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Corrosion of Superheaters and Reheaters in Fossil Fired Boilers

by

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CORROSION OF SUPERHEATERS AND REHEATERS IN FOSSIL FIRED BOILERS

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Abstract

The corrosion of superheaters and reheaters in fossil fired boilers can be related to both fire and steam side conditions. Oil fueled boilers exhibit ash corrosion by low melting point slags of vanadium, sodium, and sulfur oxides, coal fired boilers by complex sulfates. In both cases, increasing tube metal temperature exacerbates corrosion rates. On the inside of the tube, steam reacts with steel to form iron oxide, an insulating layer which reduces heat transfer. The net effect is increased tube metal temperature. A heat flow analysis is presented that relates overall heat transfer, boiler design parameters, the internal scale thickness, and tube metal temperature. Case histories of oil and coal ash corrosion failures are interpreted in light of the current understanding.

INTRODUCTION

Since the mid-1950s, the Metallurgy Laboratory of the Riley Stoker Corporation has been investigating boiler component failures. Superheater and reheater tube failures comprise more than 50 percent of the total. About a quarter of these failures are directly caused by fire side ash corrosion. The perspective of the following paper is that of failure analyses done over a number of years. The information provided with the tube samples to be studied is usually sketchy and incomplete. However, what information is provided does follow a consistent pattern.

Almost without exception, the customer tells us that "nothing" has changed in several years of successful and trouble-free operation. The coal analyses are no different now than previously used. No changes have occurred in the operation of the boiler. Steam temperatures are within expected or designed range. Yet, O.D. corrosion and a rapid increase in the frequency of the superheater or reheater tube failures "suddenly" appears. The failures all exhibit similar features:

1. Excessive tube wastage and wall thinning occur as a result of the fire side ash corrosion.
2. The inside shows magnetite scale up to 20 mils thick.
3. The tube metal microstructure of ferritic steels indicates metal temperatures have been above the design level for an extended period of time.
4. The final failure usually occurs by a creep mechanism.

The paper will be divided into four parts. A thermal analysis is presented to estimate the crown metal temperature as a function of internal scale thickness. The next two parts will discuss the possible influence on

coal and oil ash corrosion as a result of the tube metal temperature increase. The final section will discuss two case histories of superheater or reheater tube failures that can be explained by the ideas presented.

THERMAL ANALYSIS

The reaction of steam and steel to form magnetite leaves the tube with an insulating layer on the I.D. A calculation may be done to estimate the metal temperature as a result of the oxide scale. The scheme follows the heat flow analysis of Kreith¹ for the steady-state condition.

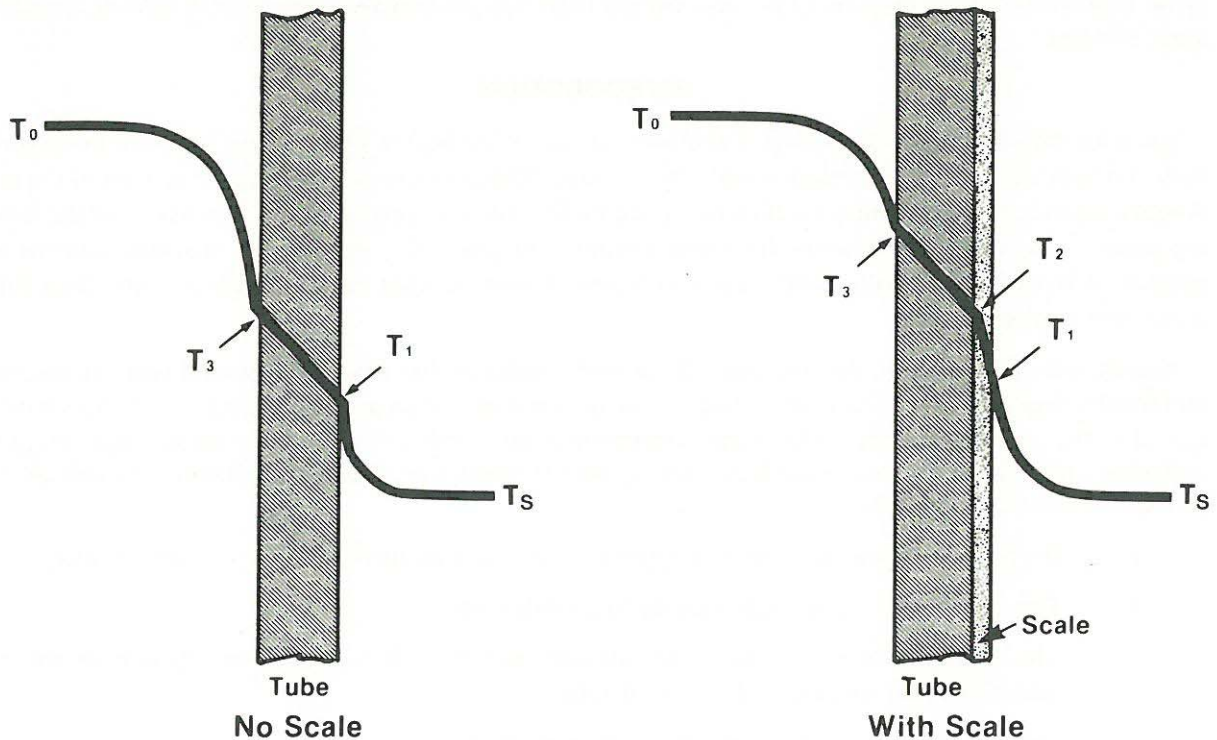
NOMENCLATURE:

