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Material Considerations in Boiler Design

by

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INTRODUCTION

The service conditions of a fossil fueled boiler are among the most severe of any large engineered structure. Flame temperatures may reach more than 3000°F. Flue gas and ash contain many species that are corrosive to the materials of construction. The steam side environment for superheaters and reheaters is generally nearly pure steam but even steam reacts with steel to form iron oxide:

$$3\ Fe + 4H_2O = Fe_3O_4 + 4H_2 \tag{1}$$

Superheaters and especially reheaters have difficult operating conditions, particularly during start-up. The highest metal temperatures are in the finishing legs where they reach 1100°F or higher. Since metal temperatures are the highest, the fire-side oxidation and corrosion potential are the greatest, and steam side scale formation is the most rapid. It is for these reasons that the actual life is about half that of the rest of the boiler, about fifteen years or so.

GAS PHASE OXIDATION

The rate at which scale thickness forms by the reaction of steam with steel decreases with increases in scale thickness but the rate never reaches zero. The relationship in the parabolic law[1]; the scale thickness, X, is proportional to the square root of time, t:

$$x = k\sqrt{t} \tag{2}$$

where k is a constant. The first derivative gives the time rate of change in scale thickness:

$$\frac{dx}{dt} = \frac{k}{2\sqrt{t}} \tag{2a}$$

Thus, when t is large, dx/dt, the rate of scale thickness increase, is small.

Data on the scale formation of steel in steam are sparse and inconsistent. Figure 1, shows scale formation of chromium-molybdenum steels in 1100°F steam for times up to 16,000 hours[2]. Tests were done by placing test coupons in a high temperature superheater outlet header so the steam temperature was nearly constant. However, as we shall see later the internal scale can dramatically increase the metal temperature. In effect, scale forms on a metal whose temperature is constantly increasing.

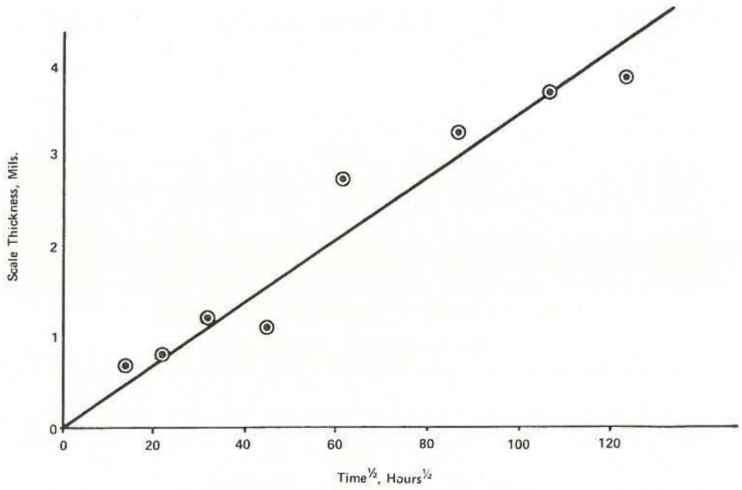


Figure 1 A plot of scale thickness vs. the square root of time for times up to 16,000 hours for the oxidation of Cr-Mo steels in 1100°F steam, data from reference 2

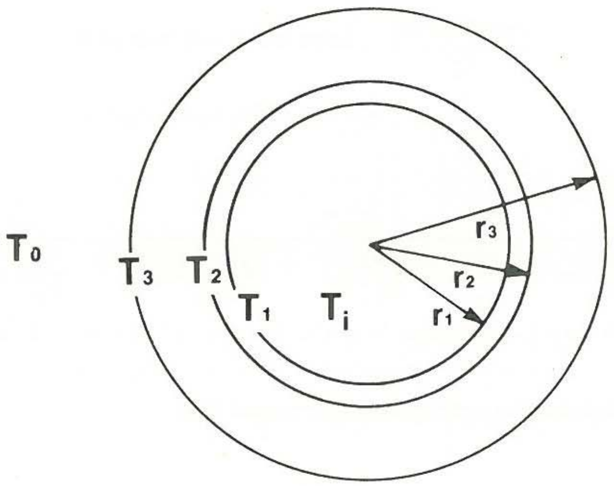
Exfoliation of the internal scale causes, really, two kinds of problems, one is the erosion of turbine blades by particles of oxide scale entrained in the steam, and two is the pluggage or partial pluggage of return bends in both superheaters and reheaters that leads to tube ruptures, see for example Thielsch[3]. It appears that reheaters are more susceptible to this problem but superheaters are not immune. Thermal shock caused by either cooling down or too rapid a start-up breaks loose the internal scale. Differences in the coefficient of thermal expansion between scale and steel cause the scale to spall off. Subsequent steam flow picks up these particles and carries them through the turbine.

