

View from the Penthouse



The DNFM Technical News Letter

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In an effort to improve air quality and reduce acidic emissions, power plant operators have been forced to change their combustion technology. Reduction in emissions of sulfur oxides (SO_x) have been achieved mainly by using lower-sulfur fuels. Reductions in nitrogen oxide (NO_x) levels have been achieved primarily by reducing combustion-flame temperatures. Of course some power plants have installed scrubbers to remove these harmful oxides.

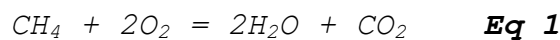
While some nitrogen oxides are present within the fuel in the form of nitrates, most NO_x comes from the reaction of atmospheric nitrogen and oxygen at combustion-flame temperatures. Under normal firing conditions, as the flame temperature increases, so does the formation of NO_x. Thus the simplest way to reduce combustion-formed NO_x is to reduce the flame temperature. The schemes for achieving this are to use off-stoichiometric or staged combustion firing. Primary air is mixed with the fuel and is less than required for complete combustion. Secondary air is added through over-fire air ports. Other schemes may use concentric ducts with the primary air port along the center and secondary air in a concentric ring displaced from the center by some distance. The intent is to burn the fuel in stages. The first stage combustion would burn the hydrogen to water vapor, and carbon to carbon monoxide. Later in the combustion sequence, the carbon monoxide would be burned completely to carbon dioxide. However, the formation of carbon monoxide leads to reducing atmospheres in the vicinity of the burners.

The advantage to this combustion technique is to reduce flame temperatures and thus prevent or at least reduce the formation of any nitrogen oxides. The drawback is to form reducing conditions in the vicinity of the burners. What may not be fully appreciated is the damage that these reducing conditions can do to stainless-steel burner components and pressure parts.

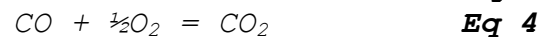
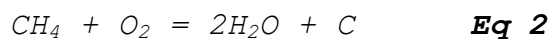
Carburization Corrosion of Stainless Steels and CSEFs

Burner parts of austenitic stainless steel, coal nozzles, gas burner rings, ignition tubes, coal spreaders, oil-burner tips and air nozzles all operate at high metal temperatures, temperatures in the neighborhood of perhaps 1500° to 1600°F. The use of austenitic stainless steel for these parts provides adequate oxidation and corrosion resistance at these elevated temperatures. However under reducing conditions, the corrosion rates of stainless steel and CSEFs are increased significantly due to carburization of these alloys.

Under fully oxidizing conditions of combustion, the fuel would be burned completely to water vapor and carbon dioxide. All fuels contain both hydrogen and carbon. To illustrate the principle consider methane. Complete combustion is as shown in *Equation 1*.



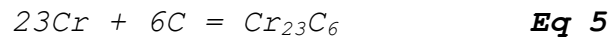
Usually a small amount of excess oxygen, perhaps 2% or so, is added to assure complete combustion to carbon dioxide (CO₂) and water (H₂O). Flame temperatures under these firing conditions would be in the neighborhood of 3000°F or higher, and the combustion would be said to be "stoichiometric". Staged combustion would reduce the amount of oxygen available in the primary flame so that the combustion would be accomplished in several steps, as shown in *Equations 2-4*.



Note that the final product is still water vapor and carbon dioxide but the carbon dioxide is formed in three steps. This is called delayed or staged combustion. The addition of over-fire air (OFA) and secondary over-fire air (SOFA) likely promote flame impingement and secondary combustion issues, resulting in localized overheating issues and higher furnace exit-gas temperature (FEGT). The rise in FEGT may lead to several issues such as plugging of vertical pendants with ash deposits, hotash corrosion, sagging and bowing of pendants, over tempering of creep-strength-enhanced ferritic steels, or reducing creep life of the superheater/reheater tubes and dissimilar-metal welds (DMWs). The advantage from a NO_x formation viewpoint is that flame temperatures are considerably lower and the formation of nitrogen oxides is considerably reduced. Note also, however, that in two stages of this combustion sequence, carbon (C) and carbon monoxide (CO), both reducing elements, are formed.

Carburization Corrosion of Stainless Steels and CSEFs

Austenitic stainless steels, similar to TP304H, and CSEFs, similar to T91, readily form carbides at pressure parts operating temperatures. The addition of carbon to a steel is called "carburization." The reaction of soot, unburned carbon, or carbon monoxide, with the surface of the steel, will form a chromium carbide by the reaction shown in **Equation 5**. The chromium carbide is quite complex and has the chemical composition of $Cr_{23}C_6$.



