Chapter

6

Low-pH Corrosion during Service

Locations

Generally, in-service acid corrosion is confined to water-cooled tubes in regions of high heat flux; slanted or horizontal tubes; locations beneath heavy deposits; and heat-transfer regions at or adjacent to backing rings at welds, or to other devices that disrupt flow.

General Description

Although relatively rare, a general depression of bulk-water pH may occur if certain contaminants gain access to the boiler. Boilers using water of low buffering capacity can realize a bulk pH drop to less than 5 if contaminated with seawater, hydrochloric acid, or sulfuric acid.

The concern of this chapter, however, is with the more common creation of localized pH conditions. Two circumstances must exist simultaneously to produce this condition. First, the boiler must be operated outside of normal, recommended water-chemistry parameters. This may happen if condenser in-leakage occurs when seawater, or water from a recirculating water system using cooling towers, is used. Another source of contamination is the inadvertent release of acidic regeneration chemicals from a makeup-water demineralizer into the feedwater system.

The second condition that must exist to produce low-pH conditions is a mechanism for concentrating acid-producing salts. This condition exists where boiling occurs and adequate mixing is hindered by the presence of porous deposits or crevices. Where deposits or crevices are present, a concentration of acid-producing salts may induce hydrolysis to produce localized low-pH conditions, while the bulk water remains alkaline.

$$M^+Cl^- + H_2O \rightarrow MOH\downarrow + H^+Cl^-$$

Wherever low-pH conditions exist, the thin film of magnetic iron oxide is dissolved and the metal is attacked. The result is gross metal loss. This loss may have smooth, rolling contours similar in appearance to caustic gouging. The gouged area will frequently be covered with nonprotective iron oxides.

Critical Factors

Two critical factors contribute to low pH. The first is the availability of free acid or acid-producing salts (i.e., salts whose solution with water may produce acid). Unintentional additions of free acid may arise from inadvertent release of acid regeneration chemicals from a makeup-water demineralizer into the makeup water. Acid-producing salts may contaminate the condensate by in-leakage through condensers, or from process streams. Because of the powerful concentration mechanisms that may operate in a boiler, in-leakage of only a few parts per million of contaminant may be sufficient to cause localized low-pH corrosion in unbuffered boiler water. Residual contamination from chemical cleaning and poorly controlled or malfunctioning feedwater-chemical equipment may also foster localized low-pH conditions.

The second contributing factor is the mechanism of concentration. Since free acid or acid-producing salts are not usually present at corrosive levels in the bulk environment, some means of concentrating them must be present. Three basic concentration mechanisms exist:

1. Departure from nucleate boiling (DNB). *Nucleate boiling* refers to a condition in which discrete bubbles of steam nucleate at points on a metal surface. Normally, as these steam bubbles form, minute concentrations of boiler-water solids will develop at the metal surface, usually where the bubble and water interface. As the bubble separates from the metal surface, the water will redissolve soluble solids (Fig. 1.1).

At the onset of DNB, the rate of bubble formation exceeds the rinsing rate. Dissolved solids, or suspended solids, will begin to concentrate (Fig. 1.3). The presence of concentrated corrosives will compromise the thin film of magnetic iron oxide, causing metal loss.

Under the conditions of fully developed DNB, a stable film or blanket of steam will form. Corrosives then concentrate at the edges of this blanket, causing metal loss at the perimeter. The metal at the interior of the blanket is left relatively intact.

2. Deposition. A similar situation occurs when deposits shield the metal from the bulk water. Steam that forms under these thermally insulating deposits escapes and leaves behind a corrosive residue that can deeply gouge the metal surface.

3. Evaporation at a waterline. Where a waterline exists, corrosives may concentrate by evaporation, resulting in gouging along the waterline. In horizontal or slanted tubes, a pair of parallel, longitudinal trenches may form. If the tube is nearly full, the parallel trenches will coalesce into a single longitudinal gouge along the top of the tube. In vertically oriented tubes, corrosive concentration at a waterline will yield a circumferential gouge.

Identification

Simple visual examination is sufficient if affected surfaces are accessible. If not, nondestructive testing techniques, such as ultrasonic testing, may be required. Steam studies using a hydrogen analyzer may also identify localized low-pH corrosion.

