AN EXPERIENCE WITH DETECTION AND ASSESSMENT OF SAC IN A RECOVERY BOILER

S. J. Pawel, A. W. Willoughby, H. F. Longmire
Oak Ridge National Laboratory
1 Bethel Valley Road
Oak Ridge, TN 37831-6156

P. M. Singh
Georgia Institute of Technology
School of Materials Science and Engineering
500 10th Street NW
Atlanta, GA 30318-5794

ABSTRACT

Stress-assisted corrosion (SAC) was observed on the waterside of mild steel recovery boiler tubes only at locations exhibiting the combination of a substantial external attachment weld and a significant internal oxide accumulation compared to the nominal Fe_3O_4 film. Penetrations of up to 30% of the tube wall thickness were observed metallographically, and the penetrations were invariably transgranular with bulbous features, rounded tips, and filled with a relatively dense oxide comprised of alternating layers of Fe_2O_3 and Fe_3O_4. Microprobe analysis also revealed the presence of trace quantities (0.1 – 1 at.%) of Cu, Cl, P, and S in the oxide, indicating at least one source of contamination in the boiler feed water. Nondestructive testing, which included two ultrasonic techniques, radiography, and visual inspection with a borescope, was not particularly successful for detecting SAC.

Key Words: stress-assisted corrosion, SAC, waterside penetration, recovery boiler, borescope, mild steel tubing, metallography, layered iron oxide, ultrasonic inspection, radiography, attachment welds, decarburization

INTRODUCTION

Stress-assisted corrosion (SAC) is a term given to waterside corrosion of steel boiler tubes that occurs as a result of a combination of stress and corrosion. In the simplest sense, the mechanism can be described[1-4] as a localized failure of a nominally protective magnetite (Fe_3O_4) film resulting from mechanical or thermal stresses on the tube, thus permitting the corrosive medium – high temperature water/steam – access to the substrate to advance steel corrosion at the location of film failure. Significant general thinning of the tubes from the waterside is not typically a factor in SAC – only localized corrosion in/around locations of frequent film failure. Depending on the water quality and heat transfer conditions during the periods of film failure, the resulting corrosion may be relatively modest with rapid repassivation or sufficiently severe to cause significant penetration of the tube wall.

Experience with SAC in boiler tubes suggests that internal surfaces adjacent to external (non-pressure) attachment welds on the boiler tubes are particularly susceptible to development of SAC, due to thermal or mechanical effects concentrated at the attachment location[1,2,5,6] or perhaps relative anodic behavior of the stressed region at/near the attachment.[7] Most commonly, SAC tends to be manifested in short clusters of indications resembling cracks perpendicular to the associated attachment weld. Because of the myriad of stress and water composition variables involved, no specific rate (or even bounding rate) has been determined for the SAC processes. In the strictest sense, the occurrence of SAC may be independent of the boiler age,[8] but it tends to be a relatively slow process and is most commonly found in boilers that have been operating for at least ten years.[3,7]

Due in part to recurring corrosion problems that included SAC, the bottom 53 ft. (16 m) of the recovery boiler at the Weyerhaeuser paper mill near Longview, Washington, was recently replaced. A large sampling of representative panels and pieces of tubing – almost 1000 linear feet (300 m) in total – was delivered to the authors for evaluation of SAC via non-destructive evaluation (NDE) techniques as well as standard metallography. The purpose of this report is to describe the NDE techniques used in an attempt to locate regions with SAC and to document the microstructure and film composition associated with the SAC that was detected.

TUBE INSPECTIONS AND RESULTS

Circumferential Wave Inspection

In the circumferential wave technique, ultrasonic waves are introduced and detected from the process side of the boiler tubing with a transducer embedded in Lucite. The working surface of the transducer is machined to the same curvature as the outside surface of the boiler tubes – in this case, 1.5 in. (38 mm) radius – and coupled to the tube surface with a standard viscous gel. To develop adequate coupling, adherent accumulations of oxide as well as any loose rust/debris must be removed, most typically with a power wire brush. The technique detects longitudinally oriented flaws via analysis of the waves that travel around the tube circumferentially – the approximate size/penetration depth of the flaw is estimated by comparing the signal fraction that is reflected from a flaw with that which travels the entire circumference, and the relative position of the flaw is determined by analysis of the reflected signal travel time.

Potential advantages of this relatively new technique include that it detects longitudinally oriented flaws best (because they are perpendicular to the direction of wave travel), which is consistent with the predominant orientation of SAC indications in boiler tubes. Also, since ultrasonic waves are not sent over long distances, power and attenuation issues are relatively minor for this technique. In addition, the precise location of any indication in the ultrasonic wave circuit is not critical, since only a limited length of tubing (roughly, the length of the transducer) is under evaluation at any given time.

A potential disadvantage of the technique is that, due to the limited analysis area, it is inefficient for examination of an entire boiler. As a result, analysis using this technique typically must focus on particular "suspect" areas based on experience. Also, the technique works best from the process side of the boiler opposite the external attachment locations because this position places the expected SAC location in the center of the detection range (halfway around the tube from the transducer). This means the boiler can most practically be inspected with this technique only at shutdown and, for some recovery boilers, it also means studs must be removed prior to inspection.

