Chapter

14

Hydrogen Damage

Locations

This form of deterioration is a direct result of electrochemical corrosion reactions in which hydrogen in the atomic form is liberated.* It is typically confined to internal surfaces of water-carrying tubes that are actively corroding.

Generally, hydrogen damage is confined to water-cooled tubes. Damage usually occurs in regions of high heat flux; beneath heavy deposits; in slanted or horizontal tubes; and in heat-transfer regions at or adjacent to backing rings at welds, or near other devices that disrupt flow. Experience has shown that hydrogen damage rarely occurs in boilers operating below 1000 psi (6.9 MPa).

General Description

Hydrogen damage may occur where corrosion reactions result in the production of atomic hydrogen. Damage may result from a high-pH corrosion reaction or from a low-pH corrosion reaction. Damage resulting from a high-pH corrosion reaction is simply caustic corrosion. (Refer to Chap. 4, "Caustic Corrosion.")

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*"Hydrogen in the atomic form" refers to uncombined atoms of hydrogen (H) as contrasted with molecules of hydrogen (H_2).

Concentrated sodium hydroxide dissolves the magnetic iron oxide according to the following reaction:

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

With the protective covering destroyed, water is then able to react directly with iron to evolve atomic hydrogen:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H\uparrow$$

The sodium hydroxide itself may also react with the iron to produce hydrogen:

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + 2H\uparrow$$

If atomic hydrogen is liberated, it is capable of diffusing into the steel. Some of this diffused atomic hydrogen will combine at grain boundaries or inclusions in the metal to produce molecular hydrogen, or will react with iron carbides in the metal to produce methane.

$$Fe_3C + 4H \rightarrow CH_4 + 3Fe$$

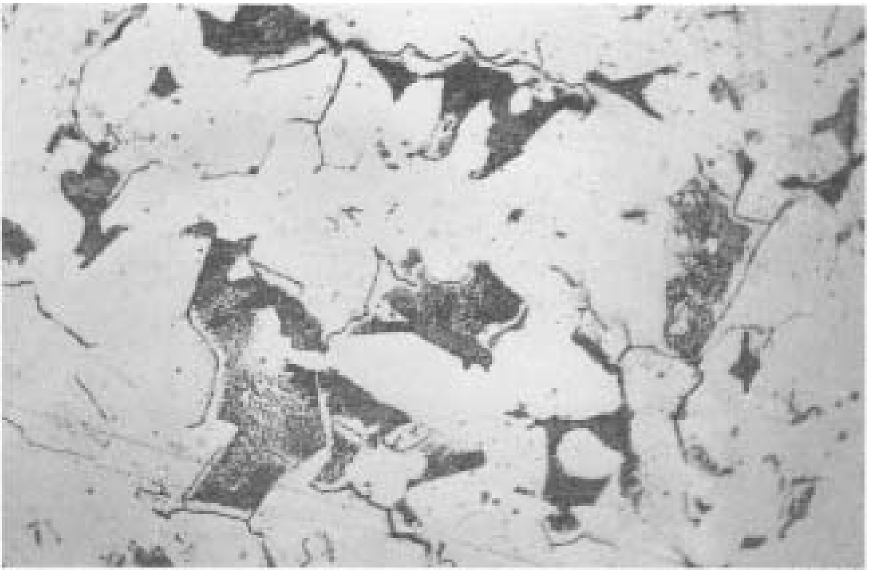

Figure 14.1 Discontinuous intergranular microcracks resulting from methane formation in the grain boundaries. Note decarburization of adjacent pearlite colonies (dark islands). (Magnification: 500X.)

Since neither molecular hydrogen nor methane is capable of diffusing through the steel, these gases accumulate, primarily at grain boundaries. Eventually, gas pressures will cause separation of the metal at its grain boundaries, producing discontinuous intergranular microcracks (Fig. 14.1). As microcracks accumulate, tube strength diminishes until stresses imposed by boiler pressure exceed the tensile strength of the remaining, intact metal. At this point a thick-walled, longitudinal burst may occur (Fig. 14.2). Depending on the extent of hydrogen damage, a large, rectangular section of the wall frequently will be blown out, producing a gaping hole (Fig. 14.3).

