Chapter 4

Caustic Corrosion

Locations

Generally, caustic corrosion is confined to (1) water-cooled tubes in regions of high heat flux, (2) slanted or horizontal tubes, (3) locations beneath heavy deposits, and (4) heat-transfer regions at or adjacent either to backing rings at welds or to other devices that disrupt flow.

General Description

The terms *caustic gouging* and *ductile gouging* refer to the corrosive interaction of sufficiently concentrated sodium hydroxide with a metal to produce distinct hemispherical or elliptical depressions. The depressions may be filled with dense corrosion products that sometimes contain sparkling crystals of magnetite. At times, a crust of hard deposits and corrosion products containing magnetite crystals will surround and/or overlie the attacked region. The affected metal surface generally has a smooth, rolling contour.

The susceptibility of steel to attack by sodium hydroxide is based on the amphoteric nature of iron oxides; that is, oxides of iron are corroded by both low-pH and high-pH environments (Fig. 4.1). High-pH substances, such as sodium hydroxide, will dissolve magnetite:

$$4NaOH + Fe_3O_4 \rightarrow 2NaFeO_2 + Na_2FeO_2 + 2H_2O$$

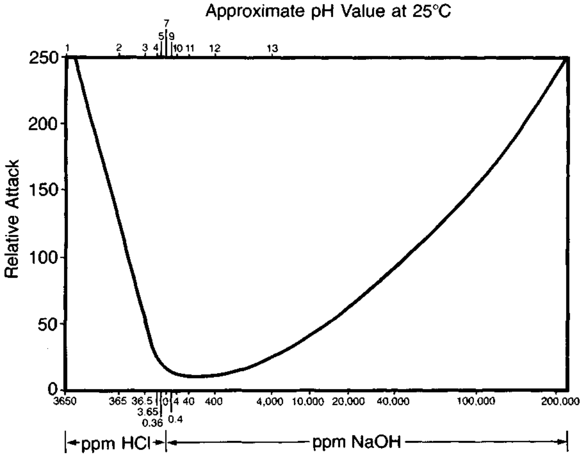

Figure 4.1 Attack on steel at 310°C (590°F) by water of varying degrees of acidity and alkalinity. (*Curve by Partridge and Hall, based on data of Berl and van Taack. Courtesy of Herbert H. Uhlig,* The Corrosion Handbook, *John Wiley and Sons, New York, 1948.*)

When magnetite is removed, the sodium hydroxide may react directly with the iron:

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2$$

Critical Factors

Two critical factors contribute to caustic corrosion. The first is the availability of sodium hydroxide or of alkaline-producing salts (i.e., salts whose solution in water may produce base). Sodium hydroxide is often intentionally added to boiler water at noncorrosive levels. It may also be introduced unintentionally if chemical from a caustically regenerated demineralizer is inadvertently released into makeup water. Alkaline-producing salts may also contaminate the condensate by in-leakage through condensers, or from process streams. Poorly controlled or malfunctioning chemical-feed equipment may also cause excessive alkalinity.

The second contributing factor is the mechanism of concentration. Because sodium hydroxide and alkaline-producing salts are rarely present at corrosive levels in the bulk environment, a means of concentrating them must be present. Three basic concentration mechanisms exist:

1. Departure from nucleate boiling (DNB). The term *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 concentra-

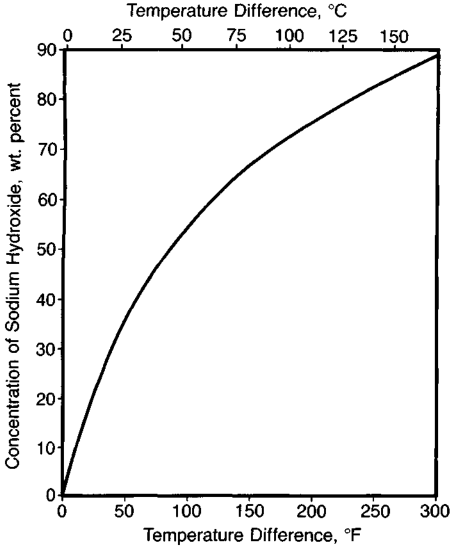

Figure 4.2 Sodium hydroxide content attainable in concentrating film of boiler water. (*Based on data from* International Critical Tables, *3:370(1928). Courtesy of Herbert H. Uhlig,* The Corrosion Handbook, *John Wiley and Sons, New York, 1948.*)

tions of boiler-water solids will develop at the metal surface, usually at the interface of the bubble and the water. As the bubble separates from the metal surface, the water will redissolve soluble solids such as sodium hydroxide (Fig. 1.1).