THERMAL ANALYSIS

Reaction of steam and steel forms a magnetite scale on the internal surface that leaves the tube with an insulating layer that will cause the metal temperature to increase. A calculation may be done to estimate the increase in tube metal temperature as a result of the oxide scale. The scheme follows the heat flow analysis of Kreith (4) for the steady state condition.

NOMENCLATURE:

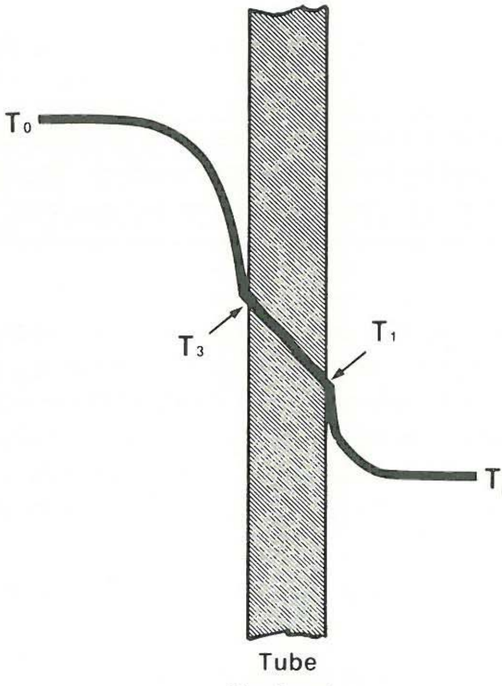
Q = heat flow, BTU/hr.
U_o = overall heat transfer coefficient, BTU/hr/ft^2.
A_o = area of the outside of the tube, ft^2.
T_o = flue gas temperature, °F.
T_3 = tube metal temperature on the OD surface, °F.
T_2 = temperature at the metal/scale interface, °F.
T_1 = temperature of the ID of the tube, °F.
T_s = bulk steam temperature, °F.
r_3 = radius of the OD of the tube, ft.
r_2 = radius of the tube metal ID, ft.
r_1 = radius of the tube ID, ft.
h_s = steam side heat transfer coefficient, BTU/hr/ft^2/°F.
h_o = gas side heat transfer coefficient, BTU/hr/ft^2/°F.
k_1 = thermal conductivity of scale, BTU/hr/ft/°F.
k_2 = thermal conductivity of metal, BTU/hr/ft/°F.



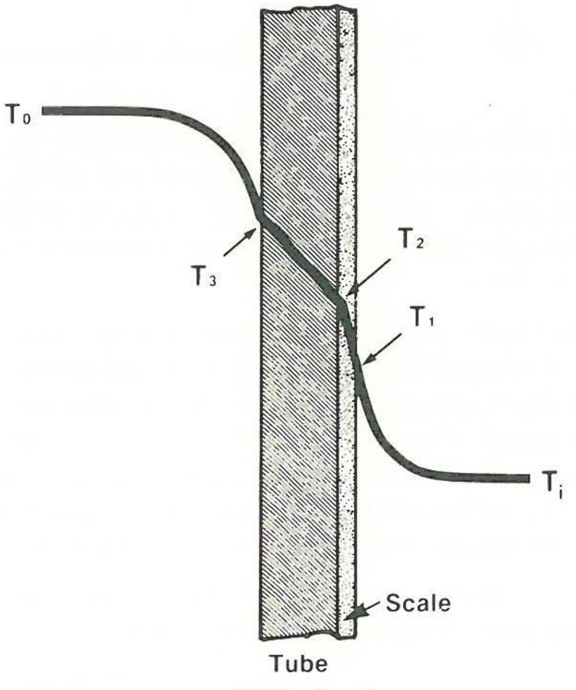
For a unit length of tube, the flow of heat, Q, is in a radial direction and is given by:

$$Q = U_oA_o\,(T_o\text{-}T_s) \tag{3}$$

Schematically, the temperature profile from flue gas , T_o, to bulk steam temperature, T_s, is:



No Scale



With Scale

$$U_o = \frac{1}{\dfrac{r_3}{r_1h_s} + \dfrac{r_3\ln\,(r_2/r_1)}{k_1} + \dfrac{r_3\ln\,(r_3/r_2)}{k_2h_o} + \dfrac{1}{h_o}} \tag{4}$$

The denominator of equation 4 has four terms, one for each of the thermal resistances:

$\dfrac{r_3}{r_ih_s}$, steam side film conductance

$\dfrac{r_3\ln\,(r_2/r_1)}{k}$, scale conductance

$$\frac{r_3 \ln (r_2/r_2)}{k_2} \text{, tube metal conductance}$$

$$\frac{1}{h_o} \text{, gas side film conductance}$$

Equation 3 may be rewritten:

$$\frac{Q}{\quad} = \frac{T_o - T_s}{\frac{r_3}{r_1 h_s} + \frac{r_3 \ln (r_2/r_1)}{k_1} + \frac{r_3 \ln (r_3/r_2)}{k_2 h_o} + \frac{1}{h_o}} \tag{5}$$

Equation 5 may be separated into its components as the quantity of heat that flows through each is the same.

$$\frac{Q}{A_o} = \frac{T_1 - T_s}{\frac{r_3}{r_1 h_s}} \text{, temperature drop through steam film} \tag{6}$$

$$\frac{Q}{A_o} = \frac{T_2 - T_1}{\frac{r_3 \ln (r_3/r_2)}{k_1}} \text{, temperature drop through scale} \tag{7}$$

$$\frac{Q}{A_o} = \frac{T_3 - T_2}{\frac{r_3 \ln (r_3/r_2)}{k_3}} \text{, temperature drop through metal} \tag{8}$$

$$\frac{Q}{A_o} = \frac{T_o - T_3}{\frac{1}{h_o}} \text{, temperature drop on the gas side} \tag{9}$$

In order to calculate the surface temperature, T_3, as a result of ID scale formation, h_o is first calculated from equation 4 given the design parameters of U_o, r_3, r_1, h_s, and k_2 for the bare tube condition. The scale conductance is zero and $r_1 = r_2$, that is there is no ID scale. Using this value of h_o, the design value of Q/A_o and T_o, the value for T_3 is calculated. In practice, T_3 is set at the oxidation limit plus a small margin; for T-22 T_3 is 1075°F.

The addition of internal scale alters the heat flow; to calculate the effect of scale, the scale term is added to the denominator of equation 5. Final calculation of T_3 (or T_2) is a two step procedure. Using h_o, just calculated, and appropriate values for the other terms in equation 5, (note hs is nearly unaffected by scale and is assumed to be constant in this exercise), T_o and T_s are taken from design conditions, a new and smaller value of Q/A_o is found. From equation 9, T_3 is calculated from this smaller Q/A_o. Figure 2, plots $\triangle T$, the increase in OD crown temperature over the scale free condition for several Q/A_o values. Figure 3-6 are plotted for specific superheater or reheater conditions.

It is instructive to calculate the various contributions to the overall flue gas temperature to steam temperature drop each component makes.

	Without Scale	With Scale (0.019 inch)
Steam film	29°F	27°F
Scale	0	38°F
Scale	8°F	7°F
Gas Side	449°F	412°F
Q/A_o	7300 Btu/hr/ft^2	6700 Btu/hr/ft^2

From this comparison, it is evident that, aside from the metallurgical implications of higher tube metal temperatures, there is a slight loss of overall thermal efficiency of the boiler. The calculation is not meant to be precise, but to show generally the effects of scale on tube temperature. It is safe to say that if the original design limit was 1075°F, the present condition is some 40°F hotter.

The next step in our attempt to get a handle on the effects of internal scale is to come to grips with the rate

