FAILURE ANALYSIS OF REHEATER TUBES INVOLVING CREEP AND SULFIDISATION

F. Vodopivec, B. Ralić, J. Žvokelj and B. Dobovišek*

The partial substitution of lignite by brown coal was followed by an increased frequency of failures. Experimental findings in connection with a theoretical analysis indicate that the leakage is due to overheating and sulfidisation of the tube steel. Iron sulfide forming prevents the closing of longitudinal scale cracks, caused by partial expansion of the tubes. A model is proposed to explain the sequences of the failure process.

INTRODUCTION

An increased frequency of failures of re heater tubes was observed in a power station some months after lignite was partially substituted by brown coal. At a first view the leakage (figure 1) was similar to those which are found to develop on tubes from small longitudinal surface defects after long operation times. The increased frequency of leakages threwd doubt upon this explanation. For this reason, a careful examination of boiler tubes was carried out. Samples for microstructural examination and electron microprobe analysis were prepared from different parts of the re heater on the longitudinal and the transverse section of the tubes. Tensile properties, microstructure, thickness of scale and of magnetite, and residual wall thickness were established on two typical points, the flame and the chimney side of tubes. As flame side the side of tubes facing the flue gases is denoted, while the chimney side is the diametral one.

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EXAMINATION OF DAMAGED TUBES

The examination of several tubes of two different steels showed very similar features. The microstructure of the steel was considerably different between chimney and flame side, because on this side the spheroidisation of cementite lamellae in pearlitic grains was much more advanced. This indicates that the metal temperature has been considerably higher on the flame side of the tubes. In Table 1 the composition and the mechanical properties of the steel, determined on specimens taken from the flame and chimney side of the tubes, are shown.

The difference in microstructure is connected with small differences in mechanical properties at room and at operation temperature. Tensile properties show somewhat lower values on the flame side, but are however very close to the nominal properties of the steel. It can be therefore concluded that the overheating of the flame side of tubes does not affect significantly the strength of tubes.

Table 1a - Composition of the two tube material types.

<table>
<thead>
<tr>
<th>Steel type</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.13</td>
<td>0.33</td>
<td>0.56</td>
<td>0.82</td>
<td>0.37</td>
</tr>
<tr>
<td>B</td>
<td>0.15</td>
<td>0.38</td>
<td>0.52</td>
<td>2.3</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Table 1b - Mechanical properties at room and operation temperature of steel type A.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>BH N/mm²</th>
<th>YP N/mm²</th>
<th>TS N/mm²</th>
<th>RA %</th>
<th>BH N/mm²</th>
<th>YP N/mm²</th>
<th>TS N/mm²</th>
<th>RA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T.</td>
<td>142</td>
<td>280</td>
<td>501</td>
<td>55</td>
<td>167</td>
<td>319</td>
<td>53⁴</td>
<td>55</td>
</tr>
<tr>
<td>500 °C</td>
<td>-</td>
<td>-</td>
<td>313</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>33⁴</td>
<td>-</td>
</tr>
<tr>
<td>R.T. nominal prop.</td>
<td>-</td>
<td>300</td>
<td>450-580</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

BH-Brinell hardness, YP-yield point stress, TS-tensile strength, RA-reduction of area, E-elongation
TABLE 2 - Thickness of scale (S) and magnetite (M) and the residual thickness of the wall (R) in mm

<table>
<thead>
<tr>
<th>Steel type</th>
<th>Flame side</th>
<th>Chimney side</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>M</td>
</tr>
<tr>
<td>A</td>
<td>0.45</td>
<td>0.28</td>
</tr>
<tr>
<td>A</td>
<td>0.90</td>
<td>0.77</td>
</tr>
<tr>
<td>B</td>
<td>0.95</td>
<td>0.10</td>
</tr>
<tr>
<td>B</td>
<td>0.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Nominal thickness of the wall 3.8 mm.

In table 2 the thickness of the scale, that of the layer of magnetite on the internal surface of the tubes and the residual thickness of the wall are shown.

The diminution of the wall thickness because of scaling of the steel on the external surface and the formation of magnetite on the internal surface of the tubes is considerable and similar for both types of steel. Residual thickness as low as 1/3 of the initial thickness are found also on non leakaged tubes. The effective stress at operation would be in such cases three times higher than the nominal stress, that is above the safety coefficient of approximately 2 which is usually considered in the calculation of the thickness of the tube wall. It can be concluded, that once the wall is diminished because of the oxidation of steel, the effective stress can at operation conditions reach the level necessary for a creep deformation of steel and the expansion of the flame side of tubes.

On the transverse section of the flame side of non leakaged tubes and on failed tubes from the leakage area, wedge shaped penetrations of the scale with orthogonal cracks in the centre were observed (figure 2). Electron microprobe analysis showed the cracks to be partially filled with iron sulfide. Small inclusions of iron sulfide were also found to be regularly distributed in the scale near to the steel surface. On some areas in the scale, also thin layers of iron sulfide alternated with oxide were observed.

The wedge shaped penetrations of the scale are in reality longitudinal grooves on the surface of the tubes and the central cracks longitudinal fissures orthogonal to the wall. Near the leakage also intergranular cracks were observed at the tip of the grooves (figure 3), while deeper also areas with porosity at triple boundary points were found (figure 4).