It was of course not practical to attempt to evaluate the entire lot of 300 m of boiler tubing for SAC using this technique, particularly since a large fraction of the tube specimens were studded. As a result, the operators relied on experience with related inspection efforts for SAC and concentrated on wall tubes with floor attachments (filler blocks) and on wall tubes adjacent to substantial scallop-type attachments as regions most likely to contain SAC detectable with this technique (see Fig. 1). However, following examination of approximately thirty "suspect" locations (among perhaps sixty or more available in the lot of sample material), no significant indications of SAC were detected. Given that SAC indications were subsequently located by destructive techniques in several tubes – including a few tubes specifically examined with circumferential waves – it seems likely that a factor other than examination of an insufficient number of locations limited/prevented detection of SAC with this technique. Perhaps the extreme proximity of the SAC indications to the attachment welds tended to mask the modest and relatively infrequent SAC indications due to attenuation issues associated with discontinuous wall thickness at the weld and attachment.

Longitudinal Wave Inspection

In this technique, which is also referred to as the guided wave method, ultrasonic waves are introduced on the cold side of boiler tubes with a transducer array embedded in Lucite machined with a curve to fit the outside surface of the tube. The waves travel primarily longitudinally down a length of tubing to be detected by a separate receiver or, alternatively, reflected from circumferentially oriented flaws and detected with the same unit as the input transducer. Like the circumferential wave technique, flaws can be located and sized by analysis of the pitch/catch time for reflected waves and the fraction of the input energy collected at the receiver. Similar to the circumferential wave technique, appropriate surface preparation and coupling is required.

Potential advantages of this technique include that it can be used from the cold side of the boiler, so entry into the boiler during very busy outage time is not required. Further, the technique may be developed in the future to the extent the boiler could be operating during the inspection. In addition, the technique is not necessarily a localized technique – it is theoretically possible to scan relatively large areas/lengths of boiler tube between small areas with the required surface preparation to introduce/detect waves.

A potential disadvantage of the technique is that circumferentially oriented indications are not particularly common for SAC, which limits the general utility of this method. Further, the technique needs additional development on issues related to surface preparation and attenuation to make long distance scans practical.

Similar to the situation for the circumferential wave technique, it was impractical to attempt to assess all of the available boiler tube specimens for SAC using this technique. Therefore, the engineers performing the test (see Fig. 2) concentrated on tubes with longitudinal weld attachments and/or tubes with a "corner" attachment resulting from the intersection of a longitudinal and a transverse weld. After considerable effort, which included detailed examination of about a dozen tube panels meeting the above criterion, no significant indications of SAC were detected. Since several tubes with SAC (found by subsequent destructive analysis) were among those examined with longitudinal waves, it seems likely that the longitudinal orientation of all of the SAC indications among the Longview boiler tubes masked these from detection with this technique.

Radiographic Inspection

Select portions of tube panels were radiographed using two techniques. The first, which is similar to that which is possible in a field evaluation of a boiler, utilized the double wall/double image technique in which the x-ray source and film are both outside of the tube/weld being investigated. The second takes advantage of the fact the tubes were cut into manageable pieces and utilized the single wall/single image technique, in which the film is placed inside the tube of interest. The latter technique is not routinely used in a field inspection because it requires section of tubing to be cut/removed.

The sections subjected to radiography were selected from among those with attachment welds deemed high probability areas for SAC based on experience, but that showed no significant indications (or perhaps only a "maybe" indication) with either the circumferential or longitudinal wave techniques. In addition, a few randomly selected tube panels with substantial attachment welds were selected from among the sections that had not been inspected by either of the ultrasonic wave methods for radiography. Figure 3 contains a representative example of the radiographic technique employed.

In total, eight panels (with several tubes each) were extensively examined with these radiographic techniques. A few small indications were identified, but none were judged by the radiographer to be significant and each was associated with the external attachment weld (not the tube ID).

Borescope/Visual Inspection

All of the boiler tube sections were examined internally with a borescope. The borescope had an adjustable power light at the tip and an optics system capable of approximately 5x magnification. This process was quite slow and tedious and did not reveal any indication of SAC, although there were a few observations of areas where the normally smooth and uniform oxide film seemed somewhat rough/graveled with scattered debris (discussed more below).

Following the borescope inspection, all of the boiler tube panels with an indication of any kind, however minor, resulting from any of the inspection techniques, as well as many with no indications, were split longitudinally with a band saw to facilitate visual inspection of the waterside of the tubing. The internal surfaces were found, almost without exception, to be a smooth, uniform gray with only very isolated spots of red/orange rust (no doubt resulting from the extensive handling since the removal from the boiler months earlier).