- Q = heat flow, Btu/hr.
 U_o = overall heat transfer coefficient, Btu/hr./ft.²/°F
 A_o = area of the outside tube surface, ft.²
 T_o = flue gas temperature, °F
 T_3 = tube metal temperature on the O.D. surface, °F
 T_2 = temperature at the metal/scale interface, °F
 T_1 = temperature at the I.D. of the tube, °F
 T_s = bulk steam temperature, °F
 r_3 = radius of the tube, ft.
 r_2 = radius of the I.D. of the tube metal, ft.
 r_1 = radius of the tube I.D., ft.
 h_s = steam side heat transfer coefficient, Btu/hr./ft.²/°F
 K_1 = thermal conductivity of scale, Btu/hr/ft./°F
 K_2 = thermal conductivity of tube metal, Btu/hr./ft./°F

For a unit length of tube, the flow of heat, Q , is in a radial direction and is given by:

$$Q = U_o A_o (T_o - T_s) \quad (1)$$

Schematically, the temperature profile from flue gas, T_o , is:



$$U_o = \frac{1}{\frac{r_3}{r_1 h_s} + \frac{r_3 \ln(r_2/r_1)}{k_1} + \frac{r_3 \ln(r_3/r_2)}{k_2} + \frac{1}{h_o}} \quad (2)$$

The demoninator of equation 2 has four terms, one for each of the thermal components: steam side film conductance, scale conductance, tube metal conductance, gas side film conductance.

Equation 1 may be rewritten:

$$Q/A_0 = \frac{T_0 - T_s}{\frac{r_3}{r_1 h_s} + \frac{r_3 \ln(r_2/r_1)}{k_1} + \frac{r_3 \ln(r_3/r_2)}{k_2} + \frac{1}{h_0}} \quad (3)$$

Equation 3 may be separated into its components as the quantity of heat that flows through each is the same.

$$Q/A_0 = \frac{\text{Gas}}{T_0 - T_3} = \frac{\text{Metal}}{T_3 - T_2} = \frac{\text{Scale}}{T_2 - T_1} = \frac{\text{Steam}}{T_1 - T_s} \quad (4)$$

$$Q/A_0 = \frac{T_0 - T_3}{\frac{1}{h_0}} = \frac{T_3 - T_2}{\frac{r_3 \ln(r_3/r_2)}{k_2}} = \frac{T_2 - T_1}{\frac{r_3 \ln(r_2/r_1)}{k_1}} = \frac{T_1 - T_s}{\frac{r_3}{r_1 h_s}}$$

In order to calculate T_3 for a scaled tube, h_0 is first calculated from equation 2 for the clean tube condition using design values U_0 , r_3 , r_1 , h_s , and k_2 . Using this value of h_0 and the design values for Q/A_0 and T_0 , T_3 (clean tube) is calculated from equation 4. For a scaled tube, a fourth term is added to the denominator of equation 3 and a smaller value of Q/A_0 is calculated and used in equation 4 to calculate T_3 .

