Chapter

11

Waterwall – Fire-Side Corrosion

Locations

As the title of this chapter indicates, the type of corrosion next discussed affects the fire side of waterwalls in coal-fired boilers. Boilers with low burner-to-side-wall or burner-to-rear-wall clearances are often affected. Waterwall – fire-side corrosion is frequently found in the wind-box area or burner area.

General Description

Waterwall – fire-side corrosion may develop when incomplete fuel combustion occurs (reducing conditions). Incomplete combustion causes release of volatile sulfur compounds, which may form pyrosulfates. Sodium and potassium pyrosulfates ($Na_2S_2O_7$ and $K_2S_2O_7$) may have melting points of 800°F (427°C) or less. Both have a high chemical activity. These molten slags may flux the protective magnetite on tube surfaces, causing accelerated metal deterioration along the crown of the tube.

Depending on the amount of SO_3 in the salt, the melting point may be less than 770°F (396°C) for $K_2S_2O_7$ and around 754°F (387°C) for $Na_2S_2O_7$ (Fig. 11.1). As temperature increases, the amount of SO_3 required to form a liquid phase also increases significantly. Consequently, neither sodium nor potassium pyrosulfates are likely to be present as liquid except on relatively cool surfaces, such as the waterwalls.

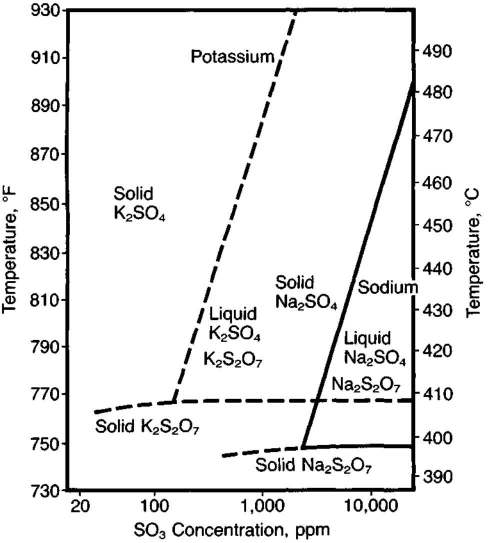

Figure 11.1 Relationships between temperature and SO_3 concentration to produce solid and liquid phase in the $Na_2SO_4 \cdot SO_3$ and $K_2S_4 \cdot SO_3$ systems. (*Reprinted with permission from William T. Reid,* External Corrosion and Deposits: Boilers and Gas Turbines, *American Elsevier, New York, 1971,* p. 106.)

Critical Factors

Insufficient oxygen in the burner zone is a primary factor in development of waterwall corrosion. Poor combustion conditions and steady or intermittent flame contact with the furnace walls, combined with coals that are capable of forming an ash with a low fusion temperature, produce a hot, fuel-rich corrosion environment.

Identification

Waterwall–fire-side corrosion is frequently characterized by metal loss along the crown of the tube and may extend uniformly across several tubes in a particular location (Fig. 11.2). Corroded regions may be covered by abnormally thick layers of iron oxide and iron sulfide corrosion products. At times, flow patterns of the liquid pyrosulfates are apparent in regions of metal wastage.

Chemical analysis of both fuel and ash may be required to determine the level of corrosive substances. A determination of the completeness of combustion can also indicate whether corrosion is occurring. Irregular combustion, malfunctioning burners, long flames, and high carbon content of the ash (3% or more), indicate that waterwall corrosion may be occurring.

In suspect areas, the use of ultrasonic thickness surveys may determine whether corrosion is occurring as well as the extent and rate of corrosion.

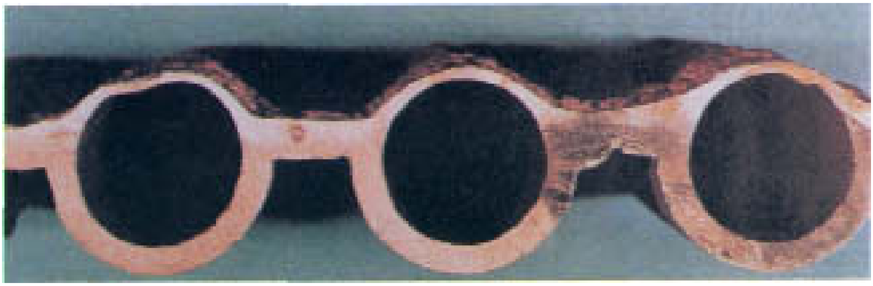

Figure 11.2 Severe fire-side metal loss on waterwall tubes. *(Courtesy of Electric Power Research Institute.)*

Elimination

Since the critical factors governing this form of deterioration relate to combustion characteristics, reduction or elimination of this problem can be realized by making appropriate changes in the combustion process. Changes might consist of improving burning efficiency by grinding coal to a finer, more uniform size; balancing fuel supply to individual burners; adjusting burners to prevent flame impingement; and increasing and redistributing secondary air.

