Abstract

Black liquor is burned in the lower furnace of a kraft recovery boiler in a high temperature, oxygen deficient environment. The gaseous and molten inorganic combustion products are extremely corrosive. The furnace walls and floor are protected against corrosion by a number of methods. Considerable operating experience with corrosion protection is available today and provides information to the boiler designer and operator for future applications. Experience is reviewed with composite tubes and with carbon steel, pin-studded tubes used in the lower furnace of many recovery boilers. The few incidents of pin stud tube wastage and failure are discussed. Composite tubes constructed of TP304L/SA210A-1 and Sandvik 3R12 material have been installed in many recovery furnaces and all boiler manufacturers have experienced cracking of the stainless clad. Experience with this material is reviewed. Research and development programs to understand the cracking mechanism and establish a better material are summarized.

Introduction

The Babcock & Wilcox Company has built recovery boilers with pin studs applied to carbon steel tubes for corrosion protection of the lower furnace walls and floor since commissioning the world’s first Tomlinson unit in 1934 (Figure 1). Pin studs were applied as the principal protection in the recovery furnace until the advent of the composite tube. In 1981, a 25 year history of pin stud tube construction was reviewed.[1] This included ten recovery boilers operating at a superheater outlet pressure above 7.5 MPa (1075 psig), including three above 10.7 MPa (1540 psig). Successful high pressure operating experience included a boiler commissioned in 1959 to operate at 10.8 MPa (1550 psig). The first use of composite tube material in a Babcock & Wilcox recovery boiler was in 1979, and there are now 50 B&W units in operation utilizing the composite tubes in the lower furnace — more than any other boiler manufacturer. Forty-five (45) percent of these incorporate a center section of the floor using carbon steel tubes with a dense pattern of pin studs.

Floor Construction With Steel Pin Studded Tubes

The dense pattern of pin studs applied on the carbon steel tube is illustrated in Figure 2. Pin studs are 25.4 mm (1 in.) length by 12.7 mm (0.5 in.) diameter and are resistance welded to the tube to achieve a density of 1980 studs/m² on membrane panels fabricated with 62.4 mm (2.5 in.) outside diameter tubes. Experience has shown that any lesser diameter or density does not provide long term corrosion protection of the tube.[1] The pin studs retain refractory or frozen smelt to provide a barrier between the molten smelt and the tube. Exposure of the carbon steel tube to a flow of molten smelt could have the effect of removing the tube wall metal.

There are 22 composite tube recovery furnaces that have been built with this construction for the central section of the floor. Figure 3 shows a typical modern recovery boiler operating in

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the southeastern USA. There have been four (4) incidents of base tube wall metal loss, three (3) with failure of the tube. These, and two (2) other failure incidents in boilers with a decanting style floor, are summarized in Table 1. The Babcock & Wilcox boilers are designed with positive inclination floor tubes for positive circulation, whereas the floor in Supplier A’s furnaces is flat for the decanting hearth design.

<table>
<thead>
<tr>
<th>Mill</th>
<th>Floor Design</th>
<th>In-Service</th>
<th>Pressure</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>8.9 MPa</td>
<td>B&amp;W</td>
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<td>Inclined</td>
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<td>10.3 MPa</td>
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</tr>
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<td>Inclined</td>
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<td>10.8 MPa</td>
<td>B&amp;W</td>
</tr>
<tr>
<td>D</td>
<td>Flat</td>
<td>1976</td>
<td>7.6 MPa</td>
<td>A</td>
</tr>
<tr>
<td>E</td>
<td>Flat</td>
<td>1973</td>
<td>10.0 MPa</td>
<td>A</td>
</tr>
<tr>
<td>F*</td>
<td>Inclined</td>
<td>1991</td>
<td>8.6 MPa</td>
<td>B&amp;W</td>
</tr>
</tbody>
</table>

*Localized Wastage Only
The failures in carbon steel floor tubes that have pin studs are characterized by stud wastage, or burn-back, and thinning of the tube wall. In all cases of either failure, or discovery of a floor area that had been subjected to metal loss but not failed, the stud wastage that reduces the tube protection was in small, localized areas. Metallurgical examination determined that the tube in the failure area had been subjected to a high metal temperature in the range of 700 to 800 °C (1300 to 1500 °F). The conclusion reached from all of the evidence was that the failures or loss of metal were due to corrosion of the tube as a result of liquid smelt contact with the tube at a high metal temperature.