An example of the only significant exceptions to smooth/uniform oxide on the waterside of the tubes is shown in Fig. 4. Viewed at right angles (light and view port on the borescope perpendicular to the tube surface), locations like these appear slightly graveled, but with oblique lighting it is obvious that the oxide at these locations is significantly thicker than the nominal oxide thickness. Oxide accumulations almost 500 μm (20 mils) thick were observed in a few of these positions, which invariably were located on the tube waterside directly adjacent to an external attachment weld. Not every attachment weld exhibited such an oxide accumulation on the tube waterside, but no accumulations were observed that were not immediately adjacent to an attachment weld. When several tubes from a panel were examined together (such as the four-tube panel shown in Fig. 5), oxide accumulations were observed on the ID of the tube crown associated with each attachment weld location, but the degree of oxide accumulation typically varied significantly among the attachment welds in the group.

The cause of the oxide accumulations is perhaps related to subtleties of the internal heat transfer conditions at the attachment weld locations. For example, depending on the efficiency (in the thermal sense) of the weld attachment, the attachment may act as something of a cooling fin to encourage heat transfer from the tube and thereby precipitation from the water on the internal surfaces of the tube at these locations. Alternate thermal conditions at the attachment might lead to slightly increased temperatures at the attachment locations encouraging more rapid growth of oxide. In any case, it is not apparent that the oxide accumulations directly cause SAC at these locations, but it is likely the thermal conditions that contribute to the oxide accumulation also contribute to the stress state and corrosion conditions at this location.

A sampling of tubes exhibiting the oxide accumulation was cut into short lengths and chemically cleaned with inhibited hydrochloric acid (ASTM G-1-1990 procedure C.3.5) to remove the oxide with no appreciable attack of the underlying steel. A representative result is shown in Fig. 6. Directly beneath every oxide accumulation, longitudinally-oriented SAC was observed. The indications in Fig. 6 are typical of all of the SAC observed among these tubes in that they appear as a cluster of short, roughly parallel indications on the ID near the tube crown, and are centered on the attachment weld location. The total longitudinal length of each cluster was less than 3 cm in every case for the tubes in this investigation.

Metallography and Microhardness Evaluation

Following the discovery of SAC under the oxide accumulations, tubes were sectioned to facilitate metallographic examination in regions with and without oxide accumulations. Figure 7 compares the nominal appearance of the internal oxide layer – observed over the entire boiler tube ID except for very limited areas adjacent to some attachment welds – with an area exhibiting the oxide accumulation. Nominally, the oxide is approximately 50 μm thick, relatively free of porosity, very adherent, and uniform in color. In locations with an oxide accumulation, the film tends to exhibit significant porosity (contributes to poor adhesion in some areas) and irregular thickness nominally near 300 μm but in some locations up to 400-500 μm. In addition, the color of the thick films is not generally uniform, suggesting a range of oxide stoichiometries and compositions, including trace contaminants (Cu, Cl, P, and S were sporadically detected, generally near 0.1 at.%, but Cu and Cl occasionally were present up to almost 1 at.%).

Figure 8 is representative of the most common characteristics of the SAC indications observed in this investigation. The waterside penetrations are consistently transgranular, relatively straight with bulbous features and rounded tips, and filled with an adherent, layered oxide. The relative width of the deepest penetrations varies significantly, with depth/width ratios commonly in the range 1-5. The SAC penetrations are invariably located within 1 cm or so of an attachment weld location, and the deepest penetration observed among these boiler tubes was about 30% of the tube wall thickness. In some instances, the penetrations are generally narrow with somewhat bulbous features, consistent with periodic intense corrosion events. Apparently, during periods of relatively high corrosion (probably associated with simultaneous rupture of the protective film and poor water chemistry), the penetration advances until the stress or water chemistry (or both) return to nominal levels, at which time the corrosion tends to spread laterally until full passivation is restored. In the most favorable cases, the number of "bulbs" on the penetrations can be related to the number of aggressive corrosion events[4] in the boiler.

Another common feature revealed by the metallography in Figure 8 is that the waterside surfaces rather routinely exhibit a decarburized layer approximately 200-300 μm deep in which the ferrite grains have grown significantly larger than the nominal size. Microhardness scans across the tube thickness indicate that the decarburized layer with large grains (85-100 HV) is generally somewhat softer than the nominal base material (100-115 HV). For comparison, the welds examined on these tubes exhibit somewhat higher hardness at 160-250 HV, with intermediate hardness in the weld heat-affected zone. In some regions with SAC indications, the decarburized layer was not observed on the tube waterside, suggesting sufficient general corrosion/wastage at this location to remove the thin layer of somewhat softer material. In general, the external surfaces of the boiler tubes also exhibit the decarburized layer with some grain growth (see area adjacent to the weld at the top of Fig. 8), but where extensive surface preparation for an external attachment has occurred, the decarburized layer has typically been removed by grinding.

If the SAC process is initiated when boiler tubes experience sufficient strain to fracture the nominally protective oxide,[9-11] then that process is perhaps aided by boiler tubes with a slightly weakened (decarburized, large grains) internal surface. Increased resistance to SAC might be realized by utilizing boiler tubes that do not exhibit a soft layer or, alternatively, selecting a somewhat stronger tube material in general, at least for application in areas of the boiler susceptible to SAC.