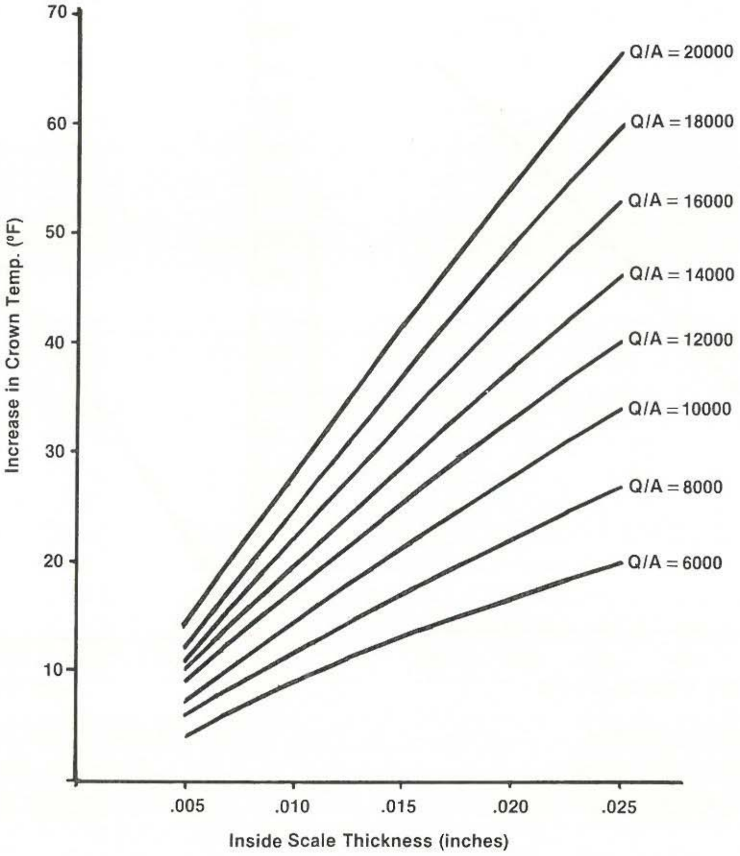


Figure 2 Increase in Crown Temperature vs. Inside Scale Thickness for Varying Q/A (Steam Cooled Tubes)

