Chapter 7

Low-pH Corrosion during Acid Cleaning

Locations

Corrosion of the internal surfaces of a boiler that results from low-pH exposure may occur during acid cleaning if proper procedures are not followed. One of the first areas to be affected is the tube ends inside the mud and steam drums. Hand-hole covers, drum manholes, and shell welds may also be affected. Heat-transfer surfaces (Fig. 7.1) and weldments (Fig. 7.2) may experience vigorous attack. Shielded regions within crevices, behind backing rings, and under remaining deposits may prevent proper neutralization of the cleaning acid. This results in vigorous localized attack of the metal once the boiler is returned to service. In general, any surface exposed to acid is susceptible (Fig. 7.3).

General Description

Attack of any metal surface of a boiler by strong acid is generally unmistakable. The surface usually has a rough or jagged appearance, depending on the severity of the attack (Figs. 7.1 and 7.4). A close examination will disclose discrete pits, which are frequently undercut. On boiler tubes, the pits will frequently be aligned longitudinally along the tube wall (Fig. 7.1).

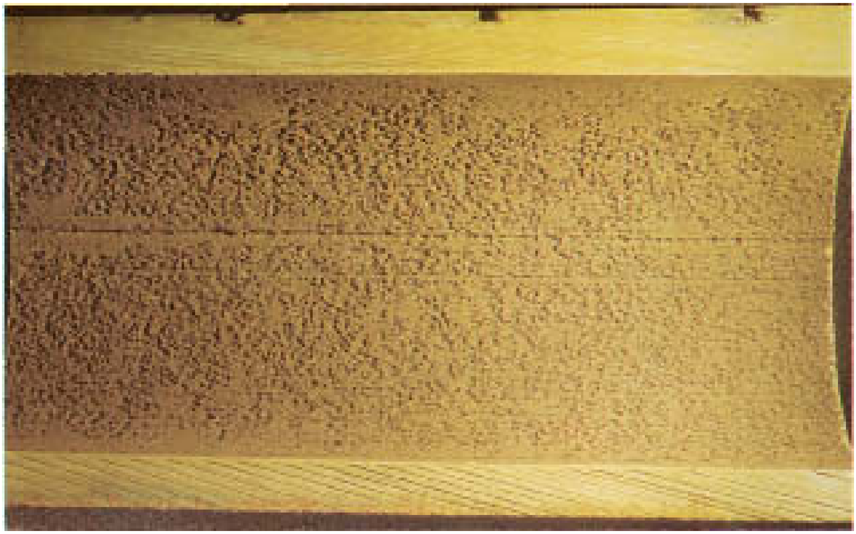

Figure 7.1 Acid corrosion on the internal surface of a wall tube. *(Courtesy of Electric Power Research Institute.)*