Scanning Electron Microscopy and Microprobe Evaluation

Scanning electron microscopy of representative SAC penetrations revealed a layered oxide structure within the penetrations as well as in portions of the oxide accumulations on the tube internal surface. An example of the layered oxide appearance is shown in Fig. 9. While not analytically identified, the relatively dark layers of iron oxide have a uniform Fe/O ratio consistent with Fe_2O_3 and the relatively light layers have a similarly uniform Fe/O ratio consistent with Fe_3O_4. While multiple alternating layers of oxide have not been previously reported within SAC penetrations, inner and outer oxide layers (similar to that shown in Fig. 7b) have been observed following field and laboratory tests associated with SAC investigations.[12-15] The alternating oxide layers observed here provide visual confirmation of the concept that the corrosion conditions in the boiler tubes – and within the penetrations into the tube wall – vary periodically and that pitting/cracking is cyclic in nature.

Trace amounts of Cl, Cu, P, and S were detected throughout the oxide layers by microprobe chemical analysis; however, isolated concentrations of Cl and Cu were found to approximately 1 at.%. In addition, Cu tended to be located in clusters of significant concentration, with S always concentrated in the same particles/regions. The source(s) of the contamination has not been confirmed by the authors, but it seems likely that the Cu contamination results from corrosion of copper-bearing components in the steam/condensate system.[16-18] Chloride contamination typically results from in-leakage from the condenser or heat exchanger[18] or perhaps make-up water of marginal quality. The P contamination may result from the water-treatment process itself. The source of sulfur is unknown, but it is typically ubiquitous in the process waters in a paper mill.

CONCLUSIONS

A large sample of tubes removed from a recovery boiler experiencing SAC was examined non-destructively using a variety of techniques. The ultrasonic techniques did not detect SAC, perhaps because an insufficient number of locations among the available specimens were examined, but also because the proximity of the SAC indications to the attachment welds apparently masked the relatively small and infrequent SAC indications from the circumferential wave technique, and the longitudinal orientation of all the penetrations detected visually or metallographically among these tubes masked them from the guided wave technique. Radiography was employed in a more limited fashion, but there was no SAC among the components selected for examination with this technique. Evaluation with the borescope was slow and tedious, and did not detect direct indications of SAC and was not efficient for detecting oxide accumulation without oblique lighting.

Oxide accumulations – up to approximately ten times the nominal oxide thickness – were observed on the tube waterside directly adjacent to a number of external attachment welds. Not all attachment welds exhibited an oxide accumulation, but SAC was found associated with each oxide accumulation via chemical cleaning of the tube and/or metallographic evaluation.

The SAC observed among these tubes extended up to 30% of the tube wall thickness, and appeared as transgranular penetrations of variable width and rounded/bulbous features filled with alternating sets of layered oxide. Metallography also revealed the tube ID to have large ferrite grains and decarburization to a depth of 200-300 μm, and the relative weakness of this layer may contribute to SAC susceptibility. In the alternating layers of Fe_3O_4 and Fe_2O_3 found in the SAC penetrations and some of the oxide accumulations, trace amounts of Cu, Cl, P, and S were observed, indicating the boiler tube coolant water was at least periodically contaminated by inappropriate make-up water or condenser leakage.

ACKNOWLEDGEMENTS

Representative boiler tubes were provided by D. Rittenbach (Weyerhaeuser). Tube panels were flame cut longitudinally into manageable sections for handling by L. Smarsh (ORNL). Circumferential wave inspections were performed by M. Cooper, J. Gustafson, and S. Shankles (Longview Inspections). Longitudinal wave inspections were performed by M. Quarry (Lawrence Livermore National Laboratory) and J. Brignac (Alstom Power). Radiographic inspections were performed by R. Sweet and C. Culbertson (Longview Inspections). Following the various inspections, tubes were saw cut into sections to facilitate visual inspections and metallographic sampling by B. Gaskin (ORNL). L. Walker (ORNL) performed the SEM analysis. D. Wilson and P. Tortorelli (ORNL) reviewed the draft manuscript, and F. Stooksbury and K. Choudhury (ORNL) helped prepare the final document. The project was funded by the U. S. Department of Energy Industrial Materials of the Future Program (DOE DE-FC07-01ID14243), managed at ORNL by P. Angelini.

REFERENCES

1. Electric Power Research Institute, EPRI-TR-100455, "Corrosion Fatigue Boiler Tube Failures in Waterwalls and Economizers – Volume 4: Summary Report and Guidelines for Corrosion Fatigue Evaluation," prepared by Ontario Hydro, Toronto, Canada, December 1993.

2. Sylvester, W. R., “Waterside Corrosion Fatigue Cracking – Is There a Single Cause and Solution?” ABB C-E Services TIS 8318, Combustion Engineering, Inc, Windsor, CT, 1987.

3. Sylvester, W. R. and Sidla, G., “Waterside Stress-Assisted Corrosion Cracking in Boilers,” Pulp and Paper Canada, Vol. 91, No. 6 (1990) p.T248.