At the onset of DNB, the rate of bubble formation exceeds the rinsing rate. Under these conditions, sodium hydroxide, as well as other dissolved solids or suspended solids, will begin to concentrate (Fig. 1.3 and Fig. 4.2). The presence of concentrated sodium hydroxide and other 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 (Fig. 4.3).

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 (Fig. 4.4). If the tube is nearly full, the parallel trenches will coalesce into a single longitudinal gouge along the top of the tube (Fig. 4.5). In

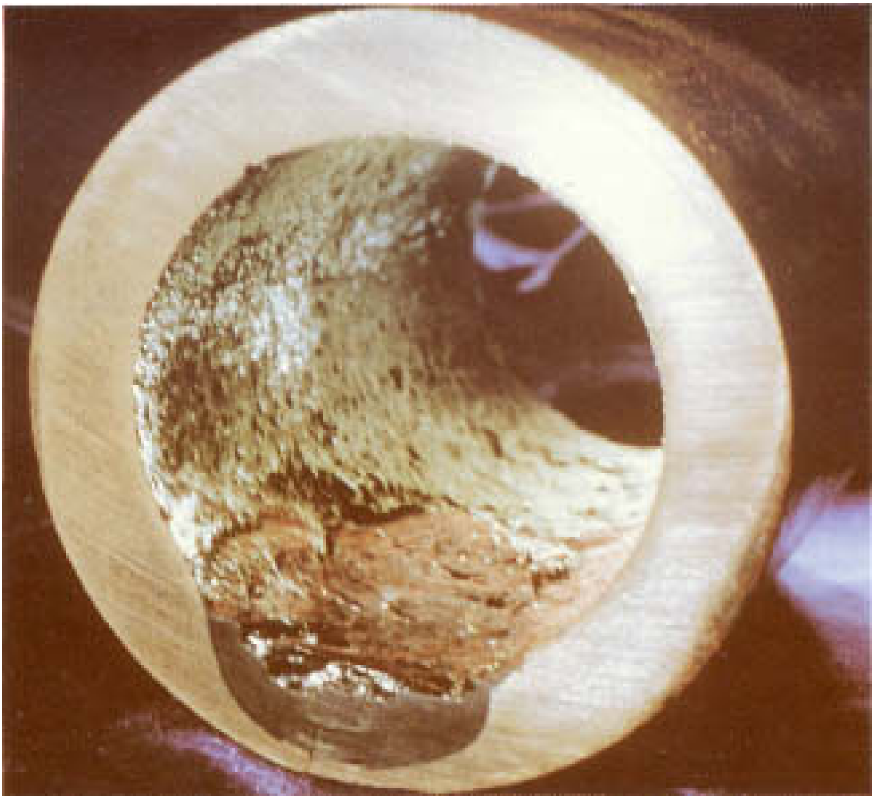

Figure 4.3 Deep caustic gouging beneath insulating internal deposits. *(Courtesy of National Association of Corrosion Engineers.)*

vertically oriented tubes, corrosive concentration at a waterline will yield a circumferential gouge.

Identification

If affected surfaces are accessible, caustic corrosion can be identified by simple visual examination. If not, nondestructive testing techniques such as ultrasonic testing may be required. Steam studies using a hydrogen analyzer may also be used to identify caustic corrosion.

Elimination

When the availability of sodium hydroxide or alkaline-producing salts and the mechanism of concentration exist simultaneously, they govern suscep-

Figure 4.4 Caustic gouging along a longitudinal waterline. *(Courtesy of National Association of Corrosion Engineers.)*

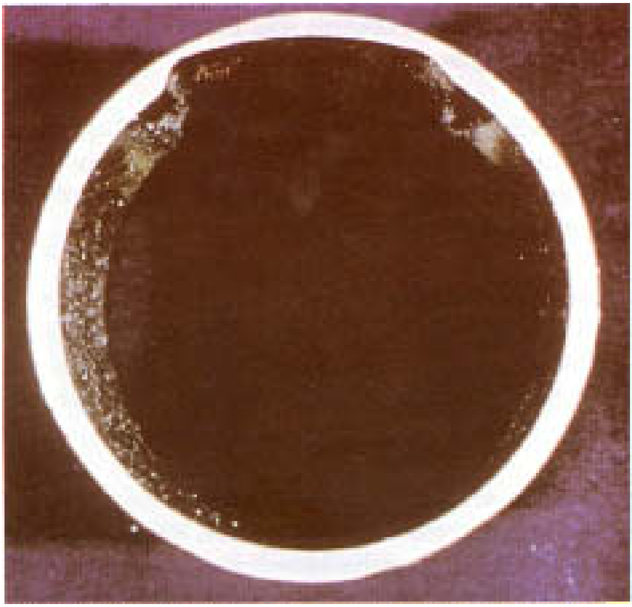

Figure 4.5 Caustic gouging resulting from evaporation at a waterline riding along the crown of the tube. *(Courtesy of National Association of Corrosion Engineers.)*

