Field corrosion tests for a low chromium steel carried out at superheater area of a utility boiler with three coals containing different chlorine contents

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Abstract

Field corrosion tests for a low chromium steel were carried out at a superheater area of a 100 MW pulverized coal-fired boiler for various times up to 500 h, when three coals having different chlorine contents were combusted. The low chromium steel had obvious metal loss due to corrosion, and comparison of the metal loss and corrosion scale structure was made among the three coals in respect to chlorine contents as well as other elements affecting its corrosion. Corrosion scales of the low chromium steel had a general two-layer structure: an inner layer containing iron, chromium, oxygen and sulfur, and an outer layer made of porous iron oxide and fly ash particles. Distinct molten phase formation, which is an indication of severe corrosion, was observed for the coal containing only the middle high chlorine, and it initiated in the outer layer of the corrosion scales.

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1. Introduction

Coal combustion in utility boilers generates complex environments that lead to heat exchange tubes being subject to corrosion. The combustion gases contain multiple corrosive components, and there are always ash and minor salt depositions that can accelerate the corrosion. Consequence of the corrosion causes not only loss in effective thickness of the heat exchange tubes, but also reduction in heat transfer due to building up of corrosion products and deposits on the surface of the tubes [1,2]. High temperature corrosion of the heat exchange tubes in the environment of coal combustion is complex. There were early reports on correlated corrosion with coal chlorine contents in coals [3–5], which has been a concern of boiler manufacturers and coal end users. Boiler manufacturers generally consider coal containing more than 0.3% chlorine to be potentially corrosive for pulverized coal units. However, a recent study based on a pilot-scale combustor did not find a clear correlation between chlorine contents in coals and corrosion [6]. It was also reported that Midwestern United States utilities had decades of experience burning high-chlorine Illinois coals in a large variety of boilers [7,8]. Although fireside corrosion problems were reported, none of them was attributed to the presence of Cl in coals. The effect of chlorine content in coals on corrosion of heat exchange tube materials needs more investigation, especially with field corrosion tests under which materials are exposed to combustion gases under an identical temperature gradient and fly ash deposition as real heat exchange tubes since there have been only limited open publications available on field corrosion tests [9,10]. In this study, field corrosion tests for a low chromium steel were carried out at the superheater area of a 100 MW low NOx pulverized coal-fired boiler when three coals containing different chlorine were combusted.

2. Field test experimental

The tested material was a low chromium steel SA-213T-22. Compositions of the material are listed in Table 1. The steel was machined into disks that had a diameter of 2.86 cm and
thickness of 0.32 cm, followed by polishing and electroplating a chromium ring. Each disk was welded to a pipe of the same material that could be connected to air compressor. Thermal couples were also connected to the disks at the side facing the pipes to monitor temperature. The gas temperature at the location where the probes were placed was 786 °C. Air flow introduced into the probe from the air compressor was used to cool the probes to give the disks a temperature around 537 °C. The schematic for the probes is shown in Fig. 1.

Deposited at one side of the disks along their circumference, the electroplated chromium was about 5 μm in thickness and had a ring width of around 0.10 cm. The chromium coating was utilized as reference for measuring metal loss from corrosion for various periods (10, 30, 70, 150 and 500 h). The metal loss was determined using optical microscopy, as it is demonstrated in Fig. 2. The corrosion scales were analyzed using X-ray diffraction (XRD), and scanning electron microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS).

The corrosion tests were carried out when the boiler was combusting there coals from different mining sources that had different chlorine contents. The chlorine contents in the coals were determined using ion chromatography and listed in Table 2. The other major elements in the coals, analyzed by X-ray fluorescence, are also given in the table.

### Table 1

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA-213T-22</td>
<td>2.27</td>
<td>8.11</td>
<td>Bal.</td>
<td>0.50</td>
<td>0.44</td>
<td>0.97</td>
<td>0.13</td>
</tr>
</tbody>
</table>

3. Results and discussion

For test time up to 500 h, the metal loss of the material from the corrosion tests for the three coals did not show a strict increase as increase of chlorine contents, as it is shown in Fig. 3. Coal 1# had the lowest chlorine content (908 ppm), but its metal loss was higher than that of coal 3# (1684 ppm) for test time up to 150 h. Although chlorine content in coal 2# (3577 ppm) was 3.94 times higher than that in coal 1# and 2.12 times larger than that in coal 3#, the metal loss from the three coals was becoming closer at 500 h compared to the test points at 150 h. The metal loss from both coals 1# and 2# showed a trend of reduced rates with time, while that from coal 3# that had the middle high chlorine content, showed an accelerated trend.