4. Schoch, W. and Spahn, H., “On the Role of Stress-Induced Corrosion and Corrosion Fatigue in Water-Wetted Boiler Components,” in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, Houston, TX (1972) p.52.

5. Dooley, R. B., “A Vision for Reducing Boiler Tube Failures,” Power Engineering, Vol. 96 (1992) p. 33.

6. Gabrielli, F., “An Overview of Water-Related Tube Failures in Industrial Boilers,” Materials Performance, Vol. 27, No. 1 (1988) p.51.

7. Esmacher, M. J., “Stress-Enhanced Corrosion of Boiler Tubing,” Materials Performance, Vol. 26, No. 5 (1987) p. 17.

8. Masterson, H. G., Castle, J. E., and Mann, G. M. W., “Waterside Corrosion of Power Station Boiler Tubes,” Chemistry and Industry (1969) p. 1261.

9. Hancock, P. “Mechanical Considerations of the Growth and Breakdown of Surface Metal Oxide Films,” Werk. und Korros., Vol. 21 (1970) p. 1002.

10. Hurst, R. C., Davies, M., and Hancock, P., “The Determination of the Fracture Strains of Growing Surface Oxides on Mild Steels at High Temperatures,” Oxidation of Metals, Vol. 9, No. 2 (1975) p. 161.

11. Field, E. M., Stanley, R. C., Adams, A. M., and Holmes, D. R., “The Growth, Structure, and Breakdown of Magnetite Films on Mild Steel,” Proc. 2nd Int. Cong. Metall. Corrosion, London, Butterworks (1963) p. 829.

12. Fujii, C. T. and Meussner, R. A., “The Mechanism of High Temperature Oxidation of Iron-Chromium Alloys in Water Vapor,” J. Electrochem. Soc., Vol. 111 (1964) p. 1215.

13. Potter, E. C. and Mann, G. M. W., “Oxidation of Mild Steel in High Temperature Aqueous Systems,” Proc. 1st Int. Cong. Metall. Corrosion, London, Butterworks (1961) p. 417.

14. Potter, E. C. and Mann, G. M. W., “Mechanism of Magnetite Growth on Low Carbon Steel in Steam and Aqueous Solutions up to 550°C,” Proc. 2nd Int. Cong. Metall. Corrosion, London, Butterworks (1963) p. 872.

15. Eberle, F. and Anderson, C. H., “Scaling Behavior of Superheater Tube Alloys in ASME High Temperature Steam Research Tests at 1100-1500°F,” Journal of Engineering for Power, Vol. 84, No. 3 (1982) p. 223.

16. Bonner, E. H., “Water Treatment for the Prevention of Water Side Corrosion in Boiler Plant,” Power Works Engineering, Vol. 19, No. 1 (1979) p. 10.

17. Goldstein, P., “A Research Study on Internal Corrosion of High Pressure Boilers,” Trans ASME, Vol. 91A (1969) p. 75.

18. Marsh, T. F., “The Morphology of Magnetite Growth on Mild Steel in Alkaline Solutions at 316°C,” J. Electrochem. Soc., Vol. 113, No. 4 (1966) p. 313.

FIGURE 1. Circumferential wave inspection of recovery boiler tube opposite the floor attachment locations. No indications of SAC were observed in locations represented by this type of attachment.

FIGURE 2. Longitudinal wave inspection of a recovery boiler tube with a longitudinal attachment (skip weld) on the opposite side. Operators shown are Mike Quarry (left) and Jacques Brignac.

