



The DNFM Technical News Letter

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Fireside corrosion remains a leading cause of failure in superheater and reheater tubes. Tubes affected by the fireside corrosion mechanism may lose as much as 15 mpy and in extreme cases even higher corrosion rates have been observed. Fireside corrosion occurs via two modes. In the first mode of corrosion, tube wastage occurs by the formation of low melting species, which dissolve the protective iron oxides on carbon or low alloy (Cr-Mo) steels. In the second mode, the tube 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 Cr-Mo and stainless steels (**Fig. 1**), 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 austenite grain boundaries and within the surface grains reduces the corrosion resistance of stainless steel.

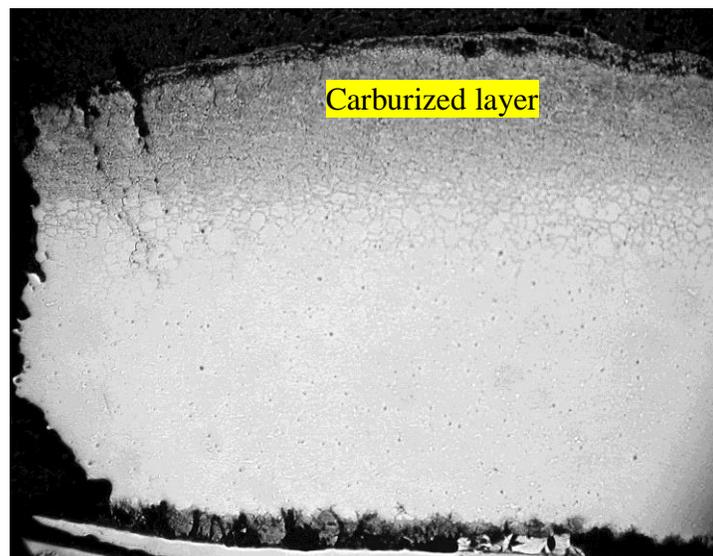


Figure 1. Carburization of stainless steel tube. 42x.

Understanding Fireside Corrosion

Fireside corrosion in the superheaters and reheaters of coal-fired units is known as coal ash corrosion, in oil-fired units as oil ash corrosion, and in refuse-fired boilers as ash corrosion. Sometimes, fireside corrosion is also referred to as hot ash corrosion. The mechanism is similar, but the low-melting species in each is different. In coal ash corrosion, the low melting species would be sodium or potassium iron trisulfates ($\text{Na}_3\text{Fe}(\text{SO}_4)_3$ or $\text{K}_3\text{Fe}(\text{SO}_4)_3$); in oil ash corrosion they would be $\text{V}_2\text{O}_5\text{-Na}_2\text{O}$ or $\text{V}_2\text{O}_5\text{-Na}_2\text{SO}_4$; and in refuse-fired boilers they would be chlorides of iron and zinc along with other constituents that form low melting chlorides. High temperatures (about 1000°F) in the superheater/reheater favor the formation of these low-melting compounds. But in refuse-fired units the low melting species form at a much lower temperature.

The corrosion rate is especially high in coal-fired units when the tubes are operating between 1100 and 1250°F. In this temperature range, complex liquid sulfates ($\text{Na}_3\text{Fe}(\text{SO}_4)_3$ or $\text{K}_3\text{Fe}(\text{SO}_4)_3$) form, resulting in rapid corrosion. **Figure 2** illustrates the view of coal ash corrosion that had occurred on the tube OD. **Figure 3** illustrates the ring section removed from a superheater tube. Note that wastage is on the flanks (arrows) of the tube, typical for hot ash corrosion. Above 1250°F, the corrosion rate is decreased significantly due to decomposition of these complex liquid trisulfates. Once the liquid phase has been removed, the corrosion is due to oxidation in contact with flue gas. The thickness of the oxide scale decreases during corrosion reactions and the metal oxidizes further to renew the oxide layer. The tube metal temperature decreases as slag thickens. At room temperature, low-melting compounds sinter the ash particles to form a tightly bound inner layer. After the slag thickness reaches equilibrium, deslagging increases because the liquid layer on the tube cannot support a thick layer of ash. This deslagging increases the tube-metal temperature. This process (slagging and deslagging) repeats in a cycle that leads to create the corrosion pattern known as ‘elephant hiding’ or ‘alligator hiding’, as shown in **Fig. 4**.

