Oxygen Corrosion of Carbon Steel Boiler Tubes

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Condominium Complex
Hot Water Boilers . 11 years old
Oxygen Corrosion

Background

The condominium has two identical horizontally oriented hot water boilers, connected in parallel, for providing heat to the residences. As we understand, only one of the boilers (typically #1, set at 150°F) is normally used to provide heat; the other boiler (typically #2, set at 120°F) is kept warm to act as a backup in the event #1 boiler goes out of service. The boilers are connected in parallel with two chillers, which are themselves connected in parallel; therefore, the same water circuit is used for both heating and cooling. Nameplate information indicates that each boiler was manufactured 32 years ago. For each boiler, the maximum working pressure for use in hot water heating is shown as 100 lbs. Each boiler is comprised of a cylindrical central firebox surrounded by a tube-in-shell heat exchanger. Each boiler is fitted with 194 carbon steel tubes. The tubes are 2.5-inch outside diameter (OD) 0.135-inch wall thickness and are 13-feet, 10-inches long. The boiler #1 was completely retubed eleven years ago (#1) while boiler #2 was retubed ten years ago. The boiler tubes are rolled and welded into the return pass tube sheet (where the failures occur), but are only rolled into the tube sheet at the other end (where the burner is located). The boiler tubes are unsupported between the two tube sheets.

For the past three years, one to three shutdowns have occurred each season to replace failed tubes. This season, nine shutdowns have occurred on #1 boiler and four shutdowns on #2 boiler. Reportedly, the tube failures have been identical: A waterside groove developed in the failed tubes at the return pass tube sheet, followed by through-wall cracking of the tubes. All failures have occurred in the lower quadrant of the heat exchanger, and most failures have typically occurred between the 10 and 2 o'clock position on the tubes.

This heating season a heating riser piping replacement project has been underway which has necessitated draining and refilling parts of the heating/cooling circuit. In addition, the records of the firm that handles water treatment indicate that a recirculating pump was leaking, though the magnitude of the leak was not described.

Findings

Examination of Failed Boiler Tubes

Ten (10), approximately 2-inch long, failed tube ends were provided to CTL for examination. Also provided was one (1) approximately 6-inch long tube end from the burner end of boiler (where no failures had occurred). Each tube end was a partial circumferential section, part of each tube having been cut away to facilitate removal from the boiler.

Each of the failed tube ends displayed the groove and crack failure features, described above, immediately adjacent to the ½-inch wide band where the tube had been rolled into the tube sheet, Figure 1. On each tube the groove was approximately 1.5-inches long, extending only part way around the circumference. In each case, the groove appeared to be the result of corrosion, mainly due to its irregular surface, rather than mechanical deformation.

Six (6) boiler tubes that had failed were available for examination at the condominium. It was noted that the general appearance of the tubes fell into two categories: Tubes that had a red, rusty appearance and tubes that had a black, shiny appearance. Closer examination of a rusty tube revealed the presence of significant pitting, accompanied by rust-colored mounds (known as "tubercles") along its length, Figure 2.

Figure 1. End of boiler tube showing typical features of failure: groove and crack adjacent to band where tube was rolled into tubesheet.

Figure 2. Pits and tubercles observed on failed boiler tube examined at the condominium. Note rusty streaks oriented at right angles to the tube length, which indicate active corrosion under stagnant conditions.

Metallography

One of the failed tube ends supplied to CTL was sectioned longitudinally through the groove and crack for metallographic examination. The presence of thick black oxide on the groove and parts of the crack surface, Figure 3, as well as lack of deformation in the microstructure, confirmed that corrosion was the cause of the grooving. Deformation of the microstructure at the crack surfaces indicated that the final failure was by ductile tearing. The microstructure itself consisted of pearlite in an equiaxed ferrite matrix, typical of low carbon steel, Figure 4. There were no indications of overheating of the tube.

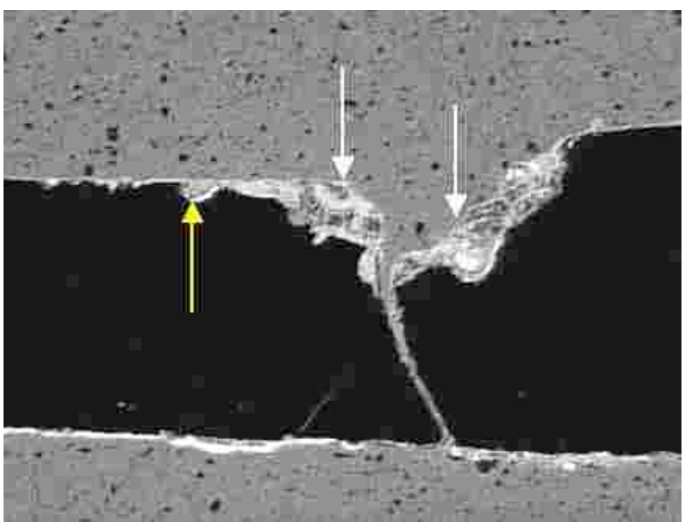

Figure 3. Polished metallographic longitudinal cross-section showing oxide-filled groove and crack. Light-colored material indicated by white arrows is oxide. Yellow arrow indicates crevice attack on part of tube rolled into tube sheet. (18X Original Magnification)

