Chapter

8

Oxygen Corrosion

Locations

Although relatively uncommon in an operating boiler, oxygen attack is a problem frequently found in idle boilers. The entire boiler system is susceptible, but the most common attack site is in superheater tubes. Reheater tubes are also susceptible, especially where moisture can collect in bends and sags in the tubes.

In an operating boiler the first areas to be affected are the economizer and the feedwater heaters. In cases of severe oxygen contamination, metal surfaces in other areas of the boiler may be affected—for example, surfaces along the waterline in the steam drum, and in the steam-separation equipment. In all cases, considerable damage can occur even if the period of oxygen contamination is short.

General Description

One of the most frequently encountered corrosion problems results from exposure of boiler metal to dissolved oxygen. Since the oxides of iron are iron's natural, stable state, steels will spontaneously revert to this form if conditions are thermodynamically favorable. Generally, conditions are favorable if steel that is not covered by the protective form of iron oxide (magnetite) is exposed to water containing oxygen. The following reaction occurs:

$$2Fe + H_2O + O_2 \rightarrow Fe_2O_3 + 2H\uparrow$$

This reaction is the basis for the intensive mechanical and chemical deaeration practices that are typical of sound water-treatment programs. These practices are generally successful. In fact, occurrences of oxygen corrosion in boilers are generally confined to idle periods.

For example, moisture condensing on the walls of an idle superheater tube will dissolve atmospheric oxygen. Fractures in the protective magnetite are caused by contraction stresses as the superheater is cooled to ambient temperatures. The fracture sites furnish anodic regions where oxygen-containing moisture can react with bare, unprotected metal. The result may be deep, distinct, almost hemispherical pits (Fig. 8.1), which may be covered at times with caps of corrosion products (Fig. 8.2). Frequently, pitting will occur at the bottom of U-shaped superheater pendants where moisture can accumulate (Fig. 8.3).

In addition to tube-wall perforation, oxygen corrosion is troublesome from another perspective. Oxygen pits can act as stress-concentration sites, thereby fostering the development of corrosion-fatigue cracks, caustic cracks, and other stress-related failures.

Figure 8.1 Oxygen pits in section of superheater tube. *(Courtesy of Electric Power Research Institute.)*

Figure 8.2 Caps of iron oxide covering pit sites.

Figure 8.3 Oxygen pits along bottom of superheater pendant. *(Courtesy of National Association of Corrosion Engineers.)*

Critical Factors

The three critical factors governing the onset and progress of oxygen corrosion include the presence of moisture or water, the presence of dissolved oxygen, and an unprotected metal surface.

The corrosiveness of water increases as temperature and dissolved solids increase, and as pH decreases. Aggressiveness generally increases with an increase in oxygen.

An unprotected metal surface can be caused by three conditions:

- The metal surface is bare — for example, following an acid cleaning.
- The metal surface is covered with a marginally protective, or nonprotective, iron oxide, such as hematite, Fe_2O_3 (red).
- The metal surface is covered with a protective iron oxide, such as magnetite, Fe_3O_4 (black), but holidays or cracks exist in the coating.

Breakdown, or cracking of the magnetite, is due largely to mechanical and thermal stresses induced during normal boiler operation. These stresses are increased — and, therefore, are more damaging — during boiler start-up, during boiler shutdown, and during rapid load swings. During normal boiler operation, the environment favors rapid repair of breaches in the magnetite. However, if excessive levels of oxygen are present, either during operation or outages, the cracks in the magnetite cannot be adequately repaired and corrosion commences.

Identification

Simple visual examination is sufficient if affected surfaces are accessible. Nondestructive testing techniques, such as ultrasonic testing, may be required if affected surfaces are not accessible.

Elimination

The three critical factors that govern oxygen corrosion in a boiler are moisture or water, oxygen, and an inadequately protected metal surface.

Operating boiler

Water is always present in an operating boiler. Also, the protective magnetite coating exists in a state of continuous breakdown and repair. At any given time, holidays and cracks in the magnetite will be present, although the percentage of the entire internal surface they represent will be very small. Therefore, since both water and corrosion sites are present, mitigation of oxygen corrosion is achieved by sufficiently diminishing dissolved oxygen levels.

