

9707 Key West Avenue, Suite 100 Rockville, MD 20850 Phone: 301-740-1421 Fax: 301-990-9771 E-Mail: <u>awt@awt.org</u>

Part of the recertification process is to obtain Continuing Education Units (CEUs). One way to do that is to review a technical article and complete a short quiz. Scoring an 80% or better will grant you 0.5 CEUs. You need 25 CEUs over a 5-year period to be recertified.

The quiz and article are posted below. Completed tests can be faxed (301-990-9771) or mailed (9707 Key West Avenue, Suite 100, Rockville, MD 20850) to AWT. Quizzes will be scored within 2 weeks of their receipt and you will be notified of the results.

Name:		
Company:		·
Address:		
City:	State:	Zip:
Phone:	Fax:	
E-mail:		

Boiler Failure Mechanisms

By Douglas DeWitt-Dick, Stephen McIntyre, and Joseph Hofilena Ashland Specialty Chemical Company

Introduction

Failure of boiler waterside components during operation may not only be costly from an operations and personnel perspective, but potential legal costs may well outstrip the actual physical costs. It is incumbent upon the system designer, the builder, the operators and the chemical treatment supplier to ensure that the systems will operate reliably. However, in this imperfect world, component failures do occur. When this happens, a full assessment of the failure mechanism(s) is required to preclude further failures due to the same factors.

Several failure modes are addressed in this article, which hopefully will give the boiler operator a better understanding of failure analyses and failure mitigation.

Overheating

Overheating failures are often classified as either short-term or long term. Short-term overheating frequently exhibits a thin-lipped longitudinal rupture, accompanied by noticeable tube bulging, which creates the large fish-mouth appearance shown in Figure 1.

Virtually all types of tubes, which carry water or steam and are exposed to high operating temperatures are susceptible to this type of failure. The more violent ruptures occur at tube metal operating temperatures well above the ASME oxidation limits of the material and typically above the eutectoid transformation temperature of 1340°F (727°C). Peak metal operating temperatures above the eutectoid can be estimated by the amount of bainite or martensite mixed with ferrite in the metal microstructure at the failure origin as shown in Figure 2.

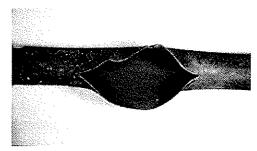


Fig. 1 - Short Term Overhealing Failure

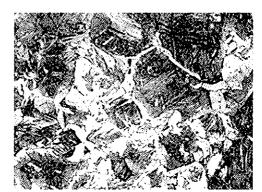


Fig. 2 - Microstructure of Overheating Failure.

Short-term failure can be caused by low water level, partial or complete

pluggage of tubes, rapid start-ups, excessive load swings and excessive heat input.

Long-term overheating usually occurs in superheaters, reheaters and waterwalls as a result of gradual accumulation of deposits or scale, partially restricted steam or water flow, excessive heat input from burners or undesired channeling of fireside gases. Horizontal or inclined tubes subjected to steam blanketing are also prone to long-term overheating failures. Tube metal operating temperatures above 850°F (454°C), or slightly above the oxidation limits of the tube steels, can lead to blistering, tube bulging or thick-lipped creep rupture failures as shown in Figure 3.

Internal and external thermal oxidation of the tube metal is often observed at the failure region as shown in Figure 4.



Fig. 3 - Long Term Overheating

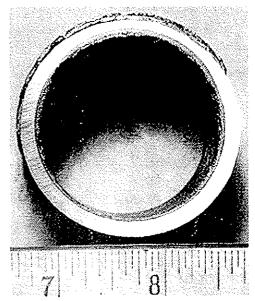
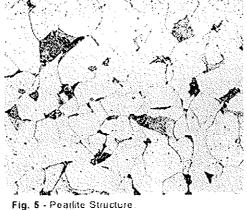


Fig. 4 - Internal and External Oxidization

Long-term failures by creep damage can occur with little or no detectable changes in the tube wall thickness. Microstructural examination is an effective means of confirming long-term overheating. The platelets of iron carbide in the pearlite structure of carbon steels will thermally decompose to spheroidized iron carbide as shown in Figures 5 through 7.

Continued decomposition will result in total degradation to graphite plus ferrite, or graphitization as shown in Figure 8.



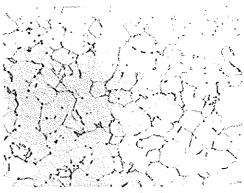


Fig. 7 - Spheroidization of Carbides

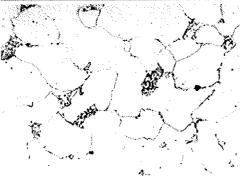


Fig. 6 - in-situ Spheroidization of Carbides

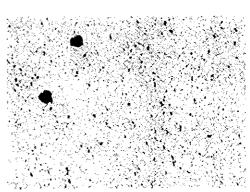


Fig. 8 - Graphitization

Creep damage is the result of permanent plastic deformation at elevated temperatures and at stresses much less than the high temperature yield stress.1 Microstructural damage is detected by the presence of creep voids at the grain boundaries as shown in Figure 9.