The corrosion scales were examined using SEM. For the corrosion tests up to 150 h, there was a similar two-layer structure for the three coals. Fig. 4a–c shows the backscattered electron images (BEIs) of the corrosion scales obtained from the tests for 70 h. The typical EDS spectra are also given in Fig. 4d.

The outer layer of the corrosion scales was made of iron oxide incorporated with fly ash particles. EDS analyses performed on the dark and gray round-shaped particles in the outer layer always gave high peak densities of both aluminum and silicon. These round-shaped particles should be fly ash incorporated. For some of the fly ash particles, significant potassium was also detected. While oxygen was the major element detected everywhere in the outer layer, iron was also detected at areas away from the incorporated fly ash particles. Oxygen peak is not shown in Fig. 4d due to the horizontal axis range selected to avoid the peak from the coated carbon thin films for SEM examination. XRD analysis performed for the corrosion scales gave most of the diffraction peaks corresponding to Fe₂O₃ (Fig. 4e), which should be the iron oxide in the outer layer.

For the inner layer, sulfur as well as iron, chromium and oxygen was detected. Some black areas were seen in the inner layer, but EDS analyses proved that they were holes or uneven areas from polishing rather than fly ash particles. The inner layer was essentially free of any fly ash particles.

The incorporation of fly ash particles into the corrosion scales was also observed from top surface images, as shown in Fig. 5. The fly ash particles were seen on surface for test time as short as 10 h. The iron oxide grew outwards and eventually surrounded the fly ash particles. Consequently the iron oxide in the outer layer is considered to form by iron migration outwards. The incorporation of the fly ash particles into the outer layer, but not into the inner layer is the evidence of the iron oxide formation by outward migration of iron through the inner layer.

Fig. 5 shows also that the iron oxide in the outer layer was porous in nature, and this plus the interface between the incorporated fly ash particles and the iron oxide, could provide the paths for inward transportation of oxygen and sulfur through the outer layer. The inner layer of the mixed iron–chromium oxide might be mainly formed by inward immigration of oxygen and
sulfur through the outer layer since there was no incorporation of the fly ash particles into the inner layer. The existence of significant amounts of sulfur in the inner, on the other hand, would cause the inner layer less protective and facilitate the outward migration of iron through it to form the porous outer layer. In any case, chlorine was not detected in the corrosion scales by EDS.

From the above examination for the corrosion scales, sulfur content in the coals would therefore be an important factor affecting the metal loss. Although coal 1# had lower chlorine content, it had higher sulfur content, and this could explain why the metal loss obtained from combusting coal 1# was higher than that obtained from coal 3# for all test points except the one for 500 h. Comparing Fig. 4a and c, the inner layer in Fig. 4a (coal 1#) is obviously thicker than that in Fig. 4c (coal 3#), showing that the inner layer formed in coal 1# was less protective.

When comparison on metal loss was made between coals 2# and 3#, it can also be considered that the higher sulfur content in coal 2# contributed to its higher metal loss. However, comparison made between coals 1# and 2# gave a more complex result for which interpretation should be beyond the sulfur contents in the coals, since the two coals had close sulfur contents but coal 2# gave higher metal loss.

Coal 2# had both higher chlorine and sodium contents compared with coal 1#. In this case, it is possible that trace of Na₂SO₄ was formed from NaCl and deposited on the coupon surface, since it is known that in the presence of sulfur species NaCl is not stable by converting it into Na₂SO₄ [11]. In a recent laboratory study [12], it was found that solid Na₂SO₄ powder coated on iron samples facilitated the formation of iron sulfide in the inner corrosion scales, and caused a higher degree of formation of iron oxides and corrosion rate, although Na₂SO₄ was seen keeping a solid coating after the corrosion tests without observing the formation of disrupted molten phase in the corrosion scales in a simulated atmosphere at a temperature far below the melting point of Na₂SO₄.

The BEIs of the cross sections of the corrosion scales from the tests for 500 h are shown in Fig. 6a–c. The corrosion scales still had the two-layer structure for the longest time, i.e., the outer iron oxide layer incorporated with the fly ash particles and the inner layer containing sulfur. However, for the corrosion scale formed from coal 3#, areas typical of disruption due to extensive formation of molten phase were seen in the outer layer, as shown by the two arrows in Fig. 6c. This is in agreement with the accelerated trend of corrosion for coal 3# shown in Fig. 3. Although the metal loss from coal 3# had lower values than that from coal 1# at all the points except the 500 h one, a higher value was obtained for the longest time.