In any case of this kind in a furnace, the first suspect is circulation. It was recognized that the recovery boiler in Mill A had operated for 15 years with no evidence of stud loss or reduced tube wall thickness in the floor. Notwithstanding, the decision was made to review the circulation design calculations for every recovery boiler operating with a superheater outlet pressure of 8.38 MPa (1200 psig) or above. Further steps were taken to install chordal thermocouples and pitot tubes in selected recovery furnace floor tubes. Figure 4 shows a typical chordal thermocouple tube. The investigation resulted in the conclusion that circulation was not the cause of the problem. Measured floor tube velocities were as predicted. Figure 5 shows velocity data from one of the furnaces investigated.

Chordal thermocouples have been installed in five (5) recovery boilers and extensive temperature data recorded for each. In four (4) of the furnaces, the chordal sections were installed in the carbon steel, pin stud section of the floor, and in two (2) of the furnaces, two (2) chordal sections were installed in the composite tube sections. Figure 6 is an example of typical data. The data showed no transient surface temperature under any significant operating condition, including start-up, shutdown, boiler trip and steady state. Temperatures were substantially below those evidenced by metallurgical examination of failed tubes. There was no recorded evidence of steam blanketing of the tube waterside under any operating condition, including start-up and burning auxiliary fuel with no bed in the furnace. The chordal thermocouples showed very low heat input to the floor when covered with the char bed. Heat fluxes were determined to be in the expected range.
by the raised smelt spouts could actually circulate to carry molten smelt downward to contact the floor tubes. The tubes in several pin stud recovery floors have been replaced using Multiple Lead Ribbed (MLR) tubes in the place of smooth bore tubes. MLR tubes (Figure 7) have helical ribs on the inside surface of the tube. The ribs generate a swirl flow resulting in a centrifugal action which forces the water to the tube wall and retards steam blanketing. The MLR tube increases the tolerance for higher heat input transients that may occur. In one case, the recovery boiler was being upgraded in capacity and the application of the MLR tubes in the floor was the economical alternative to installing additional riser circuit tubes between the upper wall headers and the steam drum. Figure 8 shows a typical example of MLR tubes installed in a recovery boiler operating at 8.5 MPa where the circulation margin for heat flux was increased by a factor of about 50%.

Figure 7 Multi-lead ribbed tube.

Composite Tube Floor Cracking

All of the recovery boiler manufacturers have reported incidents of composite tube cracking. The nature of the cracks that penetrate the layer of stainless steel and turn 90° at the interface with the carbon steel has been documented. There is general industry acceptance that the cracking of the stainless steel is the result of thermal fatigue. Table 2 presents some of the North American units that have experienced composite tube cracking in the floor and Figures 9 through 11 provide additional detail on the location of the corrosion in the various constructions.

Figure 8 Margin for heat input transient.
• 26 are installed with the complete floor of composite tubes.
• 2 are units originally installed by another manufacturer with the decanting hearth floor utilizing bare carbon steel tubes.

The Supplier B recovery furnace uses an inclined floor with raised smelt spouts and is designated as "semi-drainable." Figure 10 illustrates the areas of cracking to be most severe under the pool of smelt formed by the raised spouts. Cracking occurs at the spout openings and adjacent tubes similar to that shown in Figure 9, but also at the interface between the surface of the pool and the side wall tubes.