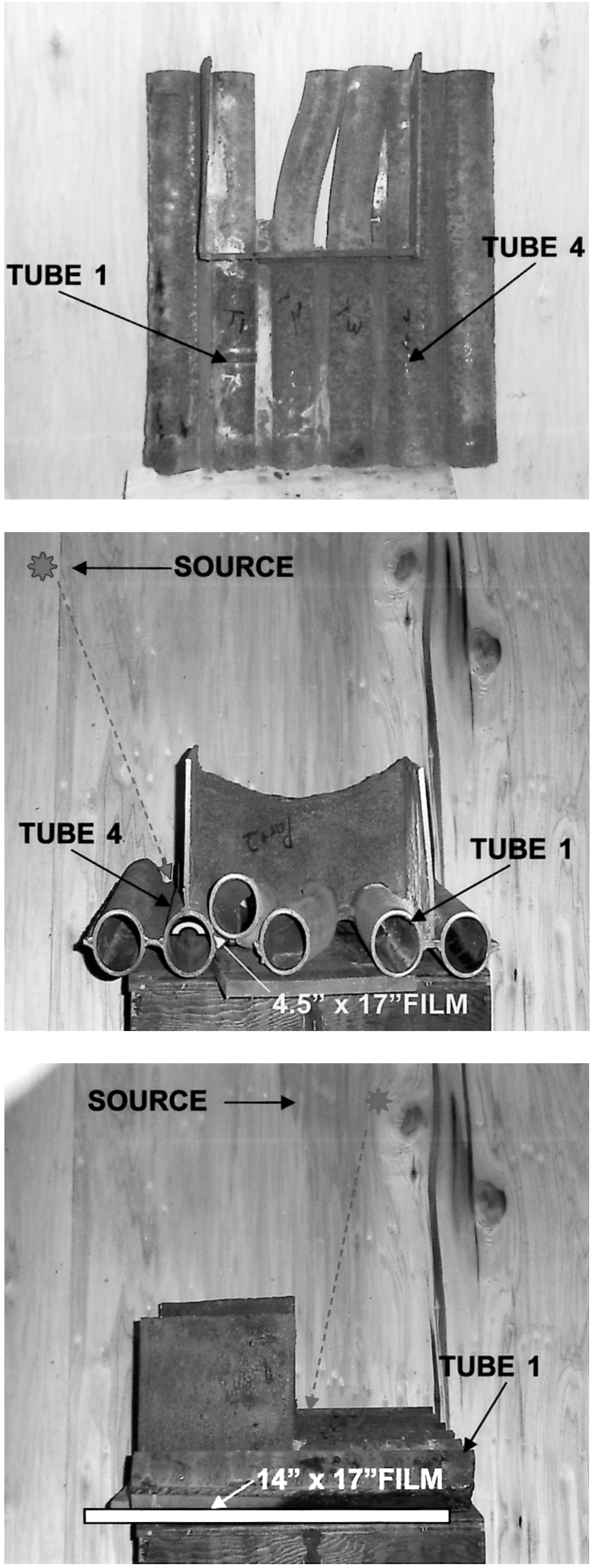


FIGURE 3. Representative example of radiographic inspection technique on a boiler tube panel with an attachment weld. Top: overview. Middle: film inside a tube. Bottom: external film.

FIGURE 4. Typical oxide accumulation on the internal surface of a boiler tube, viewed with oblique lighting. An attachment weld (scallop-type) is located immediately adjacent to the oxide build-up on the external surface of this tube.

