Fire-Side Corrosion

Introduction

In simple terms, combustion involves the rapid reaction of oxygen with the basic chemical elements in fuels — carbon, hydrogen, and sulfur — with a consequent release of heat and the formation of combustion products (Fig. 9.1). "Foreign" material present in fuel forms the combustion by-product referred to as ash.

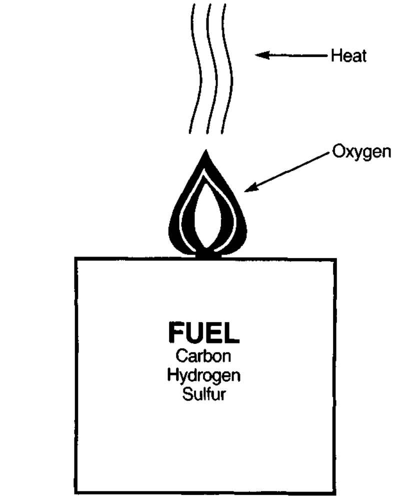

Figure 9.1 Combustion products resulting from burning of fuels.

Regardless of the original physical state of the fuel, combustion may convert fuel components to any or all of the three states of matter—solid, liquid, or gas. In a combustion device, the flue-gas temperature may range from 3000°F (1650°C) in the flame to 300°F (121°C) or less at the exhaust stack. As combustion products cool on their way to the exhaust stack, gaseous products may condense to liquids, and liquids may freeze to solids. This cooling may occur rapidly on heat-transfer surfaces that are cold relative to the flue gas, such as boiler and superheater tube walls.

In addition, combustion products rarely remain as individual oxides, but generally interact to form new families of compounds and complexes. At times, these new substances may have fusion temperatures that are lower than those of the substances from which they were formed. The presence of these liquid substances may be responsible for difficulties with fire-side corrosion.

Chapters 9 through 13 of this book discuss various types of fire-side corrosion.

Chapter

9

Oil-Ash Corrosion

Locations

Oil-ash corrosion is a high-temperature, liquid-phase corrosion phenomenon generally occurring where metal temperatures are in the range of 1100 to 1500°F (593 to 816°C). It is found in superheater and reheater sections of the boiler, especially utility boilers. It may affect the tubes, which are cooled, or it may affect support and attachment equipment, which operates at higher surface temperatures than the tubes.

General Description

Fire-side corrosion may become a problem when fuel supply or fuel type is changed. This change may result in the formation of an "aggressive" ash. Oil-ash corrosion occurs when molten slag containing vanadium compounds forms on the tube wall according to the following sequence:

1. Vanadium compounds and sodium compounds present in the fuel are oxidized in the flame to V_2O_5 and Na_2O.
2. Ash particles stick to metal surfaces, with Na_2O acting as a binding agent.
3. $V_2O_5 + Na_2O$ react on the metal surface, forming a liquid (eutectic).
4. The liquid formed fluxes the magnetite, exposing the underlying metal to rapid oxidation.

It is believed that corrosion occurs by catalytic oxidation of the metal by vanadium pentoxide (V_2O_5) or complex vanadates. The resulting rapid oxidation of the metal then reduces wall thickness, which, in turn, reduces load-carrying area. This reduction in load-carrying area results in an increase in stresses through the thinned region. The combined influence of increased stress level and high metal temperatures eventually results in failure by creep rupture.

Corrosion of superheater and reheater tubes due to slag having fusion temperatures in the 1100 to 1300°F (593 to 704°C) range was largely responsible for the deviation from the trend toward higher steam temperatures that occurred in the early 1960s. Practically all utility-boiler installations are now designed for maximum steam temperatures in the 1000 to 1025°F (538 to 551°C) range.

Critical Factors

A corrosive slag may develop when fuel oil that contains high levels of vanadium, sodium, or sulfur, or a combination of these elements, is used; when excessive amounts of excess air are available for the formation of V_2O_5; or when metal temperatures exceeding 1100°F (593°C) are achieved. As the temperature increases, the range of compositions of $Na_2O \cdot V_2O_5$ that forms liquids expands considerably (Fig. 9.2).

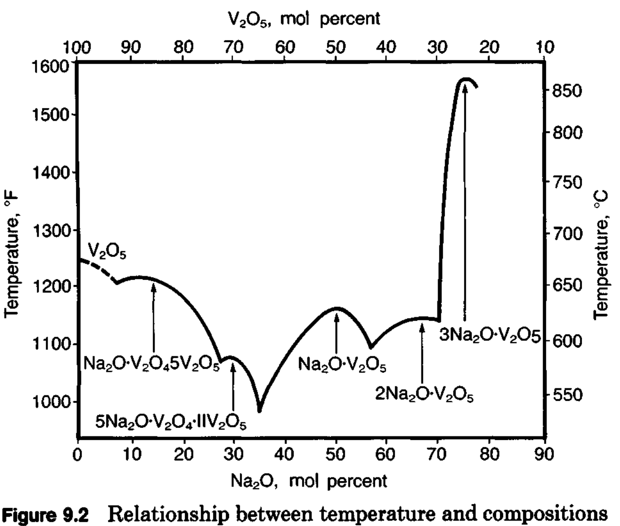

Figure 9.2 Relationship between temperature and compositions of liquid forms involving Na_2O and V_2O_5. *(Courtesy of William T. Reid,* External Corrosion and Deposits: Boilers and Gas Turbines, *American Elsevier, New York, 1971, p. 137.)*

