals the porous Fe₃O₄ film, resulting in a dense and stable "double layer protective film" formed on the steel surface [5], as shown in Figure 11a. The iron content in the feedwater is then decreased to less than 1 µg·L⁻¹.

**The Surface Difference on the Inlet Tube and Outlet Tube of the Economizer**

The status of the metal oxide films on the surfaces of the feedwater system cannot be directly analyzed and compared. This is because the sampling is difficult, and it can only be judged by means of the analysis of economizer tubes. Before 2008 in China, all feedwater oxygenated treatment was directly converted from AVT(O) while operating the boilers without first carrying out chemical cleaning. After the boiler treatment had been converted to OT (the oxygen concentration in the feedwater was about 50 to 70 µg·L⁻¹) for a period of time, tubes were sampled and metal surfaces were observed. It was found that the surface color of all tubes from the economizer to the water wall appeared brown-red due to heavy powdery iron oxides, which resulted from performing the conversion to OT without a prior chemical clean. This observed phenomenon led to some confusion regarding the theoretical effective oxygen range for OT.

After 2008, power plants in China began to focus more on saving energy and reducing the cost of running the unit. In order to completely clear out the iron oxide deposits in the feedwater system and boiler, chemical cleaning was carried out prior to OT conversions. Some tubes from
The oxide film color and appearance characteristics of the economizer outlet tube samples are close to those of water wall tube samples, showing a “clean” surface compared with that of the inlet section tube although there is a very weak brown color on the tube surface. This phenomenon may also suggest that the effect of oxygen promoting the formation of a double protective layer on the metal surface by means of cathodic reduction in a corrosion cell has visibly begun to weaken. Thus, the Fe₂O₃ oxide coating layer formed by oxygen feed only extends as far as the economizer inlet section where the water temperature is still about 300 °C (water temperatures of the economizer inlet and outlet are 290 °C and 320 °C, respectively). However, the oxidation-reduction potential (ORP) of the water here has been kept at a positive value in the boiler water solution due to oxygen feeding, until oxygen in the water enters into the steam in the water wall evaporating section of the boiler.

When the water temperature of the economizer outlet exceeds 300 °C, redox reactions occurring on the metal surface may directly oxidize ferrous ions to ferric ions instantly, as illustrated in the chemical reaction Eq. (5), which also suggests that bivalent iron ion migrating outward from the metal matrix may be converted to ferric ions subsequently a Fe₂O₃ oxide coating in the oxide layer was formed under the conditions of the water temperature at the inlet section of the economizer, which is very important for inhibiting FAC at the economizer tube entrance.

This kind of Fe₂O₃ film is different from the α-Fe₂O₃ formed at high temperatures and is unstable at the temperature of feedwater [6] and the high flow rate of feedwater; it requires continuous oxygen feed (above 30 µg·L⁻¹) to maintain its stability.

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in an instant. The formation of dense magnetite oxide films has no ferrous hydroxide as a transitional product here (Eq. (5)):

\[ 3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \]

(Eq. (5))

As long as the ferric iron concentration is above a very low threshold, it precipitates and becomes a stable solid phase, because the solubility of magnetite is much lower than that of ferrous hydroxide.

In this process, Eq. (5) is in balance with no excess bivalent ferrous ions or electrons, so the oxygen molecule here has no way to participate in the formation process of the oxide film reaction.

In other words, the metal oxide film is in a passive state due to the temperature (above 300 °C) and ORP (above 100 mV of the water, and an excess of oxygen in the water and elevation of water pH are not important in this pure water system. The scaling rate on the tube surface here also indicates that the oxidation film is very thin in the economizer outlet in Table 1. Among 4 boilers, the scaling rate of the economizer of the boiler operating under OT is the lowest.

This phenomenon indicates that in metal oxidation there is a competitive relationship between hot water and a small amount of oxygen at the temperatures in the thermal system. In the lower temperature zone, oxygen in the water can promote the formation of a double protective coating layer on the metal surface. In the middle temperature zone, the oxidizing strength of the water is enhanced due to higher temperature and positive ORP of the water; water and oxygen may contribute jointly to metal oxidation. In the steam zone, the contribution of water steam and oxygen to metal high-temperature oxidation mainly depends on the gas partial pressure.

### Deposition on the Water Wall Tube Surface

The temperature of water or steam in supercritical boiler water wall tubes is high (above 350 °C), so the metal surface can be spontaneously oxidized to form a fine and dense film by water and steam with sufficient oxidizing strength. However, there are different surface appearances due to iron corrosion products depositing on tube surfaces when boiler feedwater treatments are different; Figure 13 illustrates boiler water wall tube surfaces with feedwater treatments of AVT(R), AVT(O) and OT, respectively. The outside layer of the oxide film on a water wall tube treated with AVT(R) (Figure 13a) has an oxide that has a coarse granular particle size, since the iron oxide particle comes from the upstream thermal system by corrosion product transport. The outside layer of the oxide film on a water wall tube treated with OT (Figure 13c) has a fine granular particle size since the oxide film was formed in situ and few iron oxide particles originate from the upstream thermal system water. The outer layer of the oxide film on the water wall tube treated with AVT(O) (Figure 13b) has iron oxide particles of a size between the above two scenarios; nevertheless, the oxide layer still has obvious rippled characteristics.