tibility to caustic corrosion. The following remedies may eliminate corrosion that depends on the availability of sodium hydroxide or alkaline-producing salts:

- **Reduce the amount of available free sodium hydroxide.** This is the underlying concept that serves as the basis for coordinated phosphate programs implemented in high-pressure boilers.

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

- **Prevent in-leakage of alkaline-producing salts 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 that depends on the availability of sodium hydroxide or alkaline-producing salts, preventing localized concentration is the most effective means of avoiding caustic 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, achieved by controlling the boiler's operating parameters. Hot spots are caused by excessive overfiring or underfiring, misadjusted burners, change of fuel, gas channeling, excessive blowdown, etc.

- **Prevent excessive water-side deposition.** Tube sampling on a periodic basis (usually annually) may be performed to measure the relative thickness and amount 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. Boiler operation 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. In this situation, water velocity in the boiler tubes is reduced to a fraction of its full-load value. If velocity becomes low enough, steam/water stratification occurs, creating stable or metastable waterlines.

Cautions

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

Because corrosion products may fill the depressions caused by caustic 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 very hard, a corrosion site may remain undetected. The presence of sparkling crystalline magnetite does not necessarily indicate that caustic corrosion has occurred.

Related Problems

See also Chap. 1, "Water-Formed and Steam-Formed Deposits," and Chap. 6, "Low-pH Corrosion during Service."

CASE HISTORY 4.1

Industry:	Utility
Specimen Location:	Back wall of power boiler
Specimen Orientation:	Vertical
Years in Service:	6
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	1500 psi (10.3 MPa)
Tube Specifications:	2¾ in. (7.0 cm) outer diameter

Numerous caustic attacks on the back wall of a cyclone-fired boiler (Fig. 4.6) were all observed within a month. This type of attack had occurred once previously. This boiler was acid-cleaned every 18 to 24 months. The gouge was noted 1 year after the last acid cleaning.

Visual examinations disclosed hard layers of black, crystalline corrosion products covering the attack site. Measurement revealed a 42% reduction in tube-wall thickness. Microstructural examinations disclosed moderate overheating in the gouged region. Evidence revealed that DNB, rather than deposits, was responsible for caustic concentration in this case. Overfiring during start-up and low flow rates of the feedwater were suspected.

Figure 4.6 *Region of caustic gouging along internal surface.*

CASE HISTORY 4.2

Industry:	Utility
Specimen Location:	Camera port, waterwall
Specimen Orientation:	Vertical and slanted, S-shaped
Years in Service:	25
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	2000 psi (13.8 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter
Fuel:	Ground coal

Visual examinations disclosed a thickened patch of hard corrosion products adjacent to one bend (Fig. 4.7). Perforation of the wall had not occurred, but transverse cross sections cut through the site revealed substantial metal loss (Fig. 4.8).

The gouging was caused by sodium hydroxide that concentrated to corrosive levels along the site of a stable steam blanket, or perhaps at an isolated site of thermally insulating deposits. Previous failures of this type had not occurred in this region of the boiler. The boiler had been cleaned 4 years previously with a chelant and was in peaking service. Closer control over the water-treatment program might help prevent this type of problem in the future.

Figure 4.7 Patch of hard iron oxides on internal surface.

Figure 4.8 Cratered region beneath patch of iron oxides.

CASE HISTORY 4.3

Industry: Utility
Specimen Location: Bottom slag-screen tube
Specimen Orientation: 15° slope
Water-Treatment Program: Coordinated phosphate
Drum Pressure: 2200 psi (15.2 MPa)
Tube Specifications: 3 in. (7.6 cm) outer diameter

A growing number of small leaks were occurring in lower slag-screen tubes of this boiler. One of the leaking tubes was removed for examination.

Figure 4.9 illustrates the appearance of the internal surface in the area of leakage. A small perforation of this rifled tube was observed in the center of a large, elliptical area of metal loss (Fig. 4.10). This area has a smooth, rolling metal-surface contour covered with a thick, irregular mound of coarsely stratified iron oxides. The rest of the internal surface had suffered no metal loss.