Understanding Fireside Corrosion

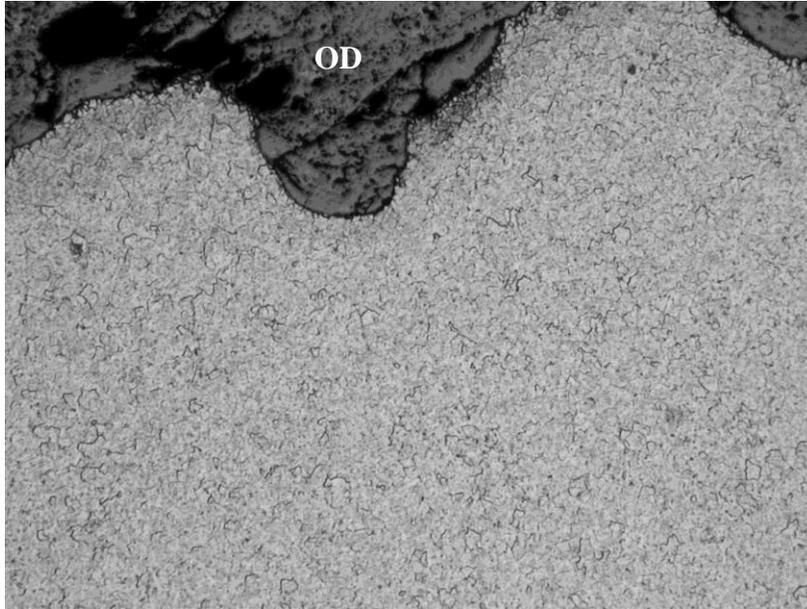


Figure 2. View of coal ash corrosion, OD, 100x.

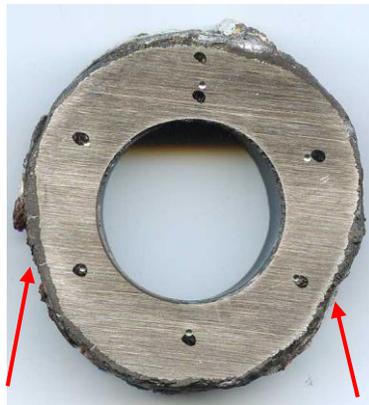


Figure 3. Sectioned ring from the tube with corroded areas noted.



Figure 4. "Alligator hiding".

Understanding Fireside Corrosion

The corrosion constituents in oil-fired units would be vanadium, sodium, potassium and sulfur. The combustion of fuel oil may produce low melting species which may consist of $V_2O_5-Na_2O$, $V_2O_5-K_2O$, $V_2O_5-Na_2SO_4$ and $V_2O_5-K_2SO_4$. The melting point of these compounds is between 1000°F and 1550°F depending on composition. The oil ash corrosion mechanism is similar to coal ash corrosion.

In refuse fired boilers, chloride and sulfate species lead to the formation, on the tube surface, of low melting species that may contain iron, zinc, lead, and sodium. These species dissolve the protective iron oxide and expose the bare steel to the corrosive environment, resulting in significant wall loss, as shown in **Fig. 5**. Reducing conditions inside the furnace may lead to the formation of iron sulfide instead of iron oxide. The presence of carbon and iron sulfide within the ash deposits indicates the presence of reducing conditions. Hydrogen chloride can more easily attack iron sulfides, rather than oxides, to form iron chloride as a corrosion product. This iron chloride has a relatively low boiling point, and therefore iron chloride vapors form in the superheater/reheater temperature range, and the corrosion mechanism is by loss of iron as a vapor. The porous sulfide formed in reducing conditions allows the easier formation and removal of iron chloride vapor. In **Fig. 6**, severe fireside corrosion led to creep damage in a relatively new superheater tube.