Using the values given in Table I for heat transfer parameters, Figures 1-3 plot the calculated temperature as a function of scale thickness for typical superheater and reheater conditions. For I.D. scale thicknesses of 10 mils, not an unusual amount, temperature increases of 40°-50°F are possible.

	h_s	U_0
Economizer	1000 Btu/hr./ft. ²	5-7 Btu/hr./ft. ²
Waterwalls	4000-8000 Btu/hr./ft. ²	20-22 Btu/hr./ft. ²
Reheaters	300-400 Btu/hr./ft. ²	11-17 Btu/hr./ft. ²
Superheaters	200-500 Btu/hr./ft. ²	11-18 Btu/hr./ft. ²
Thermal Conductivity (1100°F)		
Carbon Steel (SA-210 Al)	23.0 Btu/ft. ² /hr./°F/ft.	
SA 209-T1 (carbon + ½ Mo)	21.7 Btu/ft. ² /hr./°F/ft.	
SA 213-T11 (1¼ Cr + ½ Mo)	17.5 Btu/ft. ² /hr./°F/ft.	
Sa 213-T22 (2½ Cr + 1 Mo)	16.7 Btu/ft. ² /hr./°F/ft.	
Sa 213-TP321H (18Cr - 10 Ni)	14.0 Btu/ft. ² /hr./°F/ft.	
Fe ₃ O ₄	0.342 Btu/ft. ² /hr./°F/ft.	

Table I Range of Values for Heat Transfer Coefficients

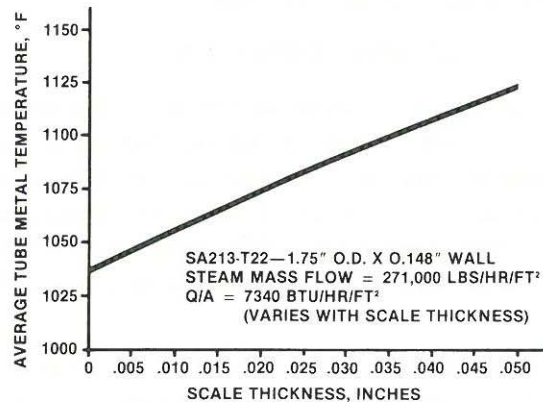


Figure 1 Tube Metal Temperatures as a Function of Scale Thickness of Reheater Tube Samples

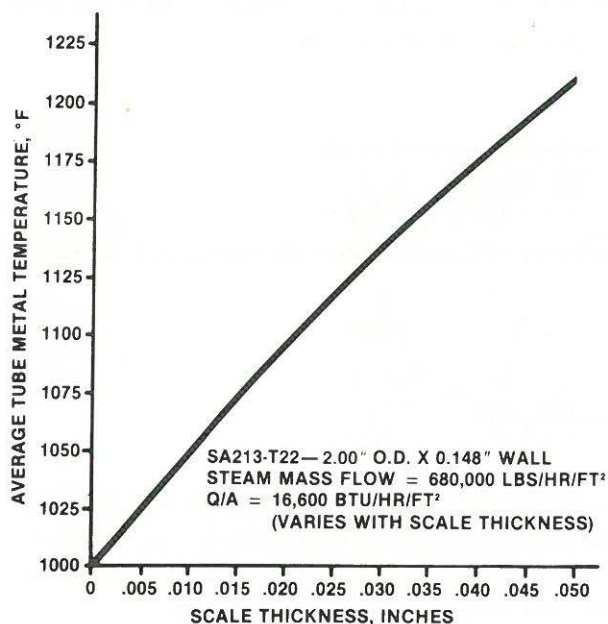


Figure 2 Tube Metal Temperature as a Function of I.D. Scale Thickness.
2" O.D. x 0.300" Wall, T-22