Since deposits were not present and evidence of a waterline was not observed, it can be assumed that concentration of the caustic material was caused by highly localized nonnucleate boiling (DNB). The rifling of the internal surface is designed to induce swirling of the water to prevent nonnucleate boiling and steam/water phase stratification. It is surprising, therefore, to find severe caustic gouging in this tube design.

However, this boiler was idle on weekends. It is possible that highly localized nonnucleate boiling may have occurred during start-up, before normal boiler-water circulation was fully established.

Figure 4.9 Thick, irregular mound of hard iron oxides covering perforation.

Figure 4.10 Perforation at bottom of crater.

CASE HISTORY 4.4

Industry:	Chemical process industry, ammonia plant
Boiler Type:	Heat-recovery boiler
Specimen Location:	Bottom of U-tube bundle
Specimen Orientation:	Horizontal on bottom, curving to vertical
Years in Service:	8
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	1500 psi (10.3 MPa)
Tube Specifications:	¾ in. (1.9 cm) outer diameter
Heat Source:	Reformer gas

A massive longitudinal perforation was evident on this tube section. The failure resulted from wall thinning on the internal surface. Metal loss was localized to the top of the tube and the area of metal loss was approximately 19 in. (48.3 cm) long (Fig. 4.11).

Examination revealed a distinct groove along the top of the internal surface; this groove diminished gradually in both depth and width as the tube assumed a vertical orientation. Vertical surfaces were not corroded. The groove surface was very smooth, slightly rolling in contour, and covered with a uniform coating of black iron oxide. The surface at the perimeter of the groove was marked by a dense population of deep, hemispherical pits that

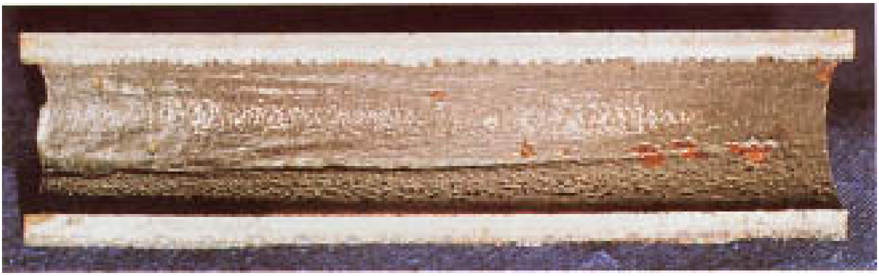

Figure 4.11 Groove approximately 14 in. (35.6 cm) from perforation.

existed in a distinct band along the sides and at each end of the groove (Fig. 4.12).

The grooving resulted from the concentration of sodium hydroxide due to steam accumulation and channeling along the upper horizontal and slanted regions of the internal surfaces. In addition to the important contribution of the tube's horizontal and slanted orientation, the accumulation of steam resulted from a condition of either excessive heat input in this region or impaired coolant flow through these tubes. This problem might be corrected by reducing heat input in this part of the boiler or by increasing water velocity through these tubes.

These types of failures have also been prevented through the use of rifled tubes. Closer control of the chemical program for the boiler water also might eliminate this type of failure.

Figure 4.12 Band of hemispherical pits adjacent to groove. (Magnification: 6.5X.)

Figure 4.13 Grooved window section cut from inner bend.

CASE HISTORY 4.5

Industry:	Sugar
Specimen Location:	Top of riser tube near entrance into steam drum
Specimen Orientation:	Slanted
Water-Treatment Program:	Polymer
Drum Pressure:	450 psi (3.1 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter
Fuel:	No. 6 fuel oil

Visual examinations revealed a longitudinal groove on the internal surface along the top of the tube (Fig. 4.13). Perforation had not occurred, but as much as 60% of the tube wall had been corroded.

The entire top side of the internal surface exhibited shallow metal loss in a distinct band (Fig. 4.14), which narrowed and ended in a "spear point" near the end of the tube in the steam drum. Sparkling black crystals of magnetite were present in and around the groove. A total of six adjacent tubes had been similarly affected.

Steam channeling along the top of the slanted section led to concentration of sodium hydroxide. Steam channeling may indicate localized or general excessive heat input. If appropriate alteration of operating parameters does not eliminate the problem, the use of rifled tubes may be effective.

The affected boiler is operated continuously during 100 to 150 days of campaign operation twice per year. The boiler is not operated during the intervening period.

Figure 4.14 Internal surface showing wasted metal.