

DAVID N. FRENCH, INC., METALLURGISTS

ONE LANCASTER ROAD

NORTHBOROUGH, MASSACHUSETTS 01532

(617) 393-3635

FALL 1984

VOL. 1, NO. 3

A VIEW FROM THE PENTHOUSE: USEFUL INFORMATION FOR THE WORLD OF BOILERS

FUEL ASH CORROSION

High temperature SH and RH of fossil fired boilers are subject to rapid corrosion by certain constituents in the ash. Both oil and coal ash under some conditions may lead to tube wastage. Regardless of the fuel, the corrosion mechanisms are similar: a low melting phase, compound, or mixture forms in the ash deposit at the surface of the tube. The liquid dissolves the protective oxide scale and leaves the bare steel exposed. At once the bare steel forms an oxide and again the oxide is dissolved. The cycle repeats. Each time the oxide layer is renewed, the tube wall is reduced in thickness. Eventually the wastage is sufficient so that the remaining metal is not strong enough to withstand the internal steam pressure. The tube ruptures and another forced outage occurs.

While the essential features of liquid ash corrosion are similar for both coal and oil fuels, the details are quite different. For coal the principle agents of destruction are sulfur and sodium or potassium. Other mineral forms, mainly calcium and magnesium, may also play important roles. All coal burned today contains some sulfur. However, the amount of sulfur does not indicate whether ash corrosion will occur. The sulfur in the coal, whether a sulfide (pyrites) or a sulfate (Na_2SO_4 , K_2SO_4 or FeSO_4), forms sulfur dioxide (SO_2) and sulfur trioxide (SO_3) in the flame. Under a nearly unique set of conditions, the SO_3 and sodium or potassium oxide (Na_2O , K_2O) migrate through the ash deposit to the cooler tube metal surface. Once there, they combine with iron oxide present in the scale. The compound that forms is an alkali iron trisulfate, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ or $\text{K}_3\text{Fe}(\text{SO}_4)_3$. Thus $3\text{Na}_2\text{O} + 6\text{SO}_3 + \text{Fe}_2\text{O}_3 = 2\text{Na}_3\text{Fe}(\text{SO}_4)_3$. A similar reaction occurs with K_2O . The melting points of trisulfates are about 1150°F.

Mixtures of these trisulfates have melting points as low as 1030°F. Both SH and RH tube metal temperatures can easily reach 1030°F. Tube metal temperatures of 1150°F are not unheard of. Thus if these trisulfates form, it is likely that rapid tube wastage will follow.

The prevention of coal ash corrosion does, however, present some difficulties. Once it is known for certain that liquid ash corrosion is the problem, tube shields are installed as the usual corrective action. In those areas where corrosion occurs, stainless steel or other high temperature alloys are welded or wrapped around the tube. The intent is to raise the surface temperature to 1300°F or slightly higher. Shields are not as well cooled by the steam, there is an air gap that functions as an insulating layer to the flow of heat from hot flue gas to cooler steam. Above 1300°F, the trisulfates are unstable and decompose. Thus above 1300°F rapid liquid ash corrosion does not continue.

Another possible way to prevent these trisulfates from forming is to make compounds of the sulfur trioxide with calcium or magnesium oxide and form the sulfate. Both calcium and magnesium sulfate have melting points well above tube metal temperatures.

Not all coals with similar ash compositions cause ash corrosion problems. The reason seems to be the form that calcium and magnesium minerals take in the coal. If they are oxides or perhaps carbonates, these will then be available to react with sulfur trioxide to form harmless sulfates. However, if the calcium and magnesium are complex minerals, silicates or clay, they cannot form harmless sulfates. Liquid ash corrosion is then likely.

Ash corrosion of furnace walls is also related to the formation of a liquid phase in the ash. Since furnace wall temperatures rarely exceed 850° - 900°F even for a supercritical boiler, the trisulfates cannot be blamed. Instead it has been suggested that pyrosulfates of sodium and potassium, $\text{Na}_2\text{S}_2\text{O}_7$ or $\text{K}_2\text{S}_2\text{O}_7$, are the bad

actors. Melting points have been measured as low as 635°F for constituents in the ash. Usually such low temperature corrosion is associated with reducing conditions along the furnace walls. High concentrations of carbon monoxide have been correlated with wall corrosion. Poor fineness control of the pulverized coal may lead to deposition of unburned carbon on the furnace walls. In either case the measured oxygen levels at the stack may be 3 - 4% but on a microenvironmental scale where the corrosion occurs there are reducing conditions.