High temperature, stress-rupture strength and oxidation resistance is increased by alloying additives of

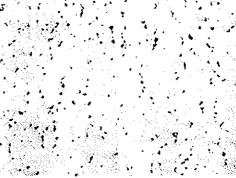


Fig. 9 - Creep Voids

chromium and molybdenum. Stress rupture failures are dependent on time, temperature and stress. This relationship can be used to estimate stressrupture life expectancy by the Larsen-Miller method² defined as:

$$P = T (20 + \text{Log t}) \tag{1}$$

Where:

P = the Larsen-Miller parameter

T = Absolute metal temperature, degrees Rankine, (°F + 460)

t = Time for rupture, hours

The Larson-Miller parameter is obtained from master rupture curves developed from high temperature tensile strength laboratory testing of the various tube metal alloys.

Hydrogen Damage

Hydrogen damage occurs in boilers operating usually above 1000 psig (6.9 MPa) and under heavy deposits or other areas where corrosion releases atomic hydrogen. Concentrated sodium hydroxide beneath the deposits can remove the protective magnetite film by the following reactions.³

$$4\text{NaOH} + \text{Fe}_3\text{O}_4 \rightarrow 2\text{NaFeO}_2 + \text{Na}_2\text{FeO}_2 + 2\text{H}_2\text{O}$$
 (2)

Concentrated sodium hydroxide can then react with freshly exposed base metal to yield sodium ferroate and atomic hydrogen:

$$Fe + 2NaOH \rightarrow Na_2 FeO_2 + 2H$$
 (3)

The hydrogen produced at the metal surface can diffuse into the steel where it can combine to form molecular hydrogen or react with iron carbide to form methane and iron:⁴

$$4H^{+} + Fe_{3}C \rightarrow CH_{4} + 3Fe$$
 (4)

Upsets in phosphate treatment programs or residual acid from chemical cleanings can also cause hydrogen damage, especially if the acids remain trapped beneath the deposits.

These failures are typically characterized as thick-lipped, brittle type ruptures as shown in Figure 10.

Sometimes, thick-walled "windows" can be completely blown out of the tube wall. Microstructural examination at the area of failure typically reveals short discontinuous intergranular cracks accompanied by decarburization as shown in Figure 11, as a result of the damage from Equation 4 above.

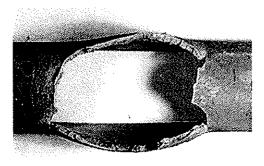


Fig. 10 - Hydrogen Damage.

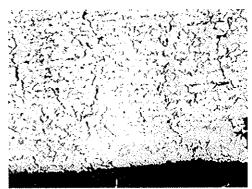


Fig. 11 - Hydrogen Damage Microstructure.

Chemically Induced Failures

Caustic Gouging

Sodium hydroxide (NaOH) is used extensively in boiler water treatment to maintain the optimum hydroxyl ion concentration range to form a protective magnetite film on steel surfaces and to help form nonadherent sludges when hardness enters the boiler water. However, excessive sodium hydroxide can destroy the protective film and corrode the base metal as shown in equations 2 and 3. NaOH can concentrate during departure from nucleate boiling (DNB), film boiling or steam blanketing conditions. Concentration also occurs when normal boiler water evaporates beneath deposits leaving behind the caustic at the metal surface. The effect of tube metal gouging beneath deposits is shown in Figure 12.

Caustic gouging can also occur due to evaporation along a waterline without significant accumulation of deposit as shown in Figure 13.

In these cases, solubilized sodium ferroite is removed from the base tube metal, but then hydrolyzes and precipitates elsewhere in the boiler as magnetite when the concentrated water is diluted by normal boiler water.⁶

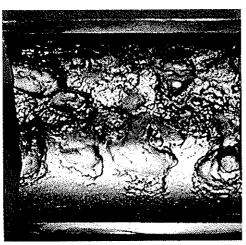


Fig. 12 - Caustic Gouging.

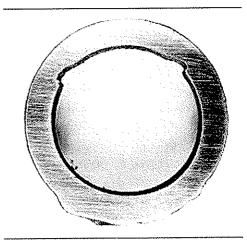


Fig. 13 - Caustic Googing.

Oxygen Attack

The presence of dissolved oxygen in boiler water causes the cathode of any corrosion cell to depolarize, thereby sustaining the corrosion process. Formation of reddish brown hematite (Fe₂O₃) or "rust" deposits or tubercles accompanied by hemispherical pitting is the most familiar form of oxygen attack as shown in Figures 14 and 15.