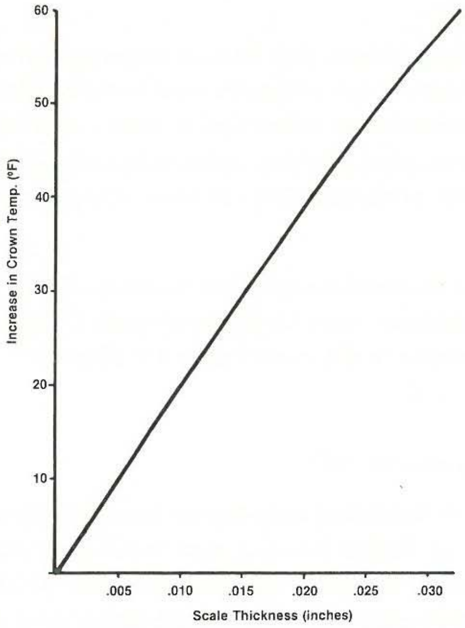


Figure 3 SA 213 T-22
1.75" OD x .148" wall
Q/A = 7340 Btu/Hr—Ft^2

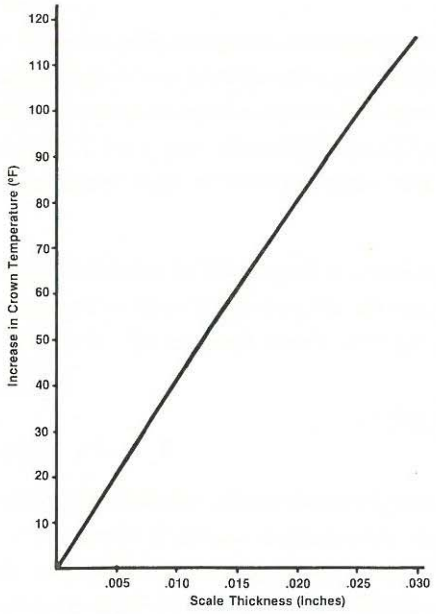


Figure 4 SA 213 T—22
1.75" OD x .148" wall
Q/A = 16,600 Btu/Hr—Ft^2

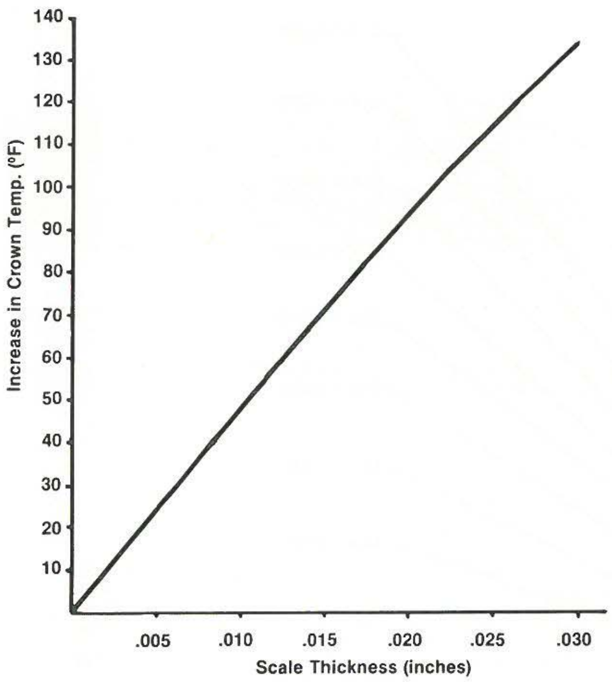


Figure 5 SS 304
2" OD x .260" wall
Q/A = 18,400 Btu/Hr—Ft²

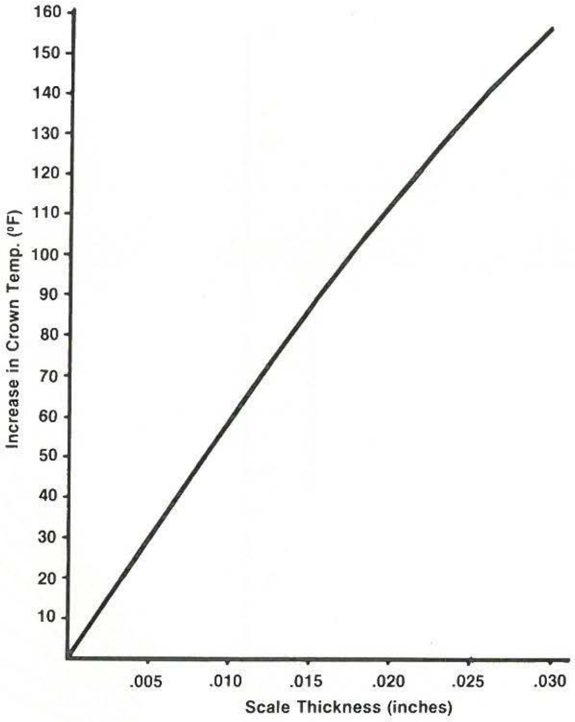


Figure 6 SA 213 T—22
2" OD x .400' wall
Q/A = 18,200 Btu/Hr—Ft²

at which scale forms in an actual boiler. As has been mentioned, most tests have been run at constant temperature but in real life, tube metal temperature increases as ID scale forms. Rehn et al[5] have used the Larson-Miller parameter[6] to correlate scale thickness as either or both temperature or time increase.

The Larson-Miller parameter, P, is:

$$P = T\,(20 + \log t) \qquad (10)$$

Where T is temperature in degrees Rankine (°F + 460), t is time in hours, and 20 is an empirical constant. P has been used to describe diffusion controlled phenomena in steels. It was originally used to extrapolate short term high temperature stress rupture and creep data to lower temperatures where similar events occur but over much longer times. Friedrich[7] has used it to describe microstructural changes, spheroidization, graphitization, etc., and relate short term high temperature changes with prolonged times at lower temperatures.

The procedure we have used to calculate the scale thickness as metal temperature increases due to the ID scale combines the data of Rehn et al[5] with our calculated temperature increase given in Figure 2 for Q/A_O of 16,000 Btu/hr/ft^2. From Rehn et al[5], X and P are scale thickness and Larson-Miller Parameter:

$$\log X = 0.0002\,P - 6.6 \qquad (11)$$

and from Figure 2:

$$T = 2.1\,X \ (Q/A = 16{,}000\ \text{Btu/hr/ft}^2) \qquad (12)$$

An iterative process is used: calculate the scale thickness from the design temperature for a time interval of 10,000 hours assuming a constant temperture. At the end of 10,000 hours a new metal temperature is calculated from X and equation 12. The new, higher temperature is used to calculate the scale thickness increase from 10,000 to 20,000 hours from equation 11. The incremental X is added to the initial value of scale thickness and the process is repeated in increments of 10,000 hours. Figure 7 plots scale growth for design temperatures of 1050°F, 1100°F, and 1125°F. Table I gives scale thickness after 100,000 hours from Figure 7 and from equation 11 (assuming constant temperature). For reference, Figure 1 is extrapolated to 100,000 hours for comparison. Final metal temperature is given as calculated from equation 12.

