Chapter

12

Cold-End Corrosion during Service

Locations

Cold-end corrosion will occur wherever the temperature of metal drops below the sulfuric acid dew point of the flue gas. Most problems caused by cold-end corrosion occur in relatively low temperature boiler components such as the economizer, air preheater, induced-draft fan, flue-gas scrubbers, and stack.

General Description

In most combustion systems, flue-gas temperatures can range from 3000°F (1650°C) in the flame to 250°F (121°C) or less at the stack. This temperature change can cause numerous chemical and physical changes in the components of the flue gas. Among the most troublesome changes is the reaction between water vapor and sulfur trioxide to form sulfuric acid.

As flue gas cools, vapor-phase sulfuric acid forms. If the sulfuric acid vapor contacts a relatively cool surface, it may condense as liquid sulfuric acid. The temperature at which sulfuric acid first condenses (sulfuric acid dew point) varies from 240 to 330°F (116 to 166°C) or higher, depending on sulfur trioxide and water-vapor concentrations in the flue gas. The corrosion resulting from condensation of sulfuric acid on metal surfaces is termed "cold-end corrosion" because it generally affects the cooler regions of the combustion system.

In general, the problem is associated with the combustion of fuel that contains sulfur or sulfur compounds. Sulfur in the fuel is oxidized to sulfur trioxide in the following sequence:

$$S + O_2 \rightarrow SO_2$$

A small fraction (1% to 3%) of the sulfur dioxide produced is additionally oxidized to sulfur trioxide by direct reaction with atomic oxygen in the flame:

$$SO_2 + O \rightarrow SO_3$$

Catalytic oxidation to SO_3 is also possible if ferric oxide, vanadium pentoxide, or nickel is present:

$$SO_2 + \tfrac{1}{2}O_2 + \text{catalyst} \rightarrow SO_3$$

The quantity of sulfur trioxide and moisture in the flue gas affects the temperature at which the dew point is reached. The graph in Fig. 12.1 illustrates the general relationship between sulfur trioxide concentration and dew point.

Corrosion may occur wherever metal temperatures are less than the

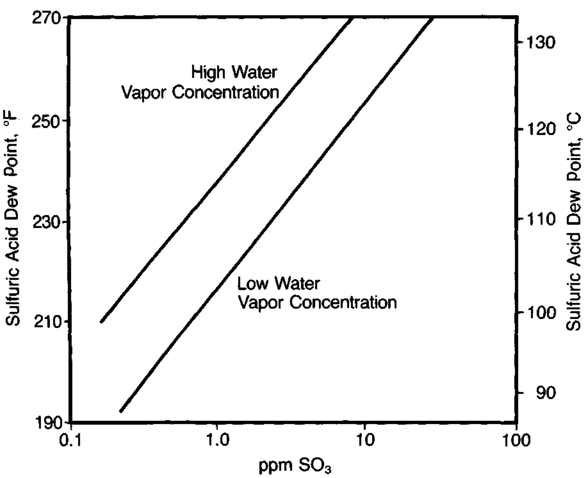

Figure 12.1 Relationship between SO_3 levels in flue gas and sulfuric acid dew point.

sulfuric acid dew point. Below this dew point, sulfuric acid forms on metal surfaces and corrodes the metal according to the following reaction:

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2\uparrow$$

Note that it is the temperature of the metal, not the temperature of the flue gas, that is critical. Even though the flue-gas temperature is well above the dew point, corrosion is a distinct possibility wherever metal temperatures are less than the dew point.

Critical Factors

The critical factors governing cold-end corrosion include the presence of corrosive quantities of sulfur trioxide, the presence of moisture in the flue gas, and the presence of metals whose surface temperature is below the sulfuric acid dew point.

The amount of sulfur trioxide produced increases with increases in the level of excess air, gas residence time, gas temperature, amount of catalyst present, and sulfur level in the fuel (Fig. 12.2).

The amount of moisture produced is dependent on many factors. Sources include moisture content in the fuel, fuel combustion, leaks in boiler tubes, and steam from soot blowing.

A metal whose surface temperature is below the sulfuric acid dew point is susceptible to cold-end corrosion. The dew point increases as the quantity of sulfur trioxide in the flue gas and the moisture content of the flue gas increase.