Elimination

When the availability of free acid or acid-producing salts and the mechanism of concentration exist simultaneously, they govern susceptibility to localized low-pH corrosion. The following remedies may eliminate low-pH corrosion based on the availability of free acids or acid-producing salts:

- **Prevent inadvertent release of acidic regeneration chemicals from makeup-water demineralizers.**

- **Prevent in-leakage of acid-producing salts, such as calcium chloride and magnesium chloride, into condensers.** Because of the powerful concentration mechanisms that may operate in a boiler, in-leakage of only a few parts per million of contaminant may be sufficient to cause localized corrosion.

- **Prevent contamination of steam and condensate by process streams.**

Although these remedies may eliminate corrosion based on the availability of free acids or acid-producing salts, preventing localized concentration is the most effective means of avoiding low-pH corrosion. It is also the most difficult to achieve. The methods for preventing localized concentration include:

- **Prevent DNB.** This usually requires the elimination of hot spots, accomplished by controlling the boiler's operating parameters. Hot spots are caused by such things as excessive overfiring or underfiring, misadjusted burners, change of fuel, gas channeling, and excessive blowdown.

- **Prevent excessive water-side deposition.** Tube sampling on a periodic basis (usually annually) may be performed to measure the relative thickness and amounts of deposit buildup on tubes. Tube-sampling practices are outlined in ASTM D887-82. Consult boiler manufacturers' recommendations for acid cleaning.

- **Prevent the creation of waterlines in tubes.** Slanted and horizontal tubes are especially susceptible to the formation of waterlines. Operation of the boiler at excessively low water levels, or excessive blowdown rates, may create waterlines. Waterlines may also be created by excessive load reduction when pressure remains constant. Under this circumstance, the water velocity in the boiler tubes is reduced to a fraction of its full load value. If it becomes low enough, steam/water stratification occurs, creating stable or metastable waterlines.

Cautions

It is very difficult to distinguish localized attack by low-pH substances from localized attack by high-pH substances simply by visual examination. Distinguishing between the two may require a formal metallographic examination. Evaluating the types of concentrateable corrosives that may be contaminating the boiler water will aid in the determination.

Because corrosion products may fill the depressions caused by low-pH corrosion, the extent and depth of the affected area, and even the existence of a corrosion site, may be overlooked. Probing a suspect area with a hard, pointed instrument may aid in the determination, but because the corrosion products are often hard, a corrosion site may remain undetected.

Related Problems

See also Chap. 4, "Caustic Corrosion," and Chap. 14, "Hydrogen Damage."

CASE HISTORY 6.1

Industry:	Utility
Specimen Location:	Side wall
Specimen Orientation:	Vertical
Years in Service:	30
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	2000 psi (13.8 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter

Numerous occurrences of the type of gouging illustrated in Fig. 6.1 had resulted in an extensive tube-replacement program. Most replacements were in one of the boiler's side walls. This type of corrosion was a recurring

Figure 6.1 Low-pH gouging.

Figure 6.2 Deep gouge on internal surface. (Magnification: 7.5X.)

problem, but the frequency had recently increased. The boiler was in peaking service.

Figure 6.2 illustrates the extent and appearance of the gouging. The crater was filled with thick, hard, iron oxides and elemental copper. (Most gouging had occurred downstream of circumferential welds.)

Analysis of corrosion products on the internal surface of the crater revealed significant amounts of chloride.

The large percentage of occurrences immediately downstream of circumferential welds indicates that disrupted water flow across the weld was instrumental in establishing a concentration site for corrosive substances.

CASE HISTORY 6.2

Industry:	Utility
Specimen Location:	Wall tube
Specimen Orientation:	Slightly off vertical
Years in Service:	26
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	1900 psi (13.1 MPa)
Tube Specifications:	3¼ in. (8.3 cm) outer diameter

Figures 6.3 and 6.4 illustrate the massive rupture that occurred in a distinct zone of deep metal loss along the internal surface of this tube. Surrounding areas of the internal surface were unaffected and quite smooth.

Figure 6.3 Rupture associated with low-pH gouging.

Figure 6.4 Metal loss at the origin of rupture.

Microstructural examinations revealed extensive hydrogen damage in the tube wall immediately below the gouged zone.

The visual and microstructural appearance of the gouged region was consistent with that of low-pH exposure. The hydrogen damage that is associated with the low-pH gouging indicates that corrosion occurred during boiler operation.