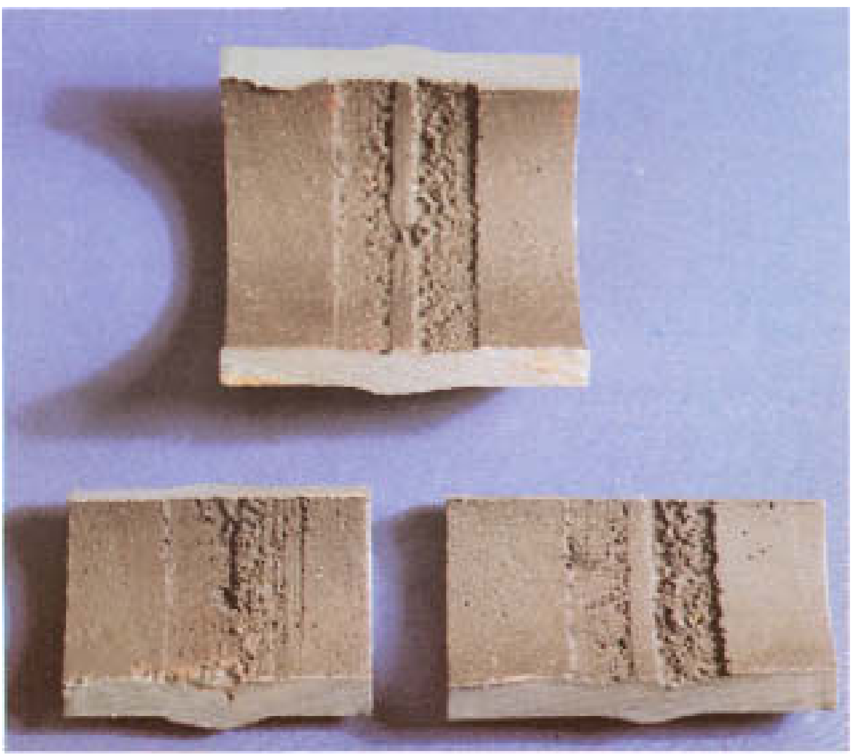

Figure 7.2 Acid corrosion at weld.

Figure 7.3 Acid corrosion of attachment hardware.

Figure 7.4 Jaggedness associated with severe acid corrosion. *(Courtesy of Electric Power Research Institute.)*

Corrosion of steel by acids is a natural consequence of steel's thermodynamic instability in these environments. Steel will corrode spontaneously in most acids. During the corrosion reaction, iron displaces hydrogen from solution. That is, the iron is oxidized and iron ions go into solution. Hydrogen ions are reduced and form hydrogen bubbles at the metal surface.

$$Fe + 2H^+ + Cl^- \rightarrow H_2\uparrow + Fe^{2+} + Cl^-$$

To stifle this corrosion process, inhibitors are added to acid-cleaning solutions used in boilers.

Critical Factors

Uncontrolled acid corrosion of a boiler during cleaning generally results from an unanticipated and unintentional deviation from standard conditions or standard practice. Many deviations are possible and may include events such as thermally induced breakdown of the inhibitor, inappropriate selection of cleaning agent or cleaning strength, excessive exposure times, excessive exposure temperatures, and failure to neutralize completely.

Identification

Simple visual examinations are generally adequate to identify acid corrosion. Attack generally can first be observed at tube ends in mud and steam drums, at ends of sheet or plate steel, and at ends of bolts. All areas of the boiler may not be affected to the same degree. Stressed metal, welded joints, crevices, and other shielded regions may suffer more intense damage. Damage assessment in visually inaccessible areas may require either nondestructive testing techniques, such as ultrasonic testing, or removal of a tube section.

Elimination

Mitigation of low-pH corrosion of boiler equipment during acid cleaning requires close monitoring of the entire cleaning procedure. The following are merely examples of the various operational parameters that must be monitored and evaluated during the procedure.

Deposit-weight determinations. Appropriate selection of several tubes for deposit-weight measurements will aid in determination of proper acid strength, exposure time, and total quantity of acid required to adequately clean the boiler.

Deposit analyses. Deposit analyses will help in determination of appropriate cleaning agents and the sequence in which the agents should be used.

Temperature of cleaning solution. Both the solution temperature and the metal temperature should be safely below the thermal breakdown point of the inhibitor.

Monitoring. Iron content, copper content, and cleaning-solution strength should be monitored at periodic intervals during the boiler cleaning. Chemistry of neutralizer should be monitored following the boiler's exposure to the acid.

Visual inspection. Inspection of tubes, mud drums, and steam drums should follow cleaning.

Cautions

Vigorous oxygen pitting and cavitation damage have been mistaken for attack by strong acid. Generally, proper distinction can be made by observing that attack by strong acid generally affects all exposed surfaces. Oxygen corrosion tends to occur in specific areas, such as the economizer, return bends in the superheater, or perhaps along the waterline in the steam drum. Cavitation damage also tends to be location-specific, and most commonly affects pump impellers. Certain forms of chelant corrosion may resemble acid corrosion, but again, chelant corrosion tends to be specific to steam drum internals.