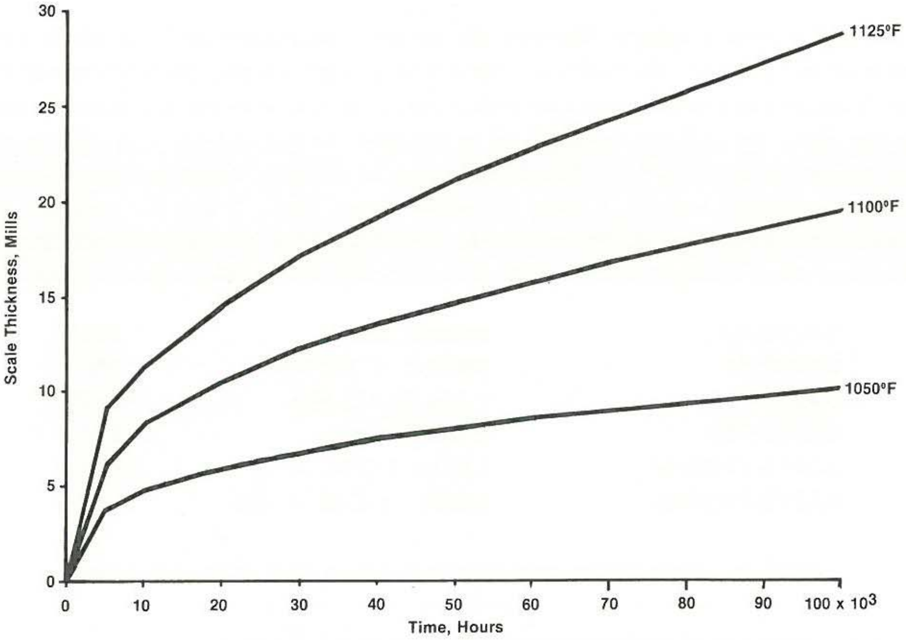


Figure 7 Scale Thickness, Mils, vs. Time, Hours for Three Initial Temperatures

Initial Temp.	Scale Thickness	Temp.	Scale Thickness	Temp.	Scale Thickness	Temp.
	Figure 7		**Equation 11**		**Figure 1**	
1050°F	**10.1 Mils**	**1072°F**	**89 Mils**	**1068°F**		
1100°F	**19.3 Mils**	**1142°F**	**15.9 Mils**	**1133°F**	**11.0 Mils.**	**1123°F**
1125°F	**28.7 Mils**	**1186°F**	**21.1 Mils**	**1170°F**		

Table I Scale Thickness and Final Metal Temperature After 100,000 Hours

The previous exercise points to one of the problems that will arise if a unit is operated above the design limits, internal scale increases faster than it would otherwise. The second problem is the deterioration of strength and microstructural properties, what takes longer at lower tempertures to occur will happen in shorter times at higher temperatures. The Larson-Miller Parameter was originally used for extrapolation of creep and stress rupture data from high to low temperatures[6]. For sake of argument, the design temperature is 1050°F and the material is T-22. From the ASME Boiler and Pressure Vessel Code, Section I[8], the allowable stress is that value of stress that given 1% creep in 100,000 hours. Using P, what time will give 1% creep at, not 1050°F but 1070°F?

$$P = (1050 + 460)(20 + \log 100{,}000) = 37{,}750$$

for P at the design temperature of 1050°F. Solving the same equation for t when the temperature is 1070°F:

$$37{,}750 = (1070 + 460)\ 20 + \log t)$$

t is found to be about 47,000 hours or a loss of about half the life from operating at 20°F over the design temperature.

While we have used SA213-T22 ferritic steel at the high end of the temperature range in our examples, similar problems occur with all steels when used above the oxidation limit for the particular steel. Most superheaters and reheaters use several alloys depending on the steam temperature and expected metal temperature. The inlet ends use carbon steel, and as the steam and metal temperatures increase progressively higher alloys are used, carbon-1/2 Mo (SA209-Tl), 1 1/4 Cr-1/2 Mo (T-11), 2 1/4 Cr - 1 Mo (t-22), and stainless steel. If the SH or RH is run hot, all of the alloys will suffer premature overheating failure at the hot end. It is for this reason that a thorough inspection of "old" superheaters and reheaters needs to include a metallurgical evaluation at all alloy transitions where metal temperatures are the highest for each alloy.