The products on the metal surfaces have been tested by XRD. The product on the water wall tube surface in a boiler with AVT(O) is a Fe₃O₄. The product on the water wall tube surface, including the economizer outlet section, in a boiler with OT is Fe₃O₄ and a small amount of α-Fe₂O₃, because hot water is strongly oxidizing under conditions of higher temperature and positive ORP; corrosive product migration and deposition can also impact the products on the water wall tube surfaces.

### Change in the Metal Oxide Film in the High-Temperature Zone of the Boiler Heating Surface

It has been a concern to chemistry personnel whether feedwater oxygenated treatment (OT) affects the oxidation behavior of the internal surfaces of superheater and reheater tubes. All collected data from field samples show that OT did not increase the oxide growth rate of superheater and reheater tube interiors. There is almost no controversy regarding this result. With regard to the oxide layer peeling off, it has been confirmed that oxide layer exfoliation of low-chromium alloy steel (T23), martensitic steel

<table>
<thead>
<tr>
<th>Unit</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>AVT(O) 1 year WOT 0.4 years</td>
<td>AVT(O) 0.83 years</td>
<td>AVT(O) 1 year</td>
<td>OT 1.17 years</td>
</tr>
<tr>
<td>Measuring point</td>
<td>EIS</td>
<td>EIS</td>
<td>EIS</td>
<td>EIS</td>
</tr>
<tr>
<td>Scaling rate (g · m⁻² per year)</td>
<td>60.6</td>
<td>46.9</td>
<td>42.9</td>
<td>35.3</td>
</tr>
</tbody>
</table>

Table 1: Scaling rate (g · m⁻² per year) at the tube surface of the economizers in one power plant.

WOT weak OT
EIS economizer inlet section
EOS economizer outlet section
(T91) and high-chromium alloy steel (HR3C) has not been affected by oxygen concentrations in steam. The focus of the argument is whether oxygen in the steam promotes the spallation of the metal oxide layer of 18 Cr series austenitic stainless steel in high-temperature zones [7,8].

It was found from the investigations and surveys in China that the issue of oxide removal from 18 Cr series austenitic stainless steel is more prominent in boilers treated with OT. The extent of serious oxide layer exfoliation is quite different when the design of the unit includes the same pipe material in boilers with or without OT. In some units, exfoliation took place in the superheater, while in other units exfoliation took place in the reheater, and in some units, the exfoliation occurred in both the superheater and the reheater, or in neither. After careful research and comparison, it was shown that temperature is the key factor in addition to the specific metal alloy. The influential factors for boiler tube temperature are the boiler model, type of coal, combustion mode, heating surface design, arrangement of superheater and reheater, etc.

Chromium Acid Ion (CrO$_4^{2-}$) Release during OT Conversion

An increase in cation conductivity in water and steam is a common phenomenon during OT conversion. This is because some anionic impurities are released from the oxide film as phase transition occurs. These anionic impurities commonly include Cl$^-$, F$^-$, SO$_4^{2-}$, formic acid and acetate ions as well as carbonate ions. As the concentration is low and release time is short, they do not jeopardize the water and steam quality. TPRI has found another anionic impurity, the chromium acid ion (CrO$_4^{2-}$) [9] released in later phases of OT conversion, as shown in Table 2, which has a higher concentration than common anionic impurities, and also contributes to the cation conductivity increase.

The source of chromium acid ion is a special concern because boiler section materials contain the element Cr. According to the data compiled after converting to OT in dozens of units, TPRI has developed a summary of the characteristic release of chromium acid ion as follows:

1. Chromium acid ion mainly appears in economizer inlet and superheated steam samples (see Table 3 below). It is usually accompanied by an oxygen content increase in the feedwater and superheated steam samples after oxygen is added to the feedwater, and the CrO$_4^{2-}$ content peaks in a short time. The higher the dissolved oxygen (DO) content, the larger the peak value is. This level gradually decreases, but this rate of decrease is not related to DO. In fact, CrO$_4^{2-}$ release does not appear in all units during the OT conversion process, which may be associated with the sample tubing material.