Figure 14.2 Thick-walled burst resulting from hydrogen damage. Note areas of gouging adjacent to burst on internal surface. *(Courtesy of Electric Power Research Institute.)*

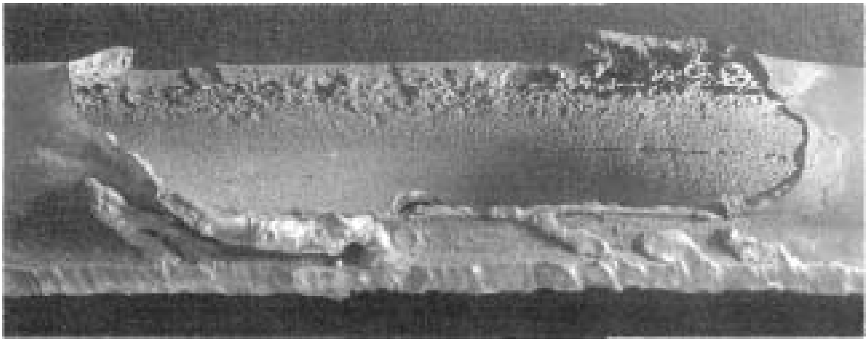

Figure 14.3 Large wall section blown out of a hydrogen-damaged tube from a 2075-psi (14.3-MPa) boiler. Note zone of gouging along fracture line. *(Courtesy of National Association of Corrosion Engineers.)*

Hydrogen damage may also result from a low-pH corrosion reaction in an operating boiler. (Refer to Chap. 6, "Low-pH Corrosion during Service.") Atomic hydrogen may be liberated during corrosion resulting from local low-pH conditions. Atomic hydrogen is capable of diffusing into the metal and reacting to form molecular hydrogen or methane, as described above. Hydrogen damage resulting from exposure to low-pH conditions is mechanistically and physically identical to that resulting from high-pH conditions. The difference is merely the source of the atomic hydrogen.

Critical Factors

The critical factors governing hydrogen damage resulting from high-pH corrosion are identical to those outlined for caustic gouging in Chap. 4, "Caustic Corrosion." The critical factors governing hydrogen damage resulting from low-pH corrosion are identical to those outlined for on-line acid corrosion in Chap. 6, "Low-pH Corrosion during Service."

Identification

It is generally not possible to visually identify hydrogen damage prior to failure. In boilers operating at more than 1000 psi (6.9 MPa), areas that have sustained either high-pH or low-pH corrosion should be considered suspect.

Generally, hydrogen damage is difficult to detect by nondestructive means, although sophisticated ultrasonic techniques have been developed to reveal hydrogen-damaged metal. Ultrasonic thickness checks may disclose corroded areas that should be considered suspect.

Gouging and hydrogen damage resulting from low-pH conditions may be distinguished from damage resulting from high-pH conditions by a consideration of the boiler-water chemistry and the chemistry of the probable sources of contamination. For example, a common source of contamination of boiler water is condenser in-leakage. The source of the cooling water determines whether the in-leakage is acid-producing or base-producing. Fresh water from lakes and rivers usually provides dissolved solids that hydrolyze in the boiler-water environment to form a high-pH substance, such as sodium hydroxide. In contrast, seawater and water from recirculating cooling-water systems incorporating cooling towers may contain dissolved solids that hydrolyze to form acidic solutions.

Elimination

Two critical factors govern susceptibility to hydrogen damage. These are the availability of high- or low-pH substances, and a mechanism of concentration. Both must be present simultaneously for hydrogen damage to occur.

To eliminate the availability of high- or low-pH substances, the following steps should be taken:

Reduce the amount of available free sodium hydroxide. This can be done in the case of hydrogen damage caused by high pH.

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

Prevent condenser in-leakage. Because of the powerful concentration mechanisms that may operate in a boiler, in-leakage of only a few parts per million of contaminants may be sufficient to cause localized corrosion and hydrogen damage.

Prevent contamination of steam and condensate by process streams.

Preventing localized concentration of corrosive substances is the most effective means of avoiding hydrogen damage. It is also the most difficult to achieve. Preventing departure from nucleate boiling (DNB), excessive water-side deposition, and the creation of waterlines in tubes may help prevent localized concentration of corrosive substances.

Prevent departure from nucleate boiling. Preventing DNB usually requires the elimination of hot spots, which is accomplished by controlling the boiler's operating parameters. Hot spots may be caused by excessive overfiring or underfiring, misadjusted burners, change of fuel, gas channeling, and excessive blowdown.