In order to provide a greater margin between the design temperature and the alarm point, the design temperature will have to be raised. All that is involved is to assume a higher metal temperature, by say 50°F. Changes in alloy from carbon steel to alloy steel will occur, in effect, at lower actual steam temperature. The result will be higher alloy, on average, superheater or reheater. In the end, the essential change would be to lower the present oxidation limits by 50°F. The finishing leg of stainless steel would have slightly thicker wall as a higher design temperature requires a lower allowable stress. Table II lists the common superheater and reheater alloys and their present oxidation limits. The lowering of the maximum temperature of use, oxidation limit would, of course, increase the cost of these components but would extend the life by some amount.

SA210-A1	**carbon steel**	**850°F**
SA209-T1	**carbon + I/2 Mo**	**900°F**
SA213-T11	**1 1/4 Cr-1/2 Mo**	**1025°F**
SA213-T22	**2 I/4 Cr-1 Mo**	**1075°F**
SA213-TP321H	**18Cr+1 ONi + Ti**	**1300°F**
SA213-TP347H	**18CR – 1 ONi + Cb**	**1300°F**

Table II Superheater and Reheater Alloys and Oxidation Limits

One example will suffice to illustrate what we have been talking about, a high temperature superheater creep rupture failure.

Boiler Statistics:

Size: 1,310,000 lbs. steam/hr.
Steam Temperature: 1005°/1005°F
Steam Pressure: 1900 psig
Fuel: Pulverized Coal
Length of Service: 10 years

The high temperature superheater tube is SA213-T22, 2.0 inch OD x 400 inch min. wall. Visual examination of the tube sample revealed the following:

A. The failure was a 1 1/2 inch long split with very little reduction in wall thickness at the rupture, see Figure 8.
B. The wall thickness one foot away from the end of the failure and in the same plane measured 0.330 inch.
C. The wall thickness 180° from the failure measured 0.400 inch.
D. The internal scale measured 0.032 inch and the OD scale and ash deposit measured 0.052 inch.

The microstructure of the sample through the lip of the failure showed a complete spheroidization of the carbide, see Figure 9. The tube surface shows a minor intergranular penetration of the OD oxide, see figure 10. The structure at the rupture shows a classic example of creep voids, see Figure 11. From Figure 4 which shows the temperature increase with scale thickness for this example, the final metal temperature is estimated to be 160°F over the scale free condition. Regardless of any margin built in or any margin increase, this particular tube would not have lasted much longer. The microstructure and creep failure attest to the fact this tube has been operated well above 1075°F for a long period of time.

It seems to me that some of the exfoliation problems that units suffer are in the older boiler, those in service more than 10 or 12 years. In the early seventies, the oxidation limit of T-22 was lowered from 1125°F to 1075°F. All things being equal, this reduction of 50°F should provide some relief of superheater and reheater high temperature problems. As older units have major modification or repair, serious consideration should be given to upgrading the alloys used. Your unique operating and fuel circumstances should be used to help the design engineer in material selection for the replacement. There is no technical reason, for example, why an all stainless superheater or reheater cannot be fabricated.