2. There is no evidence of chromate ions in the water/steam cycle. CrO$_4^{2-}$ is never detected in the condensate, low-pressure feedwater, boiler water, and high-pressure drains, or reheat steam in either the OT conversion process or under normal operating conditions of a unit. Chromium content is also not detected in deposits in steam systems and turbines. When running on normal OT, DO is 30 to 80 µg·L$^{-1}$, and CrO$_4^{2-}$ is not detected in any sampling points of the water/steam cycle. If the DO concentration is increased intentionally for testing, CrO$_4^{2-}$ will clearly increase in the economizer inlet sample. This reveals that the DO concentration plays an important role in CrO$_4^{2-}$ release.
3. In superheated steam sample tubing, \( \text{CrO}_4^{2-} \) release is only found when dry steam in the end part of the pipe segment is gradually converted to wet steam or even water. There is only a trace of \( \text{CrO}_4^{2-} \) in superheated steam sampling of some supercritical units. For one unit, it has been confirmed that the sample tubing insulation is good [10]. However, \( \text{CrO}_4^{2-} \) has not been found in low-pressure and low-temperature feedwater samples, even though the low-pressure heater tubing is made of stainless steel. This also confirms that temperature plays an important role in \( \text{CrO}_4^{2-} \) release.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Unit Capacity</th>
<th>Economizer Inlet ((\mu g \cdot L^{-1}))</th>
<th>Steam ((\mu g \cdot L^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DO</td>
<td>( \text{CrO}_4^{2-} )</td>
</tr>
<tr>
<td>A</td>
<td>600 MW supercritical once-through boiler</td>
<td>150–200</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>B</td>
<td>500 MW subcritical once-through boiler</td>
<td>200–300</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>C</td>
<td>300 MW subcritical drum boiler</td>
<td>300–350</td>
<td>4.6</td>
</tr>
<tr>
<td>D</td>
<td>600 MW supercritical once-through boiler</td>
<td>150–200</td>
<td>18.4</td>
</tr>
<tr>
<td>E</td>
<td>600 MW supercritical once-through boiler</td>
<td>150–200</td>
<td>211</td>
</tr>
<tr>
<td>F</td>
<td>300 MW subcritical once-through boiler</td>
<td>200–300</td>
<td>17</td>
</tr>
<tr>
<td>G</td>
<td>600 MW supercritical once-through boiler</td>
<td>100–200</td>
<td>7</td>
</tr>
<tr>
<td>H</td>
<td>1 000 MW ultra-supercritical once-through boiler</td>
<td>100–150</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 2: Dissolved oxygen (DO) and chromium acid ion content at some sample points during OT conversion.

Table 3: \( \text{CrO}_4^{2-} \) content at cycle sampling point in Unit E during OT conversion.

Note: < 0.3 indicates that the \( \text{CrO}_4^{2-} \) content is less than the detection limit (0.3 \( \mu g \cdot L^{-1} \)) for the chromatograph.
The analysis above reveals that CrO$_4^{2-}$ only comes from the sample tubing surface film. One possible mechanism is as follows:

In the stainless steel sample tubing of the economizer inlet, the water temperature is at 270 °C to 290 °C; there are Cr$_2$O$_3$, Cr$_2$O$_3$$_2$, (OH)$_2$ and Cr(OH)$_3$ present, from the inside to outside of the metal oxide film under AVT conditions. The higher the temperature, the higher the ratio of chromium oxide in the oxide film, due to the accelerating diffusion of chromium ions in the material. During the unit conversion to OT, as oxygen passes through the sampling tubes, the redox potential rises, and the water changes to a more oxidizing state. The metal oxide film on the surface of the sampling tube changes accordingly. Low-valence oxides in the oxide film are oxidized to high-valence oxides, such as Fe$^{2+}$, Cr$^{2+}$ and Cr$^{3+}$ being converted to Fe$^{3+}$ and Cr$^{6+}$. Part of the high-valence chromium compounds dissolve and combine with water to form CrO$_4^{2-}$. Under a certain water temperature and fluid flow velocity, if the oxygen concentration is beyond a certain range, the higher the oxygen concentration, the faster the chromium ion release from the metal [11]. Therefore, for feedwater sample tubing made of stainless steel material, specific high temperatures, water flow rate and DO concentration prove to be three key conditions for chromium acid ion release; without any of these three conditions, chromium acid ion release will not happen.

CONCLUSION

The application of feedwater oxygenated treatment technology in China is successful and has achieved technical and economic benefits. Feedwater oxygenated treatment for the pre-boiler system can significantly reduce the iron content in the feedwater system and then reduce the boiler differential pressure drop and deposit rate on boiler tubing, which eventually results in the improvement of boiler efficiency and energy savings.

Feeding oxygen to the water makes the metal surface form a reddish brown Fe$_2$O$_3$ coating layer. This layer requires continuous oxygen feed to maintain its stability. Research has confirmed that oxygen promotes the formation of a double protective film on the metal surface through the cathodic reduction effect in the corrosion cell. This mechanism is closely related to water temperature, and its effective temperature range is from room temperature to about 300 °C.

The CrO$_4^{2-}$ detected at some water sampling points during OT conversion and/or normal operation with OT does not come from the thermal equipment material but most likely is released from stainless steel sample line tubing.

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