In the case of oil ash corrosion, the components in the fuel that lead to problems are vanadium, sodium, sulfur and occasionally chlorine. The amount of ash present is a few pounds per ton; the amounts of vanadium and sodium are measured in parts per million. Even though quantities are small, in the course of a day's consumption of fuel, a few hundred pounds of vanadium pentoxide (V_2O_5) and sodium oxide (Na_2O) may be deposited on SH or RH tubes.

As noted before, the mechanism for oil ash corrosion is similar to that of coal. A liquid species forms on the tube surface, dissolves the protective oxide scale, and tube wastage proceeds. The liquid phase is a mixture of V_2O_5 and either Na_2O or sodium sulfate, (Na_2SO_4). The two oxides, V_2O_5 and Na_2O form a series of vanadates and mixtures of vanadates. The lowest melting point is less than 1000°F and occurs at a composition of about 16 wt% Na_2O - 84 wt % V_2O_5 . Mixtures of V_2O_5 and Na_2SO_4 melt at about 1000°F at a composition of 10 wt% Na_2SO_4 - 90 wt% V_2O_5 . The principle culprit, however, is not the sulfate but the sodium vanadates. I have not seen liquid ash corrosion on furnace walls in oil fired boilers.

Unlike the trisulfates in coal, the Na_2O and V_2O_5 or Na_2SO_4 compounds do not decompose at boiler temperatures. Tube shields are an ineffective solution. Since the principle liquid phase is composed of vanadates, the melting point can be raised by changing the

composition. The vanadium and sodium composition of the oil can be changed by blending oils of different V and Na content. The minimum melting point in the V_2O_5 and Na_2O system occurs at 16% Na_2O , a V_2O_5/Na_2O ratio of $5\frac{1}{4}$ (84/16). For the usual circumstance of reporting elemental analysis of V and Na in the oil in parts per million, the minimum melting point occurs at a V to Na ratio of about 4.

Additives may be blended with the oil to reduce the effects of liquid ash corrosion. The most beneficial compounds appear to be magnesium oxide or magnesium hydroxide which when heated become the oxide. MgO reacts with SO_3 to form a harmless magnesium sulfate. MgO reacts with V_2O_5 to form high melting magnesium vanadates. In either case compounds that melt at tube metal temperatures do not form.

Chlorine forms iron chloride which has a melting point below 800°F. Thus chlorine in any quantity greater than a few ppm is potentially dangerous. Of course most fuel oils are shipped by ocean freighter or barge, so the possibility exists of mixing sea water (3% chlorides) with the oil. Seawater is more dense than oil. Thus it is fairly easy to keep it out of the fuel burned.

Depending on the severity of fuel ash corrosion, stainless steel tubes offer good protection. Metals depend on oxides formed at the surface to prevent corrosion. The better the alloy for high temperature service, the more tenacious is the protective oxide. Carbon steel is safe for use to about 850°F while 304 stainless is good for over 1300°F. Stainless steel has a more tightly adhering oxide than carbon steel. These oxides on stainless are more difficult to dissolve in ash deposits than the oxides on low alloy ferritic steels, similar to SA213 T-22. I've seen coal ash corrosion on T-22 that has caused tube failures within two feet of a transition to 304 stainless. The 304 showed virtually no damage by coal ash corrosion. On the other hand, I've also seen a 321H stainless steel RH tube corroded by oil ash to a steam leak in less than 6 months. So there are no clear cut guidelines to follow without careful study by a competent metallurgist.

OTHERS WHO MAY WISH TO RECEIVE OUR NEWSLETTER:

NAME: _____ TITLE: _____

COMPANY: _____

ADDRESS: _____

TOPICS FOR CONSIDERATION: _____