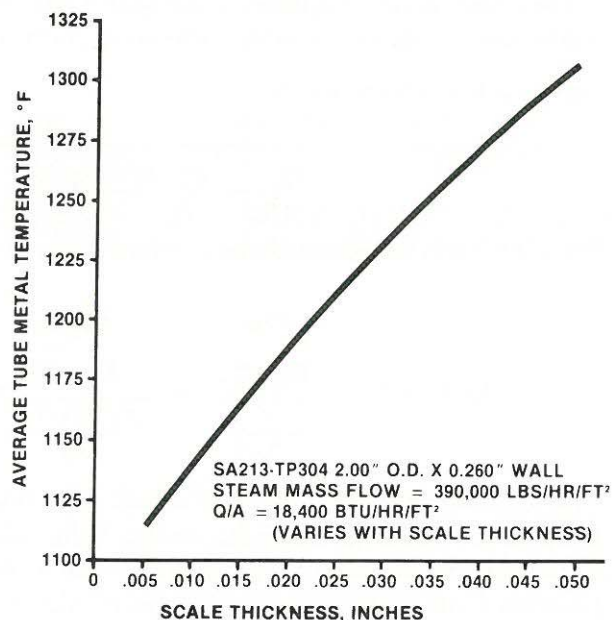


Figure 3 Tube Metal Temperature as a Function of I.D. Scale Thickness.
2" O.D. x 0.260" Wall, 304

COAL ASH CORROSION

The conventional understanding of superheater and reheater corrosion by constituents within coal ash centers on the alkali iron trisulfates, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ or $\text{K}_3\text{Fe}(\text{SO}_4)_3$. Sodium and potassium iron sulfates melt at 1155°F and 1145°F respectively, and have been frequently identified in corrosion areas.² Once the liquid phase forms, the protective iron oxide film is dissolved and tube wastage occurs either by the participation of iron oxide in the formation of the trisulfate, or the transport of oxygen to the tube metal surface by the liquid phase to form iron oxide.

Mixtures of the two have melting points as low as about 1030°F. The composition of the mixture of these two constituents will be dependent upon the relative amount of sodium and potassium oxides in the ash. If a boiler has operated for several years without serious superheater or reheater corrosion, then "all of a sudden" severe O.D. liquid ash corrosion appears, a possible explanation is that the tube metal O.D. temperature has finally reached the melting point of the mixture of sodium and potassium iron trisulfates unique to that particular circumstance. Figure 4 shows the melting point of mixtures of the two alkali iron sulfates.² Normal superheater tube metal temperatures are about 1050°F under design conditions. As has been noted, increases of 40° or 50° are certainly possible as a result of the I.D. scale.

OIL ASH CORROSION

The understanding of the causes of oil ash corrosion are similar to that of coal ash corrosion. A liquid phase is necessary, but the species that form the liquid phase are mixtures of vanadium pentoxide, sodium oxide or sodium sulfate. These vanadium salts attack a metal surface by dissolving the normally protective oxide layer and/or act as an oxygen carrier to facilitate diffusion of oxygen from the flue gas to the tube metal surface. Figure 5 shows the phase diagram for sodium oxide and vanadium pentoxide. The lowest melting point occurs at a composition of about 35 mol percent sodium oxide and has a melting point below 1000°F.

Melting point curves are shown in Figure 6 for the mixtures of sodium sulfate and vanadium pentoxide. Again, the lowest melting point is below 1000°F at a composition of about 10 weight percent sodium sulfate. Regardless of the species that causes the liquid phase, increasing the tube metal temperature opens up the range of ash composition that will form liquids.