Either unburned carbon or carbon monoxide are available to carburize the surface of these burner components. The formation of these chromium carbides reduces the surface of the stainless/CSEFs *effective* chromium and thus reduces the corrosion and oxidation resistance. Stainless steels get their excellent resistance to high-temperature oxidation by the addition of more than 12% chromium. When the chromium content is reduced to below 12%, the oxidation resistance is more ordinary. Thus the formation of chromium carbides by the reaction of stainless steels with carbon monoxide or elemental carbon leads to a depletion of chromium along the surface of the steel. With the chromium content reduced to below 12%, the oxidation resistance falls and the result is rapid loss of material. Burner components can fail in only a few months rather than several years. The wastage occurs when there are reducing conditions inside the furnace, and iron sulfide scales form instead of protective oxides. These iron sulfide scales are more porous and less protective than oxides. Reducing conditions also promote carburization of CSEFs and stainless steels, see **Figures 1 and 2**, resulting in loss of corrosion resistance. Unburnt carbon and carbon monoxide are carriers of carbon to the steel surface under reducing conditions. Formation of chromium carbides along the grain boundaries and within the surface grains reduces the corrosion resistance of stainless steels and CSEFs.

In addition to the metallographic examination, a sulfur print can be prepared to determine the presence of reducing conditions at the tube surface. A sulfur print can be prepared using a piece of photographic paper dipped in a 2% aqueous sulfuric-acid solution, and the excess acid wiped off. The polished ring sections (Grit Size #60) are pressed onto the damp photographic paper for a few seconds and removed. The sulfuric acid reacts with metallic sulfides to form hydrogen sulfide gas (H_2S); the H_2S reacts with the silver salts on the photographic paper to form silver sulfide, which is dark black or brown.

Carburization Corrosion of Stainless Steels and CSEFs

As shown in **Figure 3**, a sulfur print was prepared on the ring section to determine the effects of reducing conditions on the tube wastage. The presence of iron sulfides on the tube surface is shown in **Figure 3**, resulting in severe tube wastage.