Experience has shown, however, that only marginal improvement in combustion can be expected from these corrections. A furnace modification may be necessary to achieve substantial improvement. To date, fuel additives have not been economically successful in combating waterwall–fire-side corrosion.

Ultrasonic thickness surveys are used to determine extent and severity of existing damage. If damage is minor, patch welding of affected areas may be satisfactory. If damage is severe, installation of thicker tubes or of corrosion-resistant alloy tubes, use of thermal spray coatings, cladding of tubes, and the use of shields may be economically justifiable.

CASE HISTORY 11.1

Industry:	Utility
Specimen Location:	Roof tube
Specimen Orientation:	Horizontal
Years in Service:	35
Water-Treatment Program:	Congruent control
Drum Pressure:	2150 psi (14.8 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter, studded
Fuel:	Coal, 13% ash

Six tube failures of the type illustrated in Fig. 11.3 occurred over a period of several weeks. Only roof tubes had failed.

Visual examination of the external surface of one of the tubes revealed a deep, longitudinal fissure at the base of a stud (Fig. 11.3). This surface was covered with a hard, tenacious, light-colored slag. Chemical analysis of this fire-side slag revealed 42% sulfur and 18% sodium. The pH of a 1% slurry of the deposit was 2.9.

Microstructural examinations revealed no thermal alteration of the tube metal. However, deep, intergranular fissures filled with a complex sulfate eutectic were observed originating on the external surface.

Figure 11.3 Longitudinal fissure adjacent to stud; fissure was caused by the combined effects of stresses imposed by internal pressure and the presence of a molten phase.

Visual and microstructural examinations, coupled with chemical analysis of the slag, revealed that the cracking apparent in Fig. 11.3 resulted from penetration of molten sodium pyrosulfate along grain boundary pathways of the tube-wall metal during boiler operation. Stresses imposed by normal internal pressure acted synergistically with the molten slag to produce the intergranular penetration. Microstructural examinations reveal that this attack was localized to a small region around the primary crack.

The presence of sodium pyrosulfates indicates that reducing conditions or incomplete combustion existed in the firebox, possibly from insufficient oxygen in the burner zone or unsatisfactory grinding of the coal. Insufficient oxygen in the burner zone may be caused by insufficient excess air.

CASE HISTORY 11.2

Industry:	Pulp and paper
Specimen Location:	Adjacent to primary air port, recovery boiler
Specimen Orientation:	Vertical
Years in Service:	10
Tube Specifications:	3 in. (7.6 cm) outer diameter, stainless steel clad, carbon steel tube
Fuel:	Black liquor

Figure 11.4 shows metal loss from the external surface near a longitudinally oriented fin. Metal loss was confined to an elliptical region centered on the fin. The stainless steel cladding as well as some underlying carbon steel was corroded away.

The corroded region was covered with a layer of brown corrosion product and deposits. Chemical analysis of this layer revealed a content of 52% iron, 24% sodium, and 14% carbonate.

Visual and microstructural evidence, coupled with analysis of the corrosion products, indicated that metal loss was caused by exposure of the metal to a molten salt of sodium. The fusion temperature of this salt may have been depressed by the presence of the carbonate.

Rates of metal loss from corrosion of this type vary depending on metal temperature and furnace design. Corrosion rates of 30 mil/y (0.76 mm/y) have been reported.

Mitigation of this problem requires redesign of tube openings so that seals are tight to flue gas. In addition, crevices where corrosive substances can concentrate must be eliminated.

Repair of damage is most successful when weld overlays of high-nickel stainless steels and thermal spray coatings are used.

Figure 11.4 Metal loss around a fin resulting from exposure of a stainless steel–clad tube to a molten sodium salt.

CASE HISTORY 11.3

Industry:	Pulp and paper
Specimen Location:	Wall tube, recovery boiler
Specimen Orientation:	Vertical
Years in Service:	13
Water-Treatment Program:	Polymer
Drum Pressure:	875 psi (6 MPa)
Tube Specifications:	2½ in. (6.3 cm) outer diameter
Fuel:	Black liquor

The corrosion apparent in Figs. 11.5 and 11.6 occurred over a very small area of the wall at a position 40 ft (12.2 m) above the floor and 4 ft (1.2 m) above oil guns. A failure of this type had not occurred previously.

This sample had been water-washed before removal, which reportedly may have removed a layer of frozen smelt. The fire side of this boiler is water-washed twice per year.

Figure 11.5 Perforation in a region of severe metal loss.

Figure 11.6 Severe metal loss along crown of tube resulting from exposure to a molten phase.

The ⅜-in. hole in Fig. 11.5 is centered in a region of severe external corrosion along the crown of the tube. The corrosion has produced deep, broad depressions, which give the surface a rolling contour. Microstructural examinations revealed no evidence of overheating.

The fact that this corrosion was localized in the region of the oil guns suggests that a reducing environment, created locally during the operation of the guns, produced a corrosive molten phase having a low melting temperature. In this case, corrosion would occur only during oil-gun use, which is intermittent. However, the accumulated corrosion over 13 years of service was apparently sufficient to result in failure.