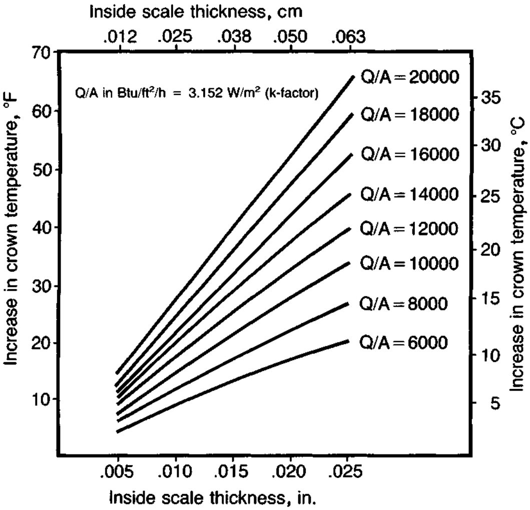

Figure 9.3 Relationship between increase in metal temperature and thickness of internal scale for steam-cooled tubes. *(Courtesy of John Wiley and Sons,* Metallurgical Failures in Fossil Fired Boilers, *by David N. French, New York, 1983.)*

Figure 9.3 indicates that as the thickness of internal scale increases, the metal temperature also increases, since the scale acts as thermal insulation. Hence, in older units, which may have established relatively thick layers of internal scale, the metal temperature will increase and may exceed temperatures at which sodium–vanadium complexes form liquids. If this occurs, sudden, unexpected problems with oil-ash corrosion may appear, even though operating parameters and fuel chemistry remain unchanged.

Identification

Figure 9.4 illustrates the appearance of oil-ash corrosion on a low-alloy steel tube. A section of a stainless steel reheater tube that has suffered oil-ash corrosion is illustrated in Fig. 9.5. Figure 9.6 illustrates the deterioration of a stainless steel tube at an attachment. The attachment, which protruded into the gas stream, acted as a heat-transfer fin, causing metal temperatures at its base to increase. Severe oil-ash corrosion resulted wherever the metal temperature exceeded 1100°F (593°C).

Figure 9.4 Wall thinning from oil-ash corrosion. Corrosion rates of 30 mil/y (0.76 mm/y) have been observed. *(Courtesy of Electric Power Research Institute.)*

Elimination

The first step in combating oil-ash corrosion is chemical analysis of both the fuel and ash to determine whether corrosive constituents are present. It is also important to know the fusion temperature of the ash. Annual surveys of tube-wall thickness using ultrasonic testing can give early warning of impending problems. If tube failure occurs, a wall-thickness survey can determine the extent and severity of the problem.

Elimination of oil-ash corrosion is accomplished by controlling the critical factors that govern it. First, if fuels containing very low quantities of vanadium, sodium, and sulfur cannot be specified, then recommendation of a fuel-treatment additive to prevent the formation of low-melting eutectics may be necessary. The use of magnesium compounds has proven to be

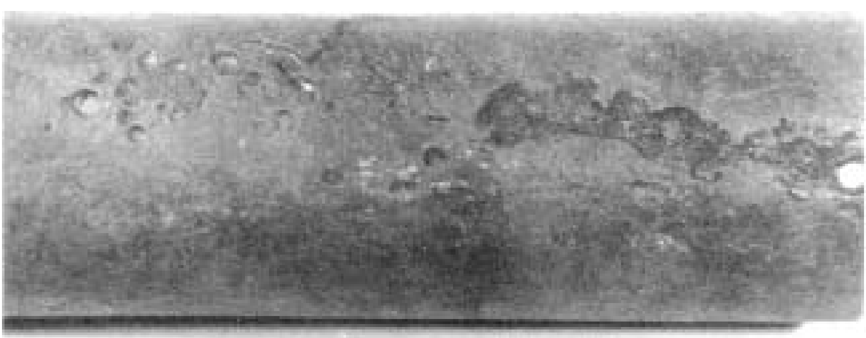

Figure 9.5 Oil-ash corrosion on stainless steel reheater tube. *(Courtesy of John Wiley and Sons,* Metallurgical Failures in Fossil Fired Boilers, *by David N. French, New York, 1983.)*

Figure 9.6 High-temperature corrosion at the base of an attachment (top of photograph) on a stainless steel reheater tube. *(Courtesy of Electric Power Research Institute.)*

economically successful in mitigating problems of oil-ash corrosion. Magnesium forms a complex with vanadium ($3MgO \cdot V_2O_5$) whose fusion temperature is significantly above that attained in most superheater and reheater sections. Second, the boiler should be fired with low excess air to retard V_2O_5 formation. Third, the superheater and reheater metals should be prevented from exceeding 1100°F (593°C). Boilers having drainable superheater and reheater sections should be chemically cleaned periodically to prevent excessive buildup of internal scale.