Possible causes of excessive levels of dissolved oxygen are, for example, a malfunctioning deaerator, improper feed of oxygen-scavenging chemicals, or air in-leakage. (See the section titled Sources of Air In-Leakage in this chapter.) Monitoring of oxygen levels at the economizer inlet, especially during start-up and low-load operation, is recommended.

Idle boiler—wet lay-up

An idle boiler during wet lay-up is subject to conditions similar to those in an operating boiler as far as oxygen corrosion is concerned. Therefore, the preventive method, reduction of oxygen content to very low levels, and continuous control that prevents these levels from rising, is the same. In general, this procedure requires complete filling of the boiler, use of sufficiently high levels of oxygen-scavenging chemicals, and maintenance of properly adjusted pH levels, as well as periodic water circulation.

Idle boiler—dry lay-up

Successful protection of an idle boiler during dry lay-up depends upon consistent elimination of moisture and/or oxygen. A procedure for boiler protection by dry lay-up can involve the use of desiccants and nitrogen blankets, or the continuous circulation of dry, dehumidified air ($<30\%$ relative humidity).

Boiler after chemical cleaning

Protection of a boiler following acid cleaning is achieved by developing a protective iron oxide coating on the metal surface. This is usually accomplished by a thorough rinsing followed with a "post boilout." A sodium carbonate solution or other alkaline substance can be used in the post-boilout–passivation step.

Cautions

The knoblike mound of corrosion products that frequently covers pit sites is sometimes misidentified as simple deposits. Correct identification of these mounds, known as *tubercles,* can be achieved through a consideration of the following:

- Tubercles will overlie corrosion sites. Under the influence of sufficient fluid velocity the tubercle may be elongated in the flow direction.

- A tubercle is highly structured and usually consists of a hard, brittle, outer shell of reddish corrosion products that encapsulates an inner core of soft, voluminous, dark corrosion products.

Sources of Air In-Leakage

Low-pressure feedwater heaters are often under negative pressure during low-load operation, allowing air to be drawn into the feedwater through leaky valves, pumps, flanges, etc. Other sources of air in-leakage are shown in Table 8.1.

TABLE 8.1 Sources of Air In-Leakage

Location	Leakage source
Turbine	Gland seals Flanges, hood, and expansion joints Penetrations Valves
Condenser	Penetrations and flanges Boot Manways Hot-well sight glass
Condensate pump suction	Valves, gauges, flanges Pump-shaft seal
Feedwater heater	Valves
Other	Perforated explosion diaphragms Valves Expansion joints Flash tanks

Related Problems

See also Chap. 15, "Corrosion-Fatigue Cracking."

CASE HISTORY 8.1

Industry:	Pulp and paper
Specimen Location:	Superheater
Specimen Orientation:	Horizontal, vertical
Years in Service:	10
Treatment Program:	Dry lay-up using nitrogen blanket
Tube Specifications:	2 in. (5.1 cm) outer diameter

The oxygen pits illustrated in Figs. 8.1 and 8.4 were discovered during a hydrotest of a recovery boiler that had been in wet lay-up over the summer. The superheater section had been in dry lay-up under a nitrogen blanket.

Gravity-induced drainage of corrosion products from sites on vertical sections is apparent in Fig. 8.1. Elliptical rings surrounding the pit on the horizontal portion of the pendant section indicate that a pool of condensate had been present (Fig. 8.4). Close examination under a low-power stereoscopic microscope revealed contraction cracks in the protective magnetite at the pit sites. It is apparent that, despite the precautions of dry lay-up, the tube had been exposed to condensed moisture and atmospheric oxygen.

Figure 8.4 Elliptical water rings surrounding oxygen pit in a U-bend. *(Courtesy of Electric Power Research Institute.)*

CASE HISTORY 8.2

Industry:	Pulp and paper
Specimen Location:	Convection bank
Specimen Orientation:	Various
Years in Service:	15
Treatment Program:	Wet lay-up, hydrazine, morpholine
Drum Pressure:	700 psi (4.8 MPa)
Tube Specifications:	2 in. (6.3 cm) outer diameter

Figures 8.5 through 8.7 illustrate typical oxygen pitting resulting from an improperly executed wet lay-up. Inadequate feed of oxygen-scavenging chemicals, and/or failure to maintain proper water circulation, may have been responsible.