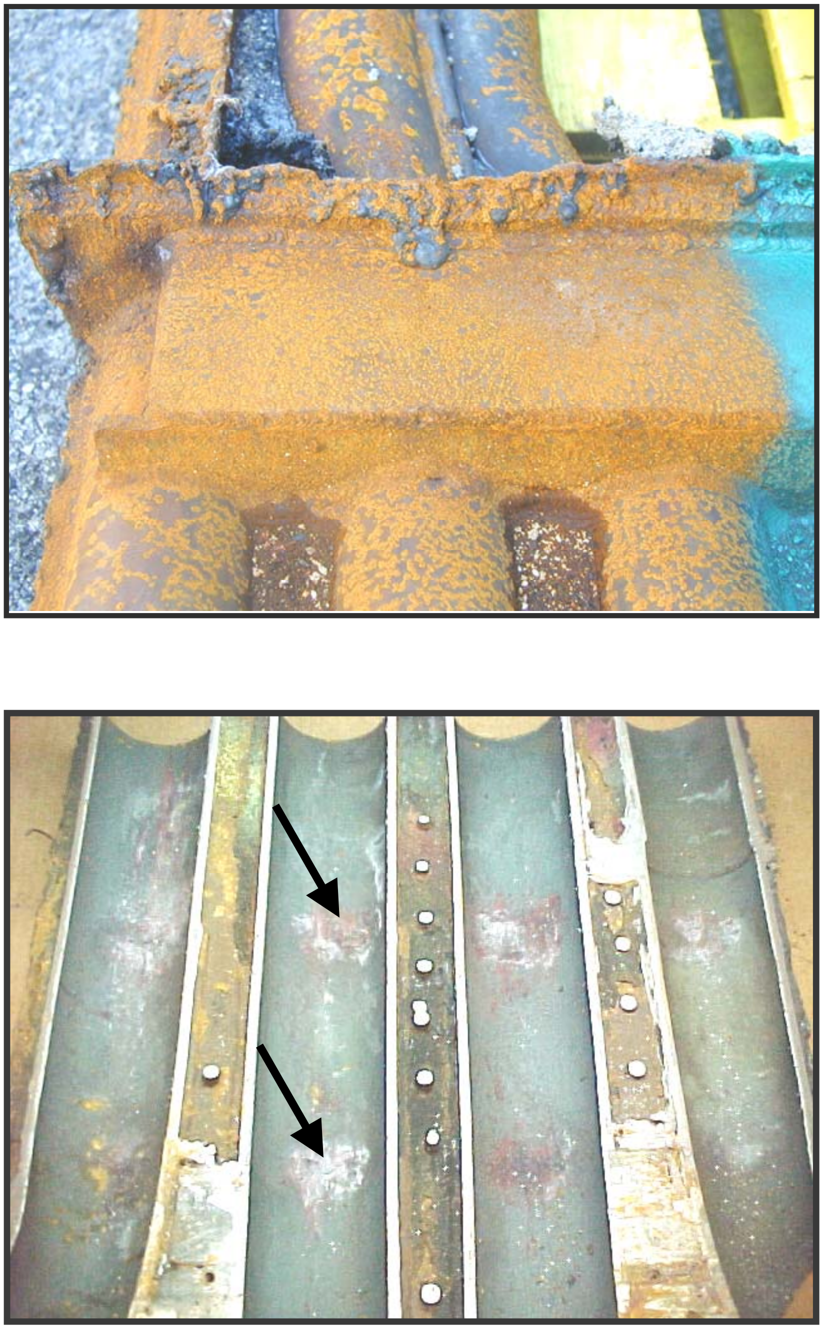


FIGURE 5. Top: Fillet welds associated with a tertiary windbox. Bottom: Internal surfaces at the fillet weld locations shown above. Note variable extent of oxide accumulation opposite each weld. One pair of oxide accumulations is marked with arrows, but a similar pair is on each tube.

FIGURE 6. Attachment weld (top) and appearance of the internal surface opposite the weld following acid cleaning.

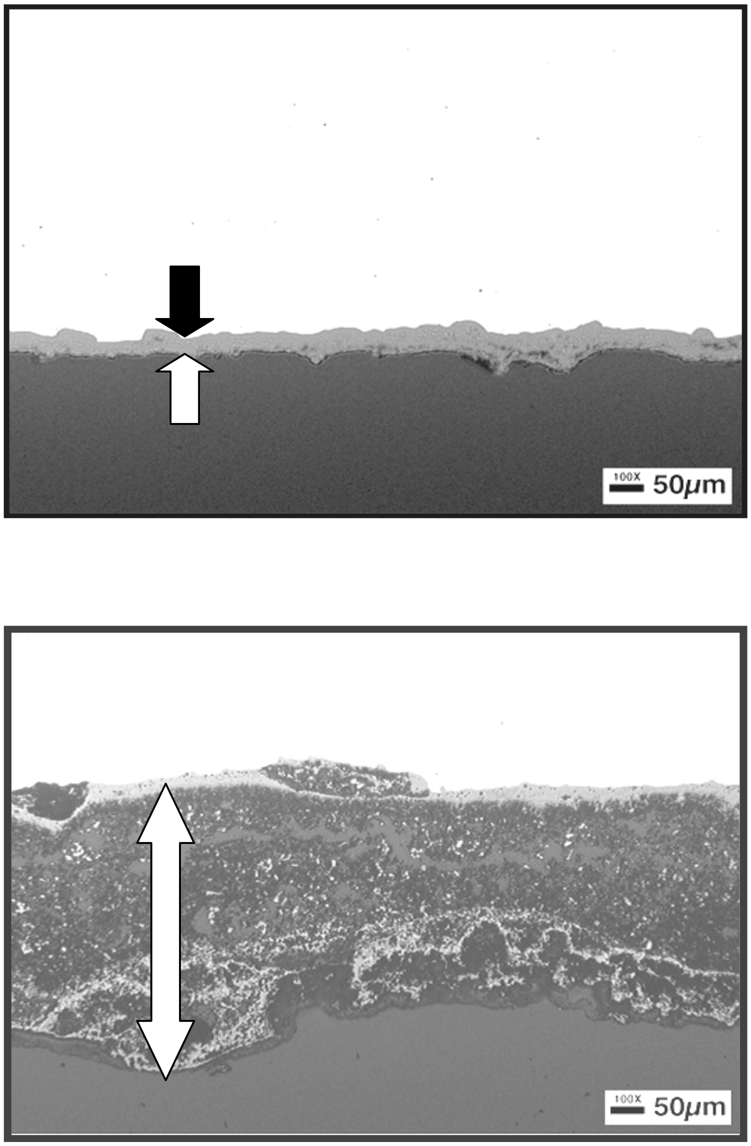
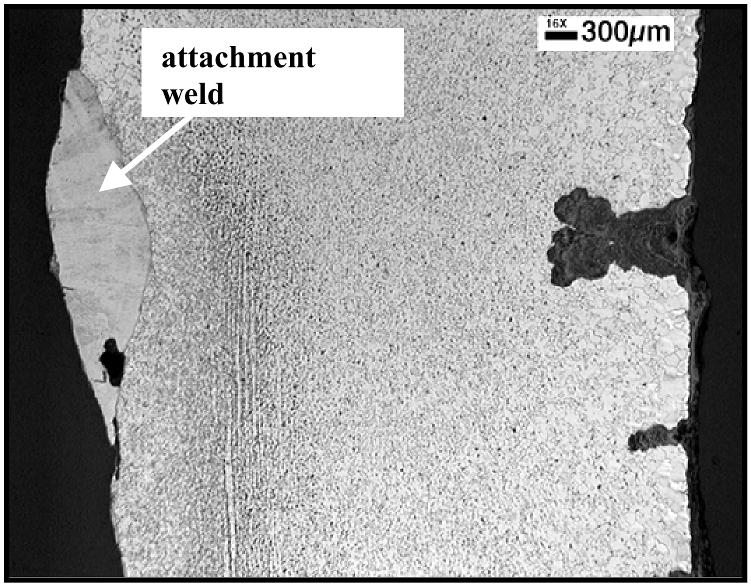


FIGURE 7. Comparison of the nominal oxide thickness (top) with an example of an oxide accumulation (bottom). In each photograph, the oxide is marked with arrows, and unetched steel is at the top (white) and the epoxy mount material is at the bottom.