The internal surface of the tubes was covered with a regular layer of magnetite with a greater thickness on the flame side of the tubes, as shown in table 2. Cracks or oxide penetrations in the wall on the internal surface of the tube walls have never been found, also not in face of grooves on the external surface. Most of the external scale and the whole internal layer consists of magnetite.
Supposing that the expansion of tubes produces cracks on the external scale, cracks would be expected to form also in the layer of magnetite on the internal surface of tubes. The absence of cracks in this area is explained by the effect of some closing process, for instance lateral growth of oxide during the expansion or once it is stopped. It can be concluded, on the other hand, that the presence of iron sulfide in cracks on external surface hinders the closing of cracks also when the expansion is stopped. Therefore, the absence of internal cracks could be considered as evidence that longitudinal grooves are not initiated by the cracking of steel but the cracking of scale. Open cracks allow a direct contact of steel and atmosphere and accelerate the local rate of steel. In this way, longitudinal grooves are formed on the external surface of the tubes.

On examined tubes it was not possible to determine the increase of size because of the expansion. The diameter was generally below the range given by the standard for the 38 mm tubes. An expansion of the tube with 1%, i.e. from 38 to approximately 38.4 mm in diameter, would cause a plastic strain of approximately 2.6%. No data were found on the deformability of scales on boiler tubes. Evidently it is small, otherwise the scale would not have cracked by the small deformation of steel.

On the basis of the kinetics of oxidation a rough evaluation of temperature difference between flame and chimney side of the tubes is possible. Pure iron is in water vapour oxidised to magnetite below 570 °C and to wustite above this limit (Benard et al. (2)). The oxidation to magnetite occurs very slow and the measured thickness of the oxide layer on the flame side on the internal surface of tubes could not be obtained in the operation time of tubes. It can be concluded that the temperature on the flame side was above 570 °C. A layer of wustite of 0.5 mm of thickness would grow at 600 °C on pure iron in approximately 6 months. Considering this, the measured thickness of oxide on the internal surface of the tubes and the fact that very probably the oxidation kinetics of pure iron is faster than that of the investigated steels, it is possible to estimate the metal temperature on the flame side to be 600 - 620 °C. At 570 the wustite layer on pure iron grow to approximately 0.25 mm in 6 months. This thickness is considerably above that measured on the chimney side. On the other hand, in the same time a layer of magnetite would reach a thickness of approximately 0.02 mm, which is below the measured values. It seems acceptable to suppose that the temperature on the chimney side was around 570 °C. It seems therefore that the temperature difference between the flame and chimney side of the tube walls has been in the range of 30 to 50 °C.
MECHANISM OF LEAKAGE

The scaling of low alloyed steel is governed by the oxidation of the matrix metal, iron (1). In dependence upon the partial pressure of oxygen, iron is oxidised to different oxides (2). Generally, hematite and magnetite with as minor components oxides of alloying elements (3), are found in the external surfaces of tubes and magnetite on the internal surfaces of boiler tubes. As required by laws of thermochemistry (Elliott and Gleiser 4) in boiler atmosphere, no reaction takes place between iron in steel and oxides with sulphur, e.g. sulphur dioxide. Iron sulfide is produced in the reaction between sulphur in elemental form or in form of compounds without oxygen, e.g. hydrogenated sulphur. No reaction occurs also between iron and sulphur bound in mineral sulfides or sulfates in coal ashes.

The presence of iron sulfide in the scale demonstrates therefore that the tubes were more or less frequently in contact with an atmosphere containing sulphur in non oxidised form. The kinetics of combustion of coal requires that the oxidation of sulphur occurs only after virtually the oxidation of compounds produced by distillation of coal and carbon is accomplished. It seems, that the contact of unoxidised sulphur with tubes is ensured through the partially burned particle of coal sintered on the flame side of tubes or sticking to it. The answer to this question was not investigated, because it is irrelevant for the purpose of this paper.

On the basis of this experimental findings and considering the thermochemistry of the reaction between the external surface of the tubes and the flue gas atmosphere the following model for the explanation of the failure of tubes is proposed. Initially, the external surface of tubes was covered with a scale of thickness corresponding to the atmosphere imposed by the combustion of lignite and the operational conditions of the boiler. Parallelly, the internal surface was covered with a layer of magnetite of thickness depending upon the wall temperature. The partial substitution of lignite by brown coal introduced uncontrolled heat transmission conditions and the temperature on flame side of tubes was increased above the allowed limit. Tempering and oxidation processes in steel were accelerated and the thickness of the wall was gradually diminished. At a critical thickness the stress in the wall exceeded that allowed for longterm operation. The consequence was a creep deformation which produced an expansion of the flame side of the tubes. In the poorly deformable scale and magnetite layer, longitudinal cracks were formed. Cracks in the magnetite closed without visible consequences, while in the scale cracks iron sulfide was formed which hindered their healing. Through partially closed cracks the oxidation of steel was accelerated. Gradually, longitudinal grooves were formed, the thickness
of the wall diminished and the stress in it increased. At a critical thickness intergranular propagation of fracture was initiated which produced a fast leakage of the wall.

CONCLUSION

Metallographical examinations were carried out on tubes taken from a boiler in which the partial substitution of fuel was followed by an increased frequency of leakage of reheater tubes. Experimental findings in connection with thermochemical considerations of the reaction between boiler atmosphere and steel showed the leakage to be due to the superposition of overheating of the flame side of the tubes and the sulfidisation of the steel, occurring simultaneously to the scaling of steel. A model is proposed in which the sequences of the process of leakage are explained.

REFERENCES

Fig. 1, Cracks in the failed tube.

Fig. 2, Scale penetrations in the wall of tube.

Fig. 3, Intergranular cracks and pores.

Fig. 4, Pores at triple boundary points of ferrite grains.

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Fig. 5, Basic sequences of the evolution of leakage.