Concentration of low-pH corrosive may have occurred beneath deposits that were dislodged from the internal surface at the time of rupture. It is also possible that concentration occurred as a result of the presence of a steam blanket that resulted from nonnucleate boiling.

CASE HISTORY 6.3

Industry:	Utility
Specimen Location:	Waterwall
Specimen Orientation:	Slanted (nose arch)
Years in Service:	10
Water-Treatment Program:	Congruent control
Drum Pressure:	2700 psi (18.6 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter

Figure 6.5 illustrates one of many tubes that had sustained similar severe corrosion. Grooves were located along the top (crown) of each tube. The convergence of the groove, apparent in Fig. 6.5, marked the position where the slanted tube assumed a vertical orientation. Metal loss was not observed downstream of this point.

Corroded areas were covered with black, powdery deposits (Fig. 6.6). These deposits covered a second layer of light-colored material that was

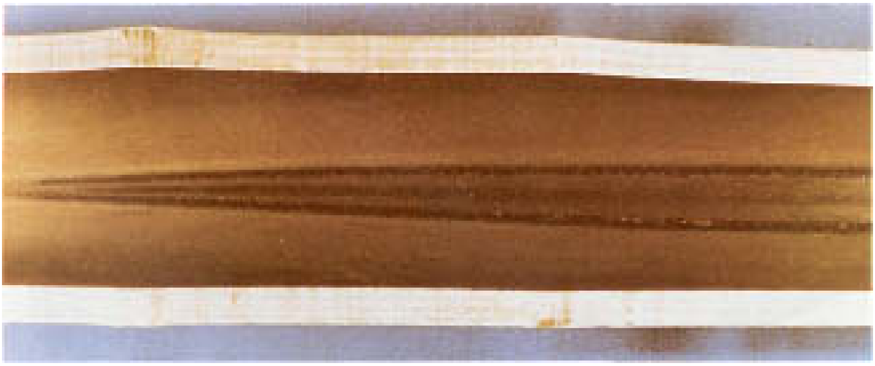

Figure 6.5 Convergence of groove.

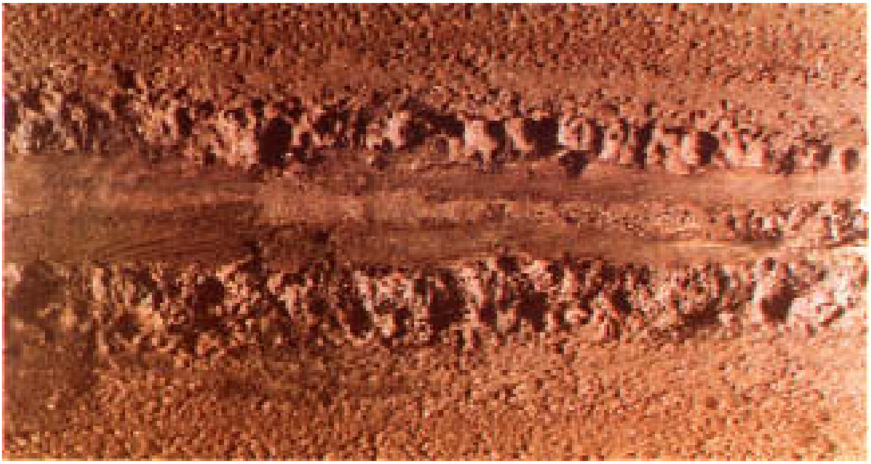

Figure 6.6 Appearance of deposits covering groove.

directly on the metal. The light-colored material was present only in corroded regions. On either side of the groove a hard coating of protective magnetite covered the smooth internal surface. The contour of the corroded surface following removal of the deposits and the light-colored material is shown in Fig. 6.7.

Figure 6.7 Contour of groove after deposit removal. *(Courtesy of Electric Power Research Institute.)*

Microstructural analyses revealed that the grooved tube wall had sustained mild overheating. Analyses of the substances covering corroded surfaces revealed that the light-colored material on the metal surface was highly crystalline and was composed of iron and phosphorus. *X*-ray diffraction studies of this material revealed iron phosphate and sodium iron phosphate.