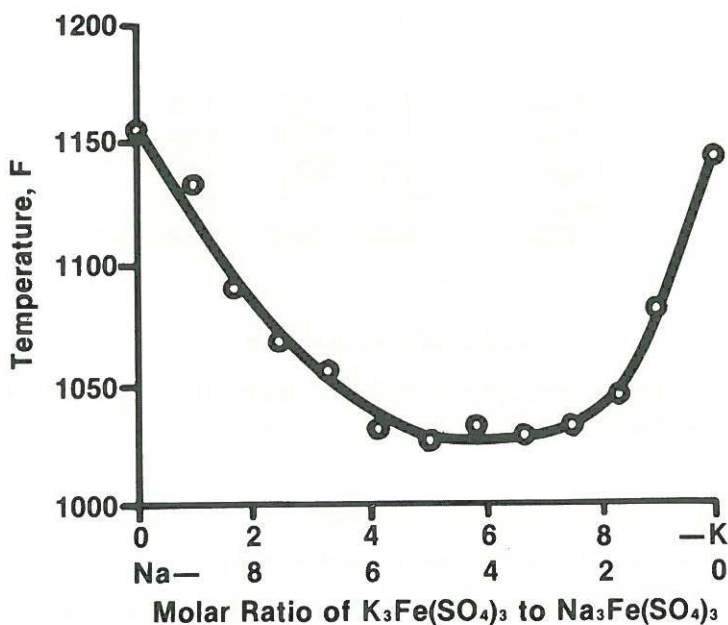


Figure 4 Melting Points in System $Na_3Fe(SO_4)_3-K_3Fe(SO_4)_3^2$

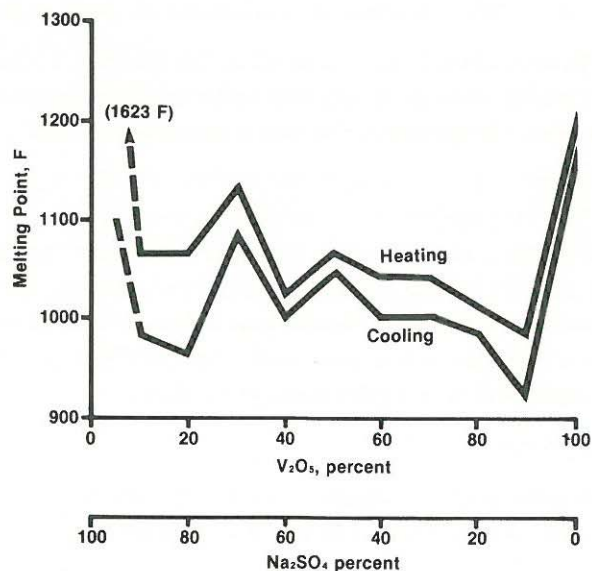
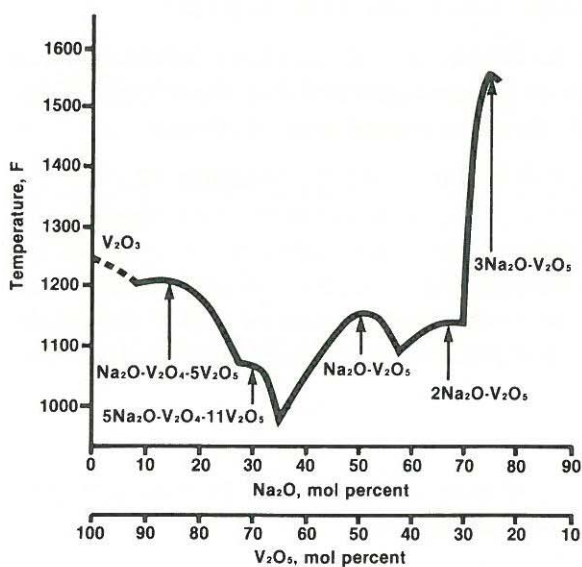


Figure 5² Phase Diagram for $Na_2O-V_2O_5$ System Figure 6² Melting Points in System $V_2O_5-Na_2SO_4$

Aside from the increases in corrosion rate from higher temperatures, serious corrosion occurs over a much wider range of ash compositions.

CASE HISTORIES

The following case histories illustrate the effects of internal scale buildup on tube metal temperature, the premature tube failure, and an explanation of the premature tube failures in light of the foregoing understanding.

Case History No. 1

This investigation covers several reheater tube samples including a tube that failed, from a coal fired utility

boiler. The tubes are 1 3/4" O.D. x 0.150" wall, SA 213-T22 material. Table II gives the ash analysis for the coals being used.