Dissolved oxygen is also a significant component in ammonia corrosion of copper alloys, stress-corrosion cracking of austenitic stainless steels and chelant corrosion.





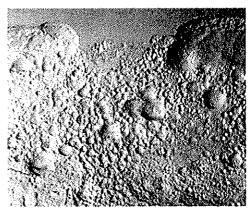


Fig. 15 - Oxygen Pitting.

Thermal Fatigue

Thermal fatigue damage typically exhibits numerous cracks and crazing as shown in Figure 16.

This damage results from cyclic and excessive thermal fluctuations accompanied by mechanical constraint. Excessive temperature gradients can add to internal strain to initiate or enhance the cracking process. Once initiated, freshly exposed metal within the cracks can undergo oxidation, creating a wedge effect at the crack tip, since the oxide occupies a greater volume than the base metal. See Figure 17.

Thermal fatigue can occur in waterwalls or other areas subjected to DNB or rapidly fluctuating flows. Low-amplitude vibrations of entire superheaters can lead to thermal fatigue.⁸

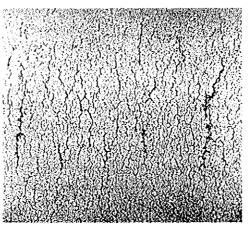
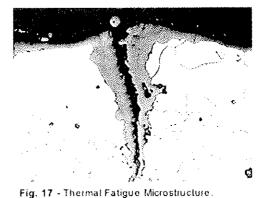


Fig. 16 - Thermal Faligue



Flow Assisted Corrosion

Flow assisted corrosion (FAC) is the localized thinning of a component related to the dissolution of the protective oxide film and the underlying base metal. The mechanisms involved in FAC are very complex due to the effect of many variables, which influence its occurrence⁹. In utility operations FAC is typically seen in single or two phase water flowing in carbon steel piping. The more common locations where FAC is detected are:

- Low pressure system bends in evaporators, risers and economizer tubes
- feedwater cycle (due to more volatile chemistry and lower pH)

There are essentially seven variables which affect FAC; with those being:

- Temperature
- pH
- Oxygen concentration
- · Mass flow rate
- Geometry
- Quality of fluid (single or two phase)
- Materials of construction

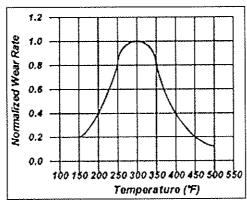


Fig. 18 - Effect of Temperature on FAC.

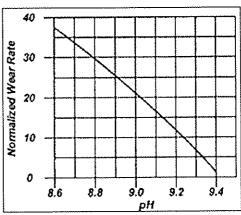
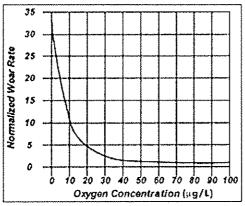


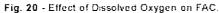
Fig. 19 - Effect of pH on FAC.

The greatest potential for normalized wear occurs at around 300°F (149°C), with very little potential for FAC below 150°F (66°C) and above 500°F (260°C). This is illustrated in Figure 18.

As with general corrosion, pH has a significant effect on the normalized wear rate of carbon steel. There is almost a forty (40) fold reduction in wear rate between a pH of 8.6 and a pH of 9.4, as shown in Figure 19.

Dissolved oxygen (DO) concentration has a direct impact of the potential for flow assisted corrosion. Above a DO concentration of 30 mg/L (ppb), the normalized wear rate on carbon steel is at a minimum. Below 30 mg/L (ppb) DO, the normalized wear rate on carbon steel increases exponentially, as depicted in Figure 20.





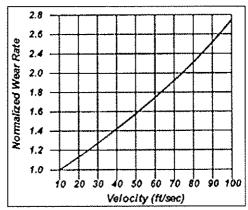


Fig. 21 - Effect of Velocity on FAC.

It only stands to reason that the mass velocity will have a significant influence on flow-assisted corrosion. Below 10 ft/sec (3.05 M/sec), the normalized wear rate is minimal, increasing 2.8 times at 100 ft/sec (30.5 M/sec). Figure 21 and Figure 22 illustrate the effect of velocity on normalized wear rate.

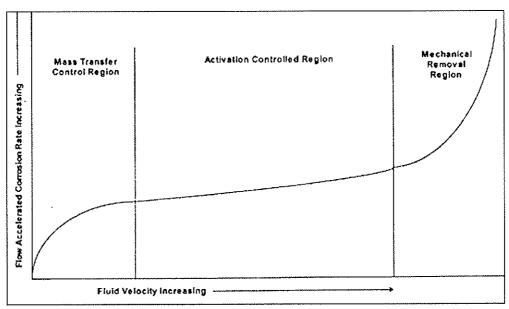
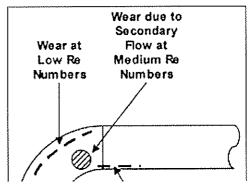


Fig. 22 - Effect of Velocity on FAC.