Gravitational stratification of water and steam established relatively stable steam channels along the tops of the slanted tubes. Evaporative concentration of dissolved solids within this channel furnished the corrodent. Careful chemical analyses revealed that iron phosphate and sodium iron phosphate were confined to corroded metal surfaces.

While a diagnosis of caustic gouging might explain this corrosion, the microstructural contours of corroded surfaces, the absence of dense iron oxide or crystalline magnetite, and the specific water chemistry of the boiler in this case all suggest corrosion by a weak, phosphorus-containing acid.

CASE HISTORY 6.4

Industry:	Chemical process
Specimen Location:	Economizer
Specimen Orientation:	Horizontal
Years in Service:	7
Water-Treatment Program:	Chelant
Drum Pressure:	155 psi (1.1 MPa)
Tube Specifications:	2⅜ in. (6.0 cm) outer diameter

Corrosion was a recurrent problem in the economizer of this gas-fired boiler. Failures occurred only in the hot end of the economizer at the beginning of the finned area (Fig. 6.8). Heat fluxes in this area were 40% higher than design values.

Corrosion formed a large elliptically shaped gouge covered with a thick, irregular layer of hard, dark iron oxides. Microstructural examinations of the iron oxides covering this gouge revealed a laminated structure typical of low-pH gouging.

Nonnucleate boiling in this area of the economizer (caused by excessively high heat fluxes) furnished the means for concentrating corrosive, low-pH substances. The source of the acid-producing salts was undetermined, but may have been caused by leakage of sodium chloride from the regeneration of a water softener.

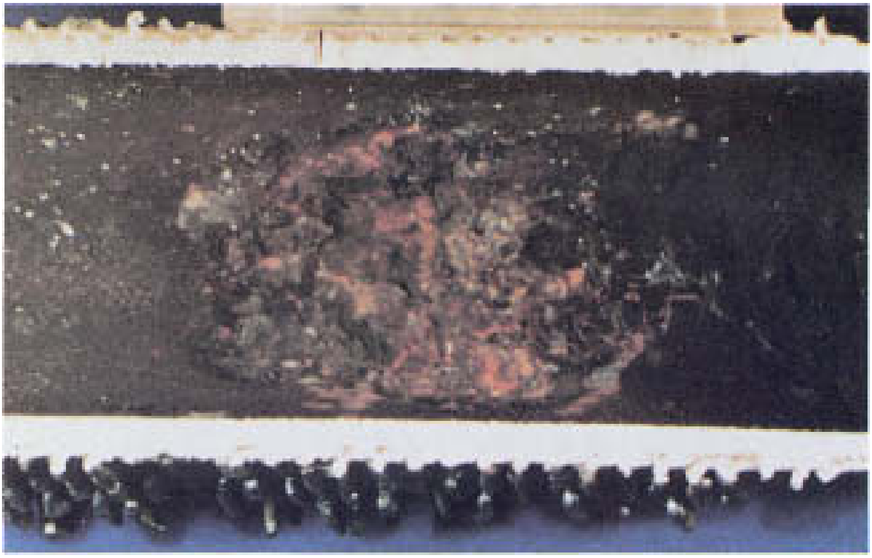

Figure 6.8 Gouging along internal surface opposite fins.

CASE HISTORY 6.5

Industry:	Chemical process
Specimen Location:	Tube from an ethylene-cracking furnace
Specimen Orientation:	Horizontal
Years in Service:	Unknown
Water-Treatment Program:	Antifoulant added
Drum Pressure:	175 psi (1.2 MPa)
Tube Specifications:	4½ in. (11.4 cm) outer diameter

The perforation illustrated in Fig. 6.9 occurred along the bottom of the first tube pass in the convection section of the furnace. Steam and ethane, in the ratio of 1 to 3, pass through the tube.

The metal loss, illustrated in Fig. 6.10, occurred on the internal surface of the tube and was responsible for the perforation. The corrosion produced a smooth, rolling surface contour.

Dark deposits, which gave a low-pH indication when wetted, surrounded the corrosion site. Analysis of these deposits and corrosion products revealed high levels of phosphorus and iron. It is possible that an acidic, phosphorus-containing substance had concentrated along the hot side of the tube, resulting in this deterioration.

Figure 6.9 Perforation resulting from corrosion of internal surface.

Figure 6.10 Appearance of metal loss on internal surface.