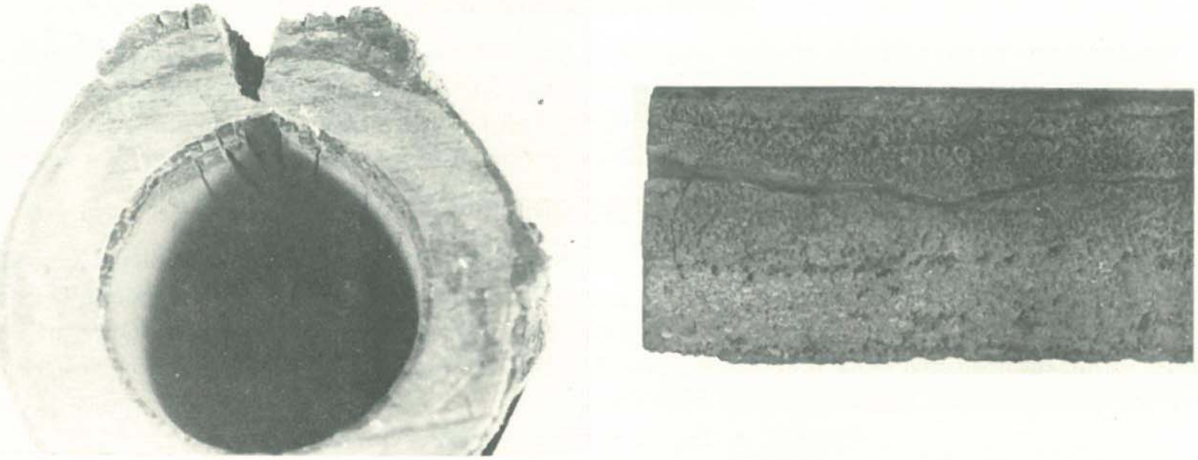


Figure 8 As-received Superheater Tube. The Failure is a Narrow Split about 1½ Inches Long. Note the ID Scale in the Transverse View.

Figure 9 Microstructure Shows Spheroidized Carbides and Ferrite (500X, Nital Etch)

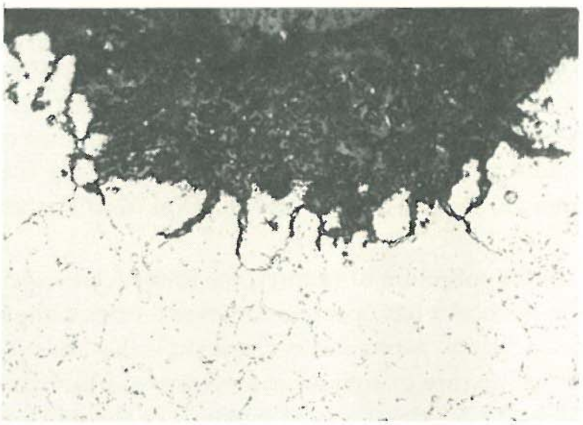


Figure 10 The OD Scale Exhibits Some Minor Grain Boundary Attack. (500X, Nital Etch)

Figure 11 The Structure at or near the Tip of the Failure. Note that the Crack is Completely Filled with Oxide Scale. The Black Specks in the Metal are Voids Indicative of a Creep Failure. (500X, Nital Etch)

LIQUID ASH CORROSION

The discussion to this point has covered only the effects of ID scale on scale thickness, metal temperature or microstructural properties. However, from what we have seen in our failure analyses, liquid ash corrosion is present to a greater or lesser extent in maybe 10-12% of all failures. As tube metal temperatures increase, the likelihood increases that fireside corrosion will cause tube metal wastage and premature tube failure.

COAL ASH CORROSION

The conventional understanding of superheater and reheater corrosion by liquid constituents in coal ash centers on the alkali iron trisulfates, $Na_3Fe(SO_4)_3$ and $K_3F_e(SO_4)_3$. Sodium and potassium iron sulfates melt at 1155°F and 1145°F respectively and have frequently been identified in corrosion areas[9]. Once the liquid phase forms, the protective oxide film on the tube is dissolved and tube wastage occurs either by the participation of iron oxide in the formation of the trisulfates,

$$3Na_2SO_4 + Fe_2O_3 + 3SO_3 = 2Na_3Fe(SO_4)3,$$

or the transport of oxygen from the flue gas to the unprotected tube 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 will be dependent on the relative amounts of sodium and potassium in the coal. However, within the high temperature portion of the flame, above 3000°F or so, the mineral matter is stripped of sodium and potassium. Volatilized alkali reacts with oxygen to form gaseous sodium and potassium oxides, Na_2O and K_2O. Within the ash deposit itself some exchange of potassium for sodium occurs and typically ash deposits contain more potassium than sodium than the fuel. It is related to the temperature that the alkali oxides vaporize, K_2O at 2690°F and Na_2O at 3210°F, thus, is a tendency to selectively deposit K_2O in the ash.

In the collection of failures, the RSC Metallurgical Laboratory has studied over the years, the usual story is that the boiler has operated for several years without incident. "All of a sudden" severe OD liquid ash corrosion appears. A possible explanation is that the tube metal temperature has finally reached the melting point of the mixture of sodium and potassium iron trisulfates unique to that particular circumstance[10]. Figure 12 shows the melting point of mixtures of these two trisulfates [9]. Normal superheater tube metal temperatures are about 1050° to 1100°F under design conditions. As has been noted, increases of 50°F and more are certainly possible as a result of the ID scale.