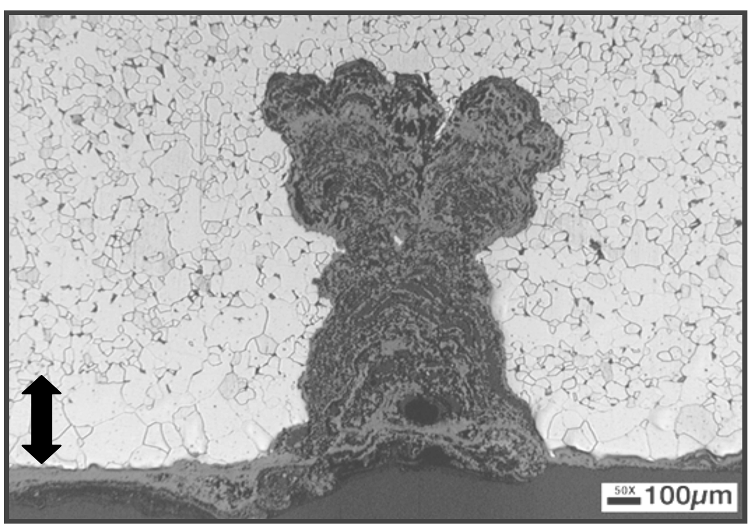
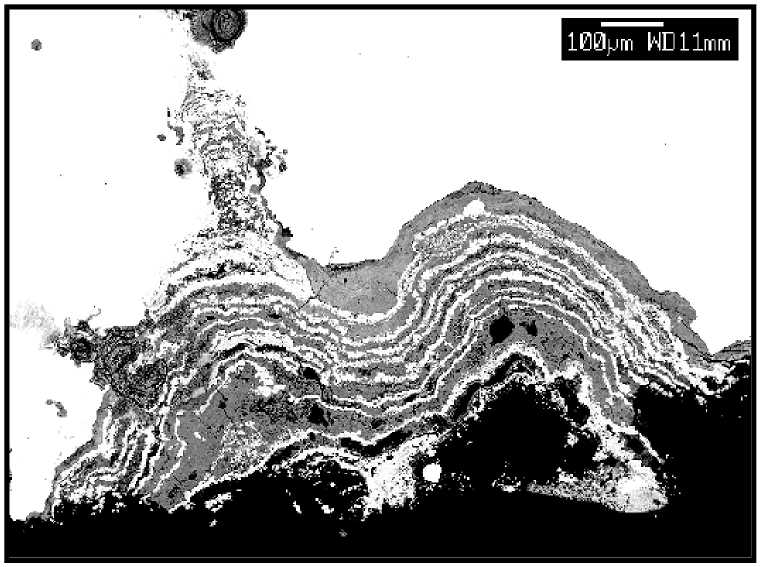


FIGURE 8. Representative photomicrographs of a tube cross section showing the attachment weld and adjacent SAC penetrations (top) and a higher magnification view of the deepest penetration associated with this particular attachment weld (bottom). The decarburized layer is marked with an arrow in the lower photograph.



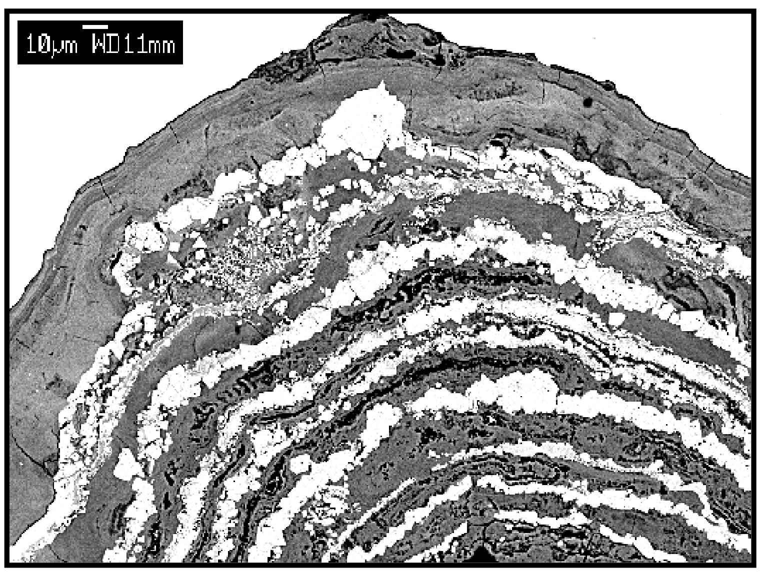


FIGURE 9. Backscattered electron microscopy of a typical SAC indication on the tube ID. The top photograph shows the entire SAC indication, and the bottom photograph is a higher magnification view of a portion of the oxide in the penetration.