Related Problems

See also Chap. 5, "Chelant Corrosion"; Chap. 8, "Oxygen Corrosion"; and Chap. 18, "Cavitation."

CASE HISTORY 7.1

Industry:	Utility
Specimen Location:	Wall tubes
Specimen Orientation:	Vertical
Years in Service:	30
Water-Treatment Program:	Phosphate and low-excess hydroxide
Drum Pressure:	875 psi (6.0 MPa)
Tube Specifications:	2½ in. (6.3 cm) outer diameter
Cleaning Solution:	Mineral acid

Following an acid cleaning of the boiler, the damage apparent in Figs. 7.5 and 7.6 was observed. Close visual examinations of these tubes revealed very fine, discontinuous fissures running longitudinally down the internal surfaces. These fissures, which appeared to coincide with a series of faint mandrel marks, were deeper at the end that had been rolled into the drum. The tube illustrated in Fig. 7.6 also shows deep transverse fissuring where it had been rolled into the drum. Examination of cross-sectional profiles of tube surfaces revealed they were jagged, undercut, and free of normally present iron oxides.

Attack by strong mineral acid is responsible for the delineation and deepening of mandrel marks running down the bore of the tube, as well as for the development of deep fissures near the end of the tubes that had been rolled into the drum. The delineation and deepening of the mandrel marks is associated with residual stresses in the metal at these sites from the tube-fabrication process. The presence of deep fissures of various orientations at the ends rolled into the drums is associated with residual stresses resulting from the tube-rolling process. Strong mineral acid characteristically attacks

Figure 7.5 Longitudinal fissures near rolled end.

Figure 7.6 Transverse fissures near rolled end.

stressed metal areas more aggressively than unstressed areas; this is because of the greater energy content of metal associated with residual stresses.

CASE HISTORY 7.2

Industry:	Utility
Specimen Location:	Wall tube
Specimen Orientation:	Vertical
Years in Service:	15
Water-Treatment Program:	Congruent control
Drum Pressure:	1960 psi (13.5 MPa)
Tube Specifications:	2½ in. (6.3 cm) outer diameter
Cleaning Solution:	Citric acid

Attack of metal surfaces by organic acids generally differs significantly from that produced by strong mineral acids. Given equivalent exposures, organic acids generally cause less corrosion. In addition, surface features of metals subject to excessive exposure to organic acids are typically less jagged and less undercut than those of metals subject to excessive exposure to strong mineral acids.

Attack by critic acid is illustrated in Fig. 7.7. Visually, the surface has an etched, bright metallic appearance. Close examination reveals irregular islands of uncorroded metal, which, in this case, stand 0.005 in. (0.12 mm) above the surrounding corroded surface. Essentially the entire internal

Figure 7.7 Appearance of attack by citric acid. (Magnification: 7.5X.)

surface, both hot and cold sides, was similarly affected. This condition is consistent with attack during acid cleaning.

CASE HISTORY 7.3

Industry:	Utility
Specimen Location:	Wall tube
Specimen Orientation:	Vertical
Years in Service:	30
Water-Treatment Program:	Congruent control
Drum Pressure:	1500 psi (10.3 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter
Cleaning Solution:	Mineral acid

Figures 7.2 and 7.8 illustrate attack of the internal surfaces of wall tubes opposite external circumferential welds. Cross-sectional profiles of the internal surface in these attacked zones revealed undercutting and jaggedness. Residual stresses remaining from the weld make these sites subject to preferential corrosion when exposed to strong acid.

Figure 7.8 Acid corrosion at welds.

CASE HISTORY 7.4

Industry:	Utility
Specimen Location:	Side-wall tube
Specimen Orientation:	Vertical
Years in Service:	30
Water-Treatment Program:	Congruent phosphate
Control Drum Pressure:	1500 psi (10.3 MPa)
Tube Specifications:	3 in. (7.6 cm) outer diameter
Cleaning Solution:	Mineral acid

A number of fairly deep, overlapping pits were observed in a circumferential zone along the internal surface opposite circumferential welds on the external surfaces of the tubes (Fig. 7.9). Other areas of attack were noted in regions where welds were not present (Fig. 7.10). Attack in these areas was more pronounced along the tube seam.