Geometry, or general layout of the piping systems has an effect on the location of FAC, regardless of the Reynold's Number (Re). Consequently, changes in flow rate may not significantly reduce FAC. Figure 23 shows areas of wear at different Reynold's Numbers. Flow assisted corrosion is most often



found in systems with all ferrous metallurgy. The incorporation of as little as 0.1% chromium into low carbon steels has been shown to have benefits in reducing FAC.



Fig. 23 - Wear Site at Different Reynold's Numbers.

References

- 1. F. Cjarofalo, Fundamentals of Creep and Stress Rupture in Metals, (Macmillam, New York, 1965.)
- 2. F.R. Larson and J. Miller, "A Time-Temperature Relationship for Rupture and Creep Stresses," Trans ASME, July 1952, pp. 765-775.
- 3. Drew Principles of Industrial Water Treatment, Eleventh Edition, (Boonton, NJ: Drew Industrial Division, Ashland Chemical Co., 1994) p 275.
- 4. D.N. French, Metallurgical Failures in Fossil Fired Boilers, (New York, NY: John Wiley & Sons, 1983) p 189.
- 5. Drew Principles of Industrial Water Treatment, p 233.
- 6. Ibid., p 234.
- 7. Ibid., p. 215.
- 8. D.N. French, p 25.
- 9. Heat Recovery Steam Generator Corrosion Causes and Control, (Weatoug, CT.: Tetra Engineering Group, Inc., 2000).

About the Authors

The authors can be reached at Ashland Specialty Chemical Company One Drew Plaza Boonton, NJ 07005

This paper was presented as part of the 61st Annual International Water ConferenceTM, which took place in Pittsburgh, PA (USA), October 22-26, 2002.

back to 2003 contents

TOP

QUIZ

Analyst Fall 2003

Boiler Failure Mechanisms by Douglas DeWitt-Dick, Stephan McIntyre, and Joseph Hofilena

- 1. Peak metal operating temperature above eutectoid can be estimated by:
 - A. the amount of bainite/martensite mixed with ferrite in microstructure at the failure origin.
 - B. the amount of austenite mixed with ferrite in microstructure at the failure origin.
 - C. the amount of austenite mixed with ferrite in microstructure remote from the failure origin
 - D. the amount of marensite mixed with austenite in microstructure at the failure origin.
- 2. What can cause short term overheating?
 - A. High Stack temperature
 - B. Low water level
 - C. High steam pressure setting
 - D. Defective steam king valve
- 3. Short term overheating usually exhibits:
 - A. Thin lip longitudinal rupture
 - B. Thick lip longitudinal rupture
 - C. Transverse cracks
 - D. Severe pitting.
- 4. Which of the following can result in long term overheating:
 - A. Undesired channeling of fireside gases.
 - B. Persistent hardness in boiler water.
 - C. Excessively high boiler water pH.
 - D. Chronically high total alkalinity.
- 5. Long term overheating exhibits:
 - A. Thin lip longitudinal rupture
 - B. Thick lip longitudinal rupture
 - C. Transverse cracks
 - D. Severe pitting.
- 6. Creep damage can be detected with:
 - A. Changes in tube wall thickness
 - B. Micro structural examination of iron carbides.
 - C. Severe bulging of tube wall.

QUIZ

Analyst Fall 2003

Boiler Failure Mechanisms by Douglas DeWitt-Dick, Stephan McIntyre, and Joseph Hofilena

- D. Transverse cracking of tube wall.
- 7. High Temperature stress rupture and oxidation resistance can be increased by:
 - A. Alloying additives of Nickel and Tin
 - B. Alloying additives of Phosphorous and Silicone
 - C. Alloying additives of Molybdenum and Chromium
 - D. Alloying additives of Aluminum and Boron.
- 8. Hydrogen damage is done thru releasing atomic hydrogen to diffuse into steel to form:
 - A. Acids
 - B. Iron hydride
 - C. Methane and iron
 - D. Positive charge resistance
- 9. Hydrogen damage is characterized with:
 - A. Thin lipped rupture
 - B. Transverse cracks
 - C. Thick lipped, brittle rupture
 - D. Severe bulging.
- 10. Caustic gouging destroys protective film by:
 - A. Dissolving carbonate scale.
 - B. Dissolving silicate scale.
 - C. Dissolving iron and magnetite to form sodium ferroate.
 - D. Depositing metal hydroxides.