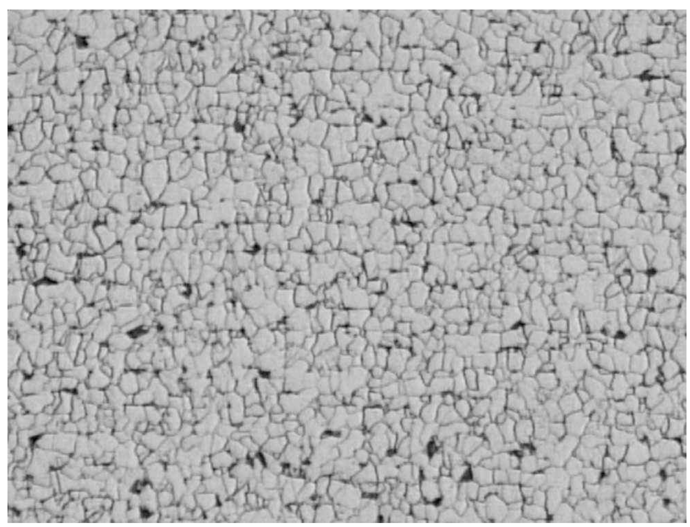

Figure 4. Microstructure of failed tube showing pearlite in equiaxed ferrite matrix. (2% nital etch) (125X Original Magnification)

Review of Water Treatment Procedures
CTL was provided with the records of eight (8) service calls made to the condominium by the water treatment provider within the last six months. The following items were noted:
A steady drop in nitrite inhibitor levels from 840 ppm to approximately 300 ppm.
Addition of molybdate inhibitor to the water treatment regimen to combat tuberculation.
Recirculating pump leak thought to be responsible for a drop in nitrite inhibitor levels.
The note of lower-than-expected nitrite levels possibly being the result of "water loss or oxygen in the system that is 'eating-up' the chemical."

Chemical Analysis of System Water
A sample of water was obtained from #1 boiler during CTL's visit. The sample was analyzed by CTL for dissolved oxygen, which had a concentration of 5ppm.

Discussion
The boiler tube failures were caused by oxygen corrosion of the tubes produced by dissolved oxygen in the boiler water. This was based on the rusty appearance of most of the failed tubes, the presence of pits and tubercles (classic oxygen corrosion features) along the lengths of some of the failed tubes, and the thick oxide present on the metallographically prepared failure site. Oxygen corrosion of the tubes at the failure locations led to the grooving described earlier. The groove reduced the tube wall thickness and subsequently acted as a stress-raiser during normal thermal cycling of the boiler. Stresses from thermal cycling eventually produced the final failure of the tubes by cracking.

The reason the failures occurred at the return end of the boiler was that the tube sheet and tubes were hottest at this end, which produced localized boiling of the oxygen-laden water. Boiling of the water produced a scouring effect on protective oxide films, which led to localized grooving. (It cannot be ruled out that tubes outside this quadrant could also be damaged, although the corrosion may have been occurring at a slower rate. It is fairly certain, however, that other boiler tubes, besides the ones that failed, have suffered pitting and may have the groove damage.)

It is possible that occluded cell (crevice) corrosion played a role in the grooving. In this scenario, a differential aeration cell is set up between the tube adjacent to the return end tube sheet and the tube just under the edge of the tube sheet (assuming leakage of boiler water under the tube sheet.). This cell will lead to corrosion of the tube just under the tube sheet, which accounts for the observed grooving. In fact, evidence of crevice corrosion is seen on the metallographic specimen (see Figure 5).

Under normal (ideal) operating conditions boiler water is deaerated (i.e., less than 0.1 ppm). Under such conditions, low residual oxygen produces a layer of black iron oxide (magnetite), which protects steel tubing. Thermal cycling can fracture the magnetite layer, which exposes underlying bare steel to the boiler water. In the presence of excessive dissolved oxygen (greater than 2 ppm) in the boiler water, accelerated corrosion of the steel tubes occurs. Our analysis shows that the boiler water contained dissolved oxygen at levels greater than 5 ppm.

Under the current situation, aeration of the boiler water occurred through the frequent additions of make-up water to the system after drain-downs for the riser replacement project and repairs to the boiler after tube failures, and as a result of the recirculator pump leakage noted in the water treatment records. The steady drop in nitrite inhibitor over the last 3 months without a simultaneous rise in nitrate levels (as indicated by our water tests) provides support for this assertion. If no make-up water had been added to the system, nitrate (oxidized nitrite) levels would be expected to be much higher than measured.

The current water treatment regimen is inadequate to prevent oxygen corrosion; boiler tube failures will continue to occur as long as dissolved oxygen is present in the boiler water.