Figure 5. Thick OD deposit and severe wastage, refuse fired SH tube.

Understanding Fireside Corrosion

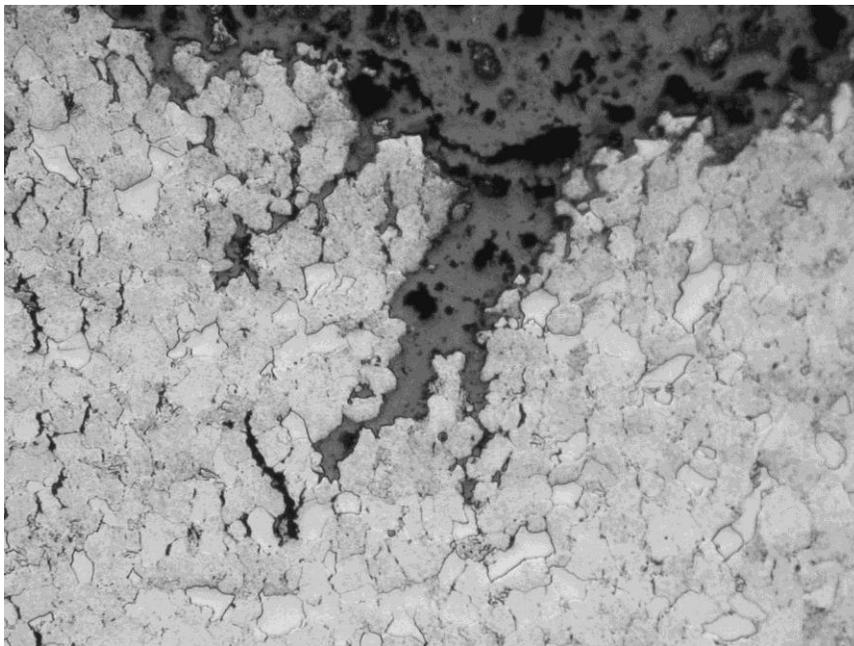


Figure 6. Creep damage due to severe wastage, OD, 200x.

Furnace wall tubes are also susceptible to fireside corrosion, but the low melting species differ from superheater/reheaters. Sodium and potassium pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$ or $\text{K}_2\text{S}_2\text{O}_7$) have been responsible for furnace wall corrosion. Both of these species melt below 800°F , where the furnace wall tubes operate. The melting points of $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$ are 750°F and 570°F , respectively. Mixtures of these two compounds could melt at even lower temperatures. Melting temperatures as low as 635°F - 770°F have been measured.

Irrespective of the boiler type, fireside corrosion affects the superheater/reheater/waterwall tubes, resulting in significant wall loss. Different methods have been proposed for controlling fireside corrosion, including reducing sulfur content, installing shields, using additives and applying corrosion-resistant weld overlays.

Coal ash corrosion rates drop drastically above 1250°F due to the decomposition of complex alkali trisulfates. Shields decrease the heat transfer, from the flue gas to the steam, resulting in an increase of the tube outside temperature above the range of stability of complex trisulfates. Also, the tube underneath the shield is not exposed to the “active” flue gas, thereby reducing the corrosion. To cause oil ash corrosion, impurities in the fuel oil (Na, V, and Pb) along with sulfur must be present. Oil ash corrosion can be minimized by reducing the impurities in the fuel and by desulphurization of fuel oil. Unfortunately, desulphurization of the fuel oil is not an economical solution. Shields are also not an

Understanding Fireside Corrosion

effective method of controlling oil ash corrosion, because, unlike in coal ash corrosion, low-melting species do not thermally decompose within the operating temperature range. Additives, such as calcium and magnesium, may be helpful to increase the melting point of compounds, but they are expensive. The increased melting temperature would be higher than superheater/reheater operating temperatures. Lowering secondary combustion reduces the hot ash corrosion, resulting from reduced SH/RH temperatures. 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-NO_x burners in coal-fired boilers has resulted in accelerated water wall wastage. These low-NO_x 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.



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