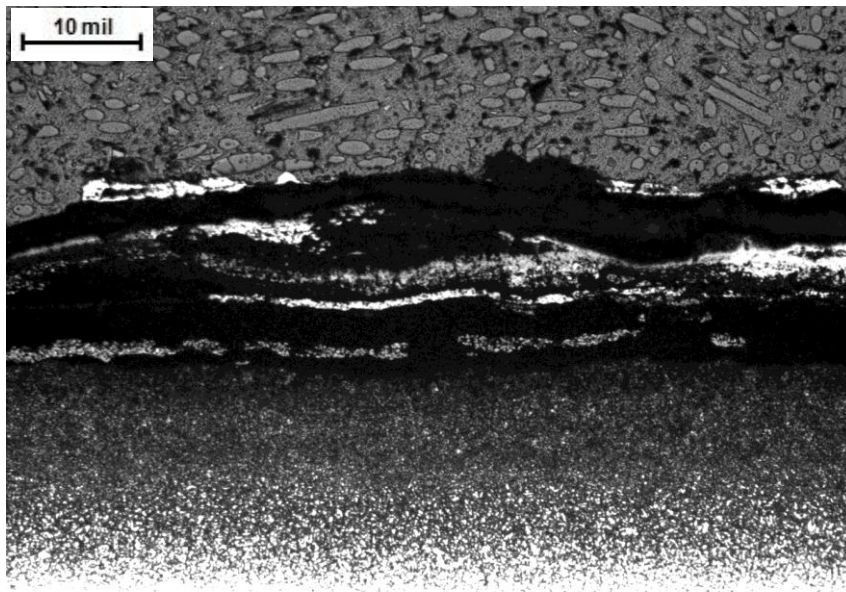


Figure 1. Carburized layer, T91 tube, OD, 63x

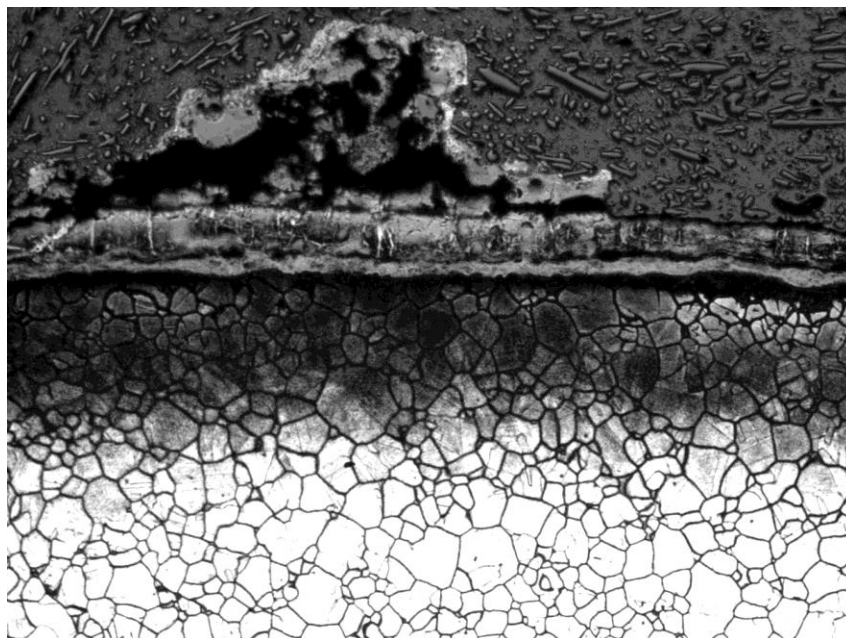


Figure 2. Carburization of TP304H stainless steel tube, OD, 63x

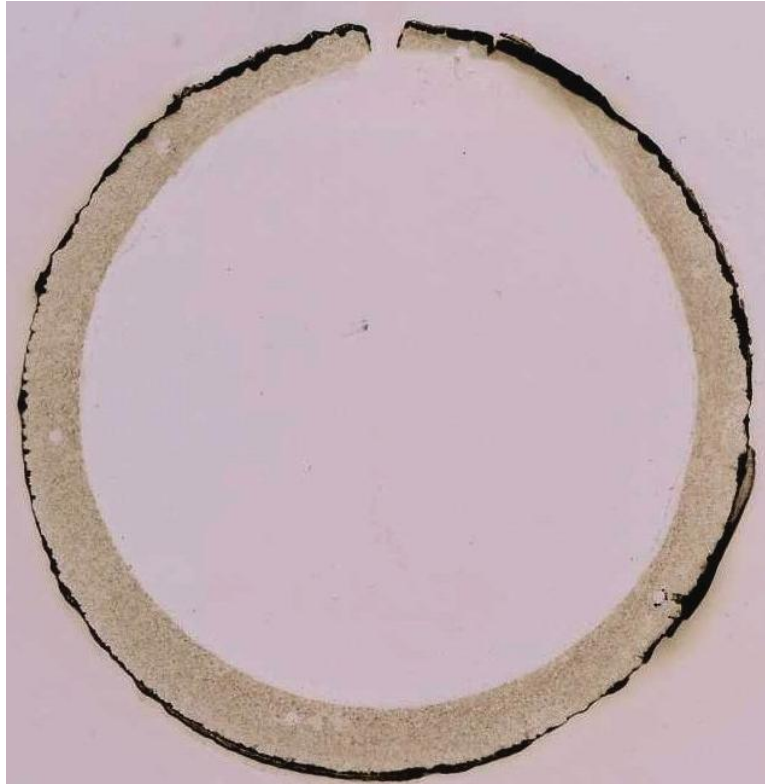


Figure 3. Iron sulfides on TP304H stainless steel tube, sulfur print, ~2x

In order to prevent this form of rapid degradation to burner components under staged-combustion conditions, alloys more resistant to carburization need to be used. Lowering secondary combustion reduces tube metal temperatures in the SH/RH circuits, which alleviates hot ash corrosion. Note that the secondary combustion issues are reduced by improving the coal finesse. Maintaining oxidizing conditions inside the furnace potentially eliminates the formation of porous iron sulfide scales instead of protective iron oxides. Wrong burner angles may result in localized reducing conditions. Therefore, burners should be adjusted per design to have the correct stoichiometric mixture. Installation of low-NOx burners in coal-fired boilers has resulted in accelerated water wall wastage. These low-NOx burners are expected to produce more H₂S, instead of SO₂ or SO₃, in the combustion gas; this promotes an increase in corrosion rates. Weld overlays of more corrosion-resistant alloys like Alloys 625 and 622 have been proven to be a long-term solution for fireside corrosion.