The decanting hearth design is used by several manufacturers of recovery boilers. Those cases in the USA where cracking is known to have occurred have composite tube floors and show a pattern of cracks for Supplier C illustrated by Figure 11. Cracking has been found in the floor and at the interface between the surface of the smelt pool and the wall tubes.

The work of Klarin provides an explanation for the floor tube cracking. [3] For the cracking in the wall tubes, it is possible to visualize that the surface of the pool of smelt rises and falls during operation to cause temperature fluctuations in the tube and thereby induce thermal fatigue cracking.

In summary, cracks have occurred in the floor of carbon steel tubes in both the designs with a sloped floor and the decanting hearth. Cracking has occurred in the floor and walls of both

Table 2

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<thead>
<tr>
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</tr>
</thead>
<tbody>
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<td>B&amp;W</td>
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<td>Inclined</td>
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<td>8.8 MPa</td>
<td>B</td>
</tr>
<tr>
<td>K*</td>
<td>Inclined</td>
<td>1989</td>
<td>6.0 MPa</td>
<td>B</td>
</tr>
<tr>
<td>L</td>
<td>Decanting</td>
<td>1990</td>
<td>8.9 MPa</td>
<td>C</td>
</tr>
<tr>
<td>M</td>
<td>Decanting</td>
<td>1992</td>
<td>8.9 MPa</td>
<td>C</td>
</tr>
</tbody>
</table>

*Raised Spouts

Figure 9 illustrates a Babcock & Wilcox lower furnace with the standard inclined, fully drainable floor. The most prevalent area of cracking is in the smelt spout openings and/or the wall tubes adjacent to the openings. There have also been incidents of cracks in the floor, including one unit placed in-service in 1982, where a high incidence of cracks has resulted in the floor being replaced during 1996 after 14 years of operation. There are 52 operating recovery boilers where Babcock & Wilcox has installed composite furnaces. The floor construction in these units can be summarized as follows:

• 2 are installed with the complete floor of carbon steel pin stud tubes.
• 22 use carbon steel pin stud tubes in the center of the floor with the inclined tubes in the smelt flow areas adjacent to the side walls being composite tubes.

Figure 9

Zones of cracking – Babcock & Wilcox.

Figure 10

Zones of cracking – supplier A.
sloped and decanting designs that are built with the composite tubes that use the TP304L or 3R12 clad material. It appears that the frequency and extent of cracking is more severe in those designs employing the decanting hearth or raised smelt spouts. Cracks have terminated at the clad/carbon steel interface except where there are weldments at the spout openings and internal tube deposits. The mechanism is believed to be thermal fatigue with a secondary corrosion component inside of the cracks.

**Alternative Materials Research**

Recognizing the need for a better material that offered corrosion protection with reduced maintenance, and hopefully, not subject to cracking of the clad material, Babcock & Wilcox initiated a program of thermal fatigue testing of alternative materials. The materials selected for cyclic testing included:

- TP304L composite, coextruded tube
- Inconel 825 composite, coextruded tube
- Incoloy 625 weld overlay tube
- TP304L monolithic tube

The base tube material for the first three of the above is SA-210 Grade A1 carbon steel. The thermal fatigue testing was conducted at the Company's Research Center in Alliance, Ohio. Figure 12 is a schematic illustration of the test facility in which the water cooled tube is rotated to affect a rapid change in temperature of the tube wall from the controlled temperature at the point of flame impingement to a low of about 40 C (104 F). Figure 13 describes in more detail the location of thermocouples to measure the inside surface temperature and the temperature of the clad layer. Cyclic testing was conducted at both 650 C and 814 C (1200 F and 1500 F); the testing at the higher temperature was initiated when cracking of the 825 and 625 clad material was not observed at 650 C.
The results of the testing are presented in Figure 14. The sharp contrast is obvious between the life of the tubes with TP304L material and the nickel alloy tubes. Testing was arbitrarily stopped at 30,000 cycles to remove the test samples for metallurgical examination. There was no evidence of cracking of the 825 or 625 material. The Thermal Fatigue Cycling tests support the possibility of the nickel alloy tubes being superior for reduced cracking of the clad layer in the recovery furnace environment. Development of the Sanicro 38/4L7 material, similar to the 825 material, is summarized by Sandvik.\[6\]