Deposits overlying the attack sites reveal that the corrosion occurred in the past, probably during the last acid cleaning of the boiler.

Preferential attack of welds may be due to residual stresses associated with the weld, or to pores or crevices existing in the weld zone. Preferential attack of a tube seam may be due to segregated impurities in the seam, or to a crevice resulting from incomplete fusion of the seam.

Figure 7.9 Acid corrosion at weld.

Figure 7.10 Acid corrosion along internal surface. (Magnification: 7.5X.)

CASE HISTORY 7.5

Industry:	Pulp and paper
Specimen Location:	Belly plate
Specimen Orientation:	Horizontal
Years in Service:	16
Water-Treatment Program:	Polymer
Drum Pressure:	600 psi (4.1 MPa)
Cleaning Solution:	Mineral acid

Visual examinations of belly-plate surfaces revealed shallow patches of irregular metal loss on all top and bottom surfaces. The sites of metal loss tended to be aligned in parallel rows. Figure 7.11 illustrates the appearance of the metal loss, although a thin coating of iron oxide tends to soften the normally sharp edges.

This case illustrates the importance of supporting observations in establishing low-pH corrosion as the cause of metal loss. Figure 7.11 lacks the classical, jagged, undercut surface profile normally associated with attack by a strong acid. However, the following additional observations strongly support the diagnosis:

- Alignment of attack sites in parallel rows oriented in the rolling direction of the steel from which the plate was fabricated
- Preferential attack of welds and tube ends in the steam drum
- Jagged, undercut, cross-sectional profiles of belly-plate surfaces apparent in metallographic examinations

Figure 7.11 Metal loss from strong acid. (Magnification: 7.5X.)

CASE HISTORY 7.6

Industry:	Pulp and paper
Specimen Location:	Screen tube
Specimen Orientation:	Vertical
Years in Service:	13
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	1250 psi (8.6 MPa)
Tube Specifications:	2¼ in. (5.7 cm) outer diameter
Cleaning Solution:	Mineral acid

A combination of welding defects in circumferential welds, and attack of the weld area by strong mineral acid over a series of five acid cleanings during a 13-year period, resulted in tube perforations. Perforations at the weld sites led to secondary failures of adjacent tubes by erosion caused by steam escaping at high velocity.

Close examination of the internal surfaces of the welds revealed highly localized areas of corrosion, which produced jagged, undercut surface contours typical of attack by strong mineral acid (Fig. 7.12).

Open crevices, pores, and pits in weld areas are sites where acid may survive neutralization steps following acid cleaning. Acid corrosion can enlarge and deepen these sites, resulting in eventual perforation of the tube wall at the weld.

Figure 7.12 Acid attack along weld on internal surface. (Magnification: 7.5x.)

CASE HISTORY 7.7

Industry:	Textile
Specimen Location:	Fire tube
Specimen Orientation:	Horizontal
Water-Treatment Program:	Phosphate
Drum Pressure:	100 psi (0.6895 MPa)
Tube Specifications:	2½ in. (6.3 cm) outer diameter
Cleaning Solution:	Mineral acid

Hydrotesting following acid cleaning of the boiler revealed several leaking tubes. Examination of one of the leaking tubes revealed profuse pitting (Figs. 7.13 and 7.14). External surfaces were covered with a film of brown iron oxides.

Although some pitting may have occurred as a result of excessively high oxygen levels in the boiler water during idle times, the primary mode of attack was insufficiently controlled exposure to strong mineral acid during acid cleaning. Note the large population of pit sites, the general deterioration, and the appearance of fine longitudinal fissures characteristic of attack by a strong acid (Fig. 7.13).

Figure 7.13 Acid corrosion on the external surface of a fire tube.

Figure 7.14 Close-up of external surface shown in Fig. 7.13.