Gravitationally induced drainage of corrosion products is apparent in Fig. 8.5. This is evidence of stagnant or very low flow of water during lay-up. Significant water flow would have reoriented the drainage lines in the direction of water flow. Typical knoblike mounds of iron oxide corrosion products (tubercles) are shown in Figs. 8.6 and 8.7.

Figure 8.5 Oxygen pits on internal surface.

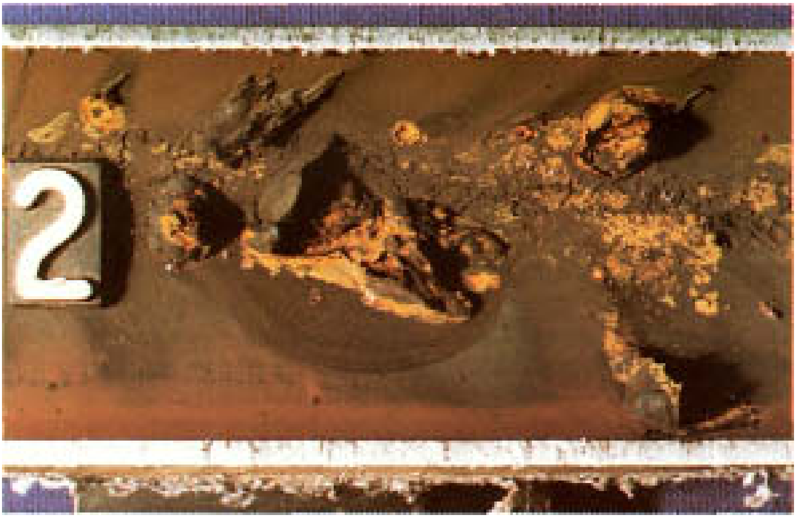

Figure 8.6 Tubercles covering oxygen pits.

Figure 8.7 Tubercles covering oxygen pits.

CASE HISTORY 8.3

Industry:	Steam heating
Specimen Location:	Fire-tube boiler
Specimen Orientation:	Horizontal
Years in Service:	4
Water-Treatment Program:	Polymer and sodium sulfite
Tube Specifications:	3 in. (7.6 cm) outer diameter

Figure 8.8 illustrates the external surface of a fire-tube boiler that has sustained severe oxygen corrosion. Interruptions of oxygen-scavenger feed lasting as long as 1 week had occurred. It is probable that the pitting initiated and progressed during these interruptions. Deposits, which can also induce pitting (deposit corrosion), were not present on the tube.

Figure 8.8 Oxygen pitting on the external surface of fire tube.

CASE HISTORY 8.4

Industry:	Steam heating
Specimen Location:	Condensate return line
Specimen Orientation:	Horizontal
Years in Service:	9
Water-Treatment Program:	Neutralizing amine
Tube Specifications:	1¼-in. (3.2 cm) outer diameter

Figure 8.9 illustrates a recurring problem in one region of the condensate system of a boiler that operated 8 to 10 hours per day. The reddish color of the iron oxides and the tubercles covering the pit sites identify the deterioration as oxygen pitting.

The condensate system is pressurized during service and carries water at 220°F (104°C). Although oxygen could be present in the system under these conditions, it is more probable that the source of oxygen is air sucked into the line as the system cooled during idle periods. A treatment utilizing filming amine, rather than a simple neutralizing amine would probably be more successful in mitigating corrosion of this type.

Figure 8.9 Internal surface of condensate line.

CASE HISTORY 8.5

Industry:	Chemical process
Specimen Location:	Economizer
Specimen Orientation:	Horizontal
Years in Service:	7
Water-Treatment Program:	Polymer and oxygen scavenger
Drum Pressure:	600 psi (4.1 MPa)
Tube Specifications:	2½ in. (6.3 cm) outer diameter

The reddish color of the iron oxides and the presence of tubercles capping iron oxide–filled pits (Fig. 8.2) is typical of exposure of economizer steel to water containing excessively high levels of dissolved oxygen. Pitting and perforation of economizer tubes was a recurrent problem at this plant. Failures were occurring every 3 or 4 months.

Oxygen content of the water was measured at 5 to 9 ppb. Excursions to higher levels were suspected but could not be documented. The boiler was operated continuously. Although the source of the oxygen was not identified, it is clear that excessively high levels existed in the affected regions of the economizer.