The suitability of these materials to resist corrosion in a furnace is indicated by a summary of laboratory testing conducted by Babcock & Wilcox.\[5\] Test samples were subjected to various caustic chemical combinations showing that the resistance of the 825 and 625 material in this environment is superior to the austenitic stainless steels tested. The environment that was not tested is that of the active sulfur compounds, such as Na$_2$S and H$_2$S.

The final proof is installed life for the application of any material used in a recovery boiler. There is North American experience with both the Inconel 825 and the Incoloy 625 tube material in the hearth zone of the recovery furnace. The earliest application of the 825 material is for smelt spout openings operating since being placed in service in 1987. The Inconel 825 material is today being used selectively in recovery furnaces. In a few boilers where the TP304L openings have a tendency to crack, 825 alloy tubes have been installed for the severe duty in spout openings. With minor exceptions, these openings have proven far superior to the TP304L openings in resistance to cracking. One composite tube furnace that experienced high maintenance as a result of cracking of the TP304L tubes forming the primary air port openings, replaced these areas with the 825 composite tubes during 1995. Field experience is confirming the apparent superiority of the material. Another furnace will be rebuilt in late 1996 with a complete 825 composite tube floor. The new Tampella recovery boiler at Metsa-Rauma in Rauma, Finland, that was commissioned in the Spring of 1996 has a floor of Sanicro 38/4L7, a material with a similar chemistry to the Inconel 825.\[7\]

The Incoloy 625 weld overlay tubes have been installed in smelt spout openings and used for replacement of wall tubes adjacent to the openings. With limited operating time, it is too early to determine the life of this material. A floor of the weld overlay tubes will be installed in a recovery furnace during the latter part of 1996.

Table 3 is a comparison of material properties for the various cladding material. The expansion coefficients for the nickel alloy materials, in particular the Incoloy 625, are much more compatible with the carbon steel base tube than is the TP304L. Reducing the differential between the expansion coefficient of the materials reduces the thermal stress.

The Oak Ridge National Laboratory has a project underway to develop materials for black liquor recovery boilers. The objective of the current phase is to “characterize the microstructural and residual stress state of as-fabricated composite tubing.” Measured residual stress data will be used in finite element models to predict the stress in tubes during boiler operation. The program is being supported by paper companies and boiler manufacturers; Babcock & Wilcox is contributing information, samples and materials.
Conclusion

The TP304L composite tube is experiencing cracking of the clad layer in a number of recovery furnaces supplied by each of the manufacturers. Alternative materials replacing the TP304L composite tube are available and initial operating results appear to establish these as being far less susceptible to cracking. The Incoloy 825 material can be integrated into the recovery hearth design for use in the floor and in the lower walls where smelt may pool and contact the tubes. For the center of the floor, a viable alternative is to utilize carbon steel tubes with pin studs for corrosion protection.

There appears to be an industry trend to use carbon steel tubes in the floor in the installation of the decanting hearth arrangement. This is expected to change. During a presentation by Tampella, now Kvaerner Pulping, on June 7, 1996, the prediction was made that that future floors will be fabricated of Sanicro 38/4L7 or equivalent because of the potassium and chloride levels in mills. The selection of tube material for this construction must consider the protection of the most vulnerable areas. One of these is the wall tubes at the fluctuating surface of the molten smelt pool in the furnace. For a decanting hearth recovery furnace, further consideration needs to be given that any movement of molten smelt downward through the pool will contact the floor tubes and suitable protection of the carbon steel tubes should be provided.

References