Coal 2# had much higher chloride, sodium and sulfur contents than coal 3#. However, apparent disruption due to the formation of molten phase was only seen for coal 3#, and corrosion from coal 3# showed an accelerated trend compared with the other two coals. Coal 3# contained the highest potassium (K₂O=3.55). While alkali elements Na and K have been considered to contribute to the formation of alkali iron sulfate causing liquid-phase corrosion, alkaline earths Ca and Mg were documented to be anticorrosion elements that inhibited formation of alkali iron sulfates and Ca was considered more effective than Mg in suppressing the liquid formation [9]. Coal 3# had the lowest Ca content (with CaO=1.08), as compared with coal 1# (CaO=1.547) and coal 2# (CaO=1.937). It is possible that the weaker anticorrosion factor led to the earlier formation of the molten phase and the accelerated corrosion trend for coal 3#, while chlorine content in the coals did not play a major role.

Considering long operation time of the boiler, the corrosion tests carried out only for 500 h revealed an earlier stage of corrosion of the material. The above results show that corrosion of the material occurred first as sulfur-affected oxidation. Sulfur content in the coals should be a critical factor at this stage, but chlorine content could also possibly affect the oxidation under the condition that its contents as well as sodium and potassium in coals were significantly high. Long time exposure of the material would have formation of molten phase in the corrosion scales. The formation of molten phase, which is an indication of severe corrosion, was found initiating in the outer layer that was made of the porous iron oxide and the incorporated fly ash particles. For the coal containing the highest chlorine content, it did not give an earlier formation of the molten phase. Consequently, corrosion severity may not be simply linked to

<table>
<thead>
<tr>
<th>Coal no.</th>
<th>Cl ppm</th>
<th>SO₃ %</th>
<th>Na₂O %</th>
<th>K₂O %</th>
<th>CaO %</th>
<th>MgO %</th>
<th>Al₂O₃ %</th>
<th>SiO₂ %</th>
<th>P₂O₅ %</th>
<th>BaO %</th>
<th>SrO %</th>
<th>Fe₂O₃ %</th>
<th>Mn %</th>
<th>TiO₂ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>908</td>
<td>1.413</td>
<td>0.340</td>
<td>2.225</td>
<td>1.547</td>
<td>1.083</td>
<td>26.927</td>
<td>53.277</td>
<td>0.300</td>
<td>0.284</td>
<td>0.211</td>
<td>9.005</td>
<td>0.017</td>
<td>1.511</td>
</tr>
<tr>
<td>2#</td>
<td>3577</td>
<td>1.320</td>
<td>1.113</td>
<td>2.834</td>
<td>1.937</td>
<td>0.710</td>
<td>23.314</td>
<td>49.422</td>
<td>0.363</td>
<td>0.064</td>
<td>0.087</td>
<td>14.950</td>
<td>0.023</td>
<td>1.364</td>
</tr>
<tr>
<td>3#</td>
<td>1684</td>
<td>0.774</td>
<td>0.332</td>
<td>3.550</td>
<td>1.108</td>
<td>1.115</td>
<td>24.236</td>
<td>47.465</td>
<td>0.220</td>
<td>0.089</td>
<td>0.065</td>
<td>17.678</td>
<td>0.028</td>
<td>1.173</td>
</tr>
</tbody>
</table>

**Table 2** Contents of major elements in the coals
chlorine contents in coals. It is thus possible that combusting coals containing higher chlorine might not always give more severe corrosion problem, or technologies in combustion could be developed to lessen the corrosion problem for more use of high chlorine coals.

4. Conclusions

The field tests showed that the low chromium steel experienced corrosion at the superheater area of the boiler, inspected from both metal loss and corrosion scales. Coal 2#, which had the highest chlorine content, had also the largest metal loss, but coal 3#, whose chlorine content was much lower, showed an increased trend of corrosion. Although coal 1# had the lowest chlorine content, the steel had higher metal loss than coal 3# for all of the test points except the one for 500 h.

The corrosion scales obtained from the three coals had similar scale structure: an outer layer consisted of porous iron oxide and the incorporated fly ash particles, and an inner layer made of iron, chromium, oxygen and sulfur. Disruption in the corrosion scale due to substantial molten phase formation that is an indication of severe corrosion was only observed for the coal containing middle high chlorine (coal 3#) for the longest test time.

Corrosion of the material was in the form of sulfur-affected oxidation at the beginning, likely followed by molten phase formation in the corrosion scales that started more severe

Fig. 4. BEI images of the cross sections of the coupons tested for 70 h: A) coal 1#; B) coal 2#; C) coal 3#. Typical EDS spectra are given in D), and E) is a typical XRD spectrum.
corrosion. The molten phase formation initiated in the outer layer that was porous and incorporated with fly ash particles. Significantly high chlorine content might affect the corrosion, especially at the sulfur-affected oxidation stage. However, there was no obvious correlation between higher chlorine content in the coals and more corrosion severity as a whole.

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