P ₂ O ₅	0.23	CaO	1.61
SiO ₂	53.95	MgO	2.30
Fe ₂ O ₃	13.34	SO ₃	1.15
Al ₂ O ₃	20.35	K ₂ O	3.73
TiO ₂	0.73	Na ₂ O	0.34

Table II Ash Analysis

COAL ASH ANALYSIS

If we assume all of the potassium and sodium oxide are converted to the trisulfates, the mole ratio of potassium to sodium iron trisulfate is 7.75. From Figure 4, the melting point for such a mixture is estimated at about 1080°F.

Visual examination of these tubes revealed the following:

- A. The internal scale measured from 0.015" to 0.026" thick.
- B. The tube wall thickness 12" away from the failure and in the same plane measured 0.127". The tube wall thickness 180° from this point measured 0.171" thick.
- C. The remaining sections of reheater tubes showed I.D. scale varying from 0.018" to 0.021" thick and O.D. scale and deposit up to 0.040" thick.
- D. Wall thickness measurements on these unfailed tubes varied from 0.170" to 0.127".

Microstructural analysis of all of the samples, including the failure, showed complete spheroidization of the carbides indicating exposure to elevated temperatures for an extended period of time. From Figure 1, the tube metal temperature increase is estimated as 40°F as a result of the internal scale of 20 mils.

The tube samples were removed from a utility boiler that had been in service approximately 12 years. For the first 10 years or so of operation, no severe ash corrosion was noted, and, according to the customer, the coal supply had not varied. It appears likely that the rapid deterioration of these reheater tubes over the last two years of service is caused by the increase in the tube metal temperature as a result of internal oxide scale formation. Given the composition of the coal ash, the increase in tube metal temperature of 40°F allowed the mixture of sodium and potassium iron trisulfates to form a liquid phase. Once the liquid ash phase had formed, rapid and severe tube wastage resulted.

Case History No. 2

Metallurgical investigation of reheater tube failure from a small utility oil fired boiler. The tube is 2" O.D. x 0.148" wall, SA 213-T22 material. Table III gives the tube deposit analysis.

V as V ₂ O ₅	37.9 wt%	Al as Al ₂ O ₃	11.3
S as SO ₃	1.0	Si as SiO ₂	7.6
Fe as Fe ₂ O ₃	9.4	Carbon	0.2
Ca as CaO	2.5	K as K ₂ O	0.2
Mg as MgO	8.1	Na as Na ₂ O	4.0
Ni as NiO	7.8	Chlorine	100 ppm

Table III Tube Deposit Analysis

OIL ASH ANALYSIS

A sulfur print revealed the presence of sulfides in the ash deposit, the 0.2%C noted assures reducing conditions on a local scale. Wastage of this sample fits the pattern of reducing condition corrosion reported

previously.³ If we assume the liquid phase to be mixtures of V_2O_5 and Na_2O , the analysis given in Table III gives about 75 mol % V_2O_5 and 25 mol % Na_2O . From Figure 5 the melting point is about 1100° F.

Visual examination of the tube showed the following:

- A. The internal scale measured 0.015" thick.
- B. The tube wall thickness measured around the tube varied from 0.158" to 0.079" on the fire side.
- C. Microstructural analysis showed spheroidization of the carbides indicating exposure to elevated temperatures for some time.

From Figure 1 the tube metal temperature increase is estimated as about 30°F as a result of the 0.015" internal scale.

It appears likely from the combination of I.D. scale, O.D. deposit analysis, and estimated tube metal temperature increase that the recent liquid ash corrosion attack is caused by the internal scale. Once the tube metal temperatures increased to about 1100°F, the liquid phase of $Na_2O - V_2O_5$ formed and rapid tube wastage formed.

CONCLUSION

Internal scale formation leads to an increase in tube metal temperature. Depending on the composition of the O.D. ash deposit, this temperature increase may allow liquid phases to form on the tube surface and rapid tube wastage follows. Several years of satisfactory operation may precede the rapid corrosion as the I.D. scale develops.

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