The severity of cold-end corrosion is most extreme with "sour" gaseous fuels, while it is less extreme with oil. Severity of corrosion is least with coal. The combined burning of sulfur- and vanadium-containing fuel oil

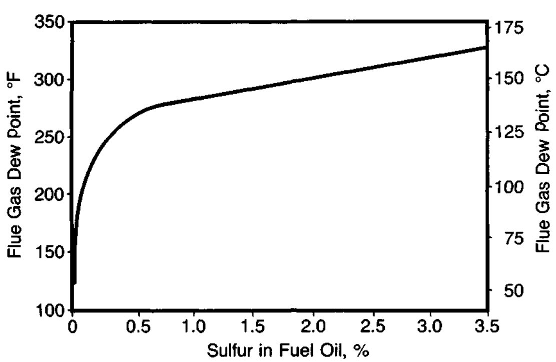

Figure 12.2 Relationship between the percentage of sulfur in fuel oil and flue-gas dew point.

with natural gas is worse than use of oil alone because of the high water-vapor content that results from burning of natural gas.

Identification

Cold-end corrosion frequently produces general, smooth, featureless metal loss. Rough, rust-colored surfaces also may be observed.

Elimination

Elimination of cold-end corrosion is achieved by gaining control of the critical factors that govern it. The critical factors include the presence of corrosive quantities of sulfur trioxide in flue gas, the presence of excessive quantities of moisture in the flue gas, and the presence of metals whose surface temperature is below the sulfuric acid dew point.

To eliminate the presence of corrosive quantities of sulfur trioxide in flue gas it is necessary to operate the boiler at or below 5% excess air to the burners, to minimize air infiltration, and to specify fuels with low sulfur content.

To eliminate the presence of excessive quantities of moisture in the flue gas, it is necessary to specify fuel with low moisture content, to prevent tube leaks, and to reduce the amount of soot blowing.

Substantial design changes are often required to eliminate metals with surface temperatures below the sulfuric acid dew point. These design changes are beyond the scope of this manual.

In boilers equipped with multiple air preheaters it is possible to isolate and perform an on-line washing of one of the preheaters.

Feeding of fuel additives and/or cold-end additives constitutes a chemical solution to this problem.

Cautions

Metal surfaces that have suffered cold-end corrosion may be covered with deposits and/or corrosion products, making visual identification difficult. In addition, cold-end corrosion typically produces smooth, uniform, featureless metal loss, such that the attacked surfaces closely resemble the original, unaffected surface contour. Thickness measurements using ultrasonic techniques serve as a nondestructive means of evaluation. Visual comparison of surface profiles and metal thicknesses on a section cut from the equipment may also reveal the occurrence of cold-end corrosion.

CASE HISTORY 12.1

Industry:	Pulp and paper
Specimen Location:	Economizer, recovery boiler
Specimen Orientation:	Vertical
Years in Service:	20
Drum Pressure:	600 psi (4.1 MPa)
Tube Specifications:	2½-in. (6.3 cm) outer diameter
Fuel:	Black liquor

Figure 12.3 is a close-up photograph of the external surface of an economizer tube that has sustained general corrosion. Note the pockmarked contour. Corrosion occurred in regions of the economizer where sulfuric acid condensed from the flue gas. Such condensation, if it occurs, generally affects the tubes at the end of the economizer where feedwater enters—i.e., the end where metal temperatures are lower.

Figure 12.3 Pockmarked contour of economizer tube exposed to condensed sulfuric acid. (Magnification: 7.5 X.)

CASE HISTORY 12.2

Industry:	Sugar
Specimen Location:	Economizer
Specimen Orientation:	Horizontal
Tube Specifications:	$1\frac{7}{8}$ in. (4.8 cm) outer diameter
Fuel:	No. 6 fuel oil (1.9% S)

The corrosion and perforations apparent in Fig. 12.4 represent a chronic problem in this boiler. The external surface, including fin surfaces, exhibited smooth, general metal loss. In many cases, severe corrosion along the attachment line had caused the fins to separate from the tube wall.

The deposits and corrosion products covering the corroded surfaces were analyzed by x-ray diffraction and identified as hydrated iron sulfate. The pH of a 1% slurry of the material was measured at 2.3. The corrosion was caused by condensation of sulfuric acid on the cold tube surfaces during boiler operation.

Figure 12.4 Corrosion and perforations of finned economizer tube resulting from exposure to condensed sulfuric acid. Note detachment of fins from tube wall.