Prevent excessive water-side depositions. To prevent excessive water-side deposition, tube sampling on a periodic basis (usually annually) may be performed to measure 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 waterline formation. 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. When load is reduced and pressure remains constant, water velocity in boiler tubes is reduced to a fraction of its full-load value. If it becomes low enough, steam/water stratification occurs and creates stable or metastable waterlines.

Cautions

Hydrogen damage typically produces thick-walled ruptures. Other failure mechanisms producing thick-walled ruptures include stress-corrosion cracking, corrosion fatigue, stress rupture, and, in some rare cases, severe overheating. It may be difficult to visually distinguish ruptures caused by hydrogen damage from other ruptures, although certain features may serve as an aid.

For example, hydrogen damage is almost always associated with metal gouging. (Note cautions listed in Chaps. 4 and 6.) The other failure modes (with the possible exception of corrosion fatigue, which frequently initiates at discrete pits) are not typically associated with gross corrosion.

Tube failures in hydrogen-damaged metal are often manifested as a blowout of a rectangular "window" of the tube wall. This is not a common feature of the other failure modes.

A definitive diagnosis of hydrogen damage may require a formal metallographic examination.

Related Problems

See also Chap. 2, "Long-Term Overheating"; Chap. 3, "Short-Term Overheating"; Chap. 4, "Caustic Corrosion"; Chap. 6, "Low-pH Corrosion during Service"; Chap. 15, "Corrosion-Fatigue Cracking"; and Chap. 16, "Stress-Corrosion Cracking."

CASE HISTORY 14.1

Industry:	Utility
Specimen Location:	Nose section
Specimen Orientation:	Slanted
Years in Service:	25
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	2075 psi (14.3 MPa)
Tube Specifications:	2 in. (5.1 cm) outer diameter

The boiler from which the section illustrated in Fig. 14.3 was taken is a forced-circulation unit that produces 2½ million pounds (1,134,000 kilograms) of steam per hour. The boiler had been in peaking service for 2 years.

Failures were recurrent in the nose section and roof tubes. An acid cleaning of the boiler was conducted. The failure shown in Fig. 14.3 is one of several that occurred after the acid cleaning.

Note the large, rectangular opening remaining after a section of the tube wall was literally blown out. Fracture edges are thick, blunt, and have an irregular contour. Numerous small, secondary cracks are present along the fracture edges.

Close examination of the illustration reveals internal wall thinning along the fracture surface in the form of intersecting patches of shallow metal loss. In places, the corroded regions are covered with a thick layer of hard, black iron oxide. Where this layer is absent, deep longitudinal cracks can be observed.

Examinations of the microstructure in the fractured region reveal numerous discontinuous intergranular microcracks. Thermal alteration of the microstructure from overheating has not occurred. Iron oxides covering corroded regions of the internal surface are slightly stratified.

The severe hydrogen damage observed in this tube resulted in the blowout of a large section of tube wall. Microstructural evidence (stratification of the iron oxides) suggests that hydrogen damage resulted when the boiler water was contaminated with acid-producing salts (such as chlorides) from condenser in-leakage.

CASE HISTORY 14.2

Industry: Utility
Specimen Location: Waterwall
Specimen Orientation: Vertical
Years in Service: 17
Water-Treatment Program: Congruent control
Drum Pressure: 2100 psi (14.5 MPa)
Tube Specifications: 2½ in. (6.3 cm) outer diameter

The failure shown in Fig. 14.2 is the last in a series of four similar failures that were localized in a region above the burners. Note the thick, blunt fracture edge, as well as the shallow gouging along the internal surface. The internal surface was free of deposits.

Microstructural examinations revealed the discontinuous, randomly oriented microcracks directly beneath the corroded regions that are typical of hydrogen damage. Thermal alteration of the microstructure from overheating had not occurred. The iron oxides covering the corroded sites were highly stratified.

Records indicated that condenser in-leakage of low-level chloride salts had induced a depression of boiler-water pH. The presence of the acid-producing salts, coupled with DNB at the rupture site, caused this failure.

CASE HISTORY 14.3

Industry: Utility
Specimen Location: Waterwall
Specimen Orientation: Vertical
Years in Service: 2
Water-Treatment Program: Coordinated phosphate
Tube Specifications: 2½ in. (6.3 cm) outer diameter

Numerous hydrogen-damage failures caused by caustic corrosion necessitated a major boiler overhaul and significant changes to the water chemistry. A coordinated phosphate program replaced a low-solids, free-alkalinity program. The failure illustrated in Fig. 14.4 occurred in a tube that had been replaced at the time this change in water chemistry occurred.

The failed tube exhibits a thick-walled rupture through a distinct area of gouging on the internal surface. The rupture is immediately downstream of a circumferential weld that protrudes on the internal surface.

Microstructural examinations reveal no thermal alteration of the micro-

Figure 14.4 Rupture resulting from hydrogen damage. Note proximity of failure to circumferential weld. *(Courtesy of Electric Power Research Institute.)*

structure as a consequence of overheating. However, fine discontinuous intergranular microcracks are present in the tube wall adjacent to gouged regions. Gouged regions are covered with thick, stratified layers of dense iron oxide.

Highly localized concentration of a corrosive substance on the metal surface caused gouging and hydrogen damage. Concentration of such substances occurred during DNB, which resulted from disrupted water flow past the protruding circumferential weld. The stratified character of the iron oxides that cover the gouged regions indicates that gouging and hydrogen damage were caused by a low-pH environment that resulted from the concentration of acid-producing salts.

CASE HISTORY 14.4

Industry:	Utility
Specimen Location:	Platen tube
Years in Service:	26
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	2080 psi (14.3 MPa)
Tube Specifications:	3¼ in. (8.3 cm) outer diameter

The massive failure illustrated in Figs. 6.3 and 6.4 (page 87) was the first tube failure to have occurred at this station. The failure occurred 6 months after an acid cleaning of the boiler.

The thick-walled, longitudinal rupture is confined to the zone of corrosion, while the remainder of the internal surface is smooth and uncorroded.

Microstructural examinations revealed no thermal deterioration of the microstructure. A population of discontinuous intergranular microcracks were present in the tube wall immediately below the corroded zone.

The visual and microstructural appearance of the tube revealed that the failure resulted from hydrogen damage caused by exposure to a low-pH substance. The exact source of the substance and mode of concentration is uncertain. Since platen regions of a boiler may be difficult to rinse following an acid cleaning, it is possible that unneutralized acid remaining beneath deposits reacted with the tube metal during boiler operation. The hydrogen damage that was responsible for this failure occurs only during boiler operation.

CASE HISTORY 14.5

Industry:	Utility
Specimen Location:	Nose slope, waterwall
Specimen Orientation:	45°
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

The thick-walled rupture shown in Fig. 14.5 is one of numerous similar failures recurring in both the nose-arch section and roof tubes, requiring this area of the boiler to be rebuilt. The boiler is in peaking service.

The rupture coincides with a distinct zone of deep metal loss on the internal surface (Fig. 14.6). The wavelike contour of the corroded region is covered with black iron oxide.

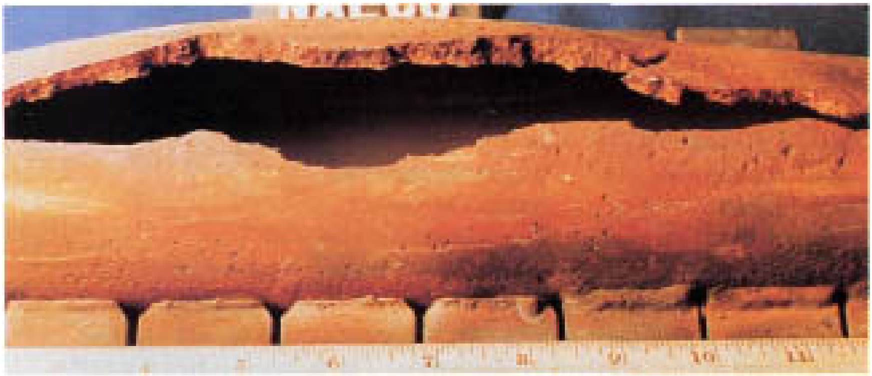

Figure 14.5 Thick-walled rupture.

Examination of the microstructure revealed no thermal alteration. Numerous randomly oriented intergranular microcracks were present in the tube wall just below the corroded region.

Localized DNB resulted in concentration of sodium hydroxide, which caused deep caustic gouging at this site. The hydrogen damage and resulting fracture were a direct consequence of the caustic gouging.

Figure 14.6 Smooth, wavelike contours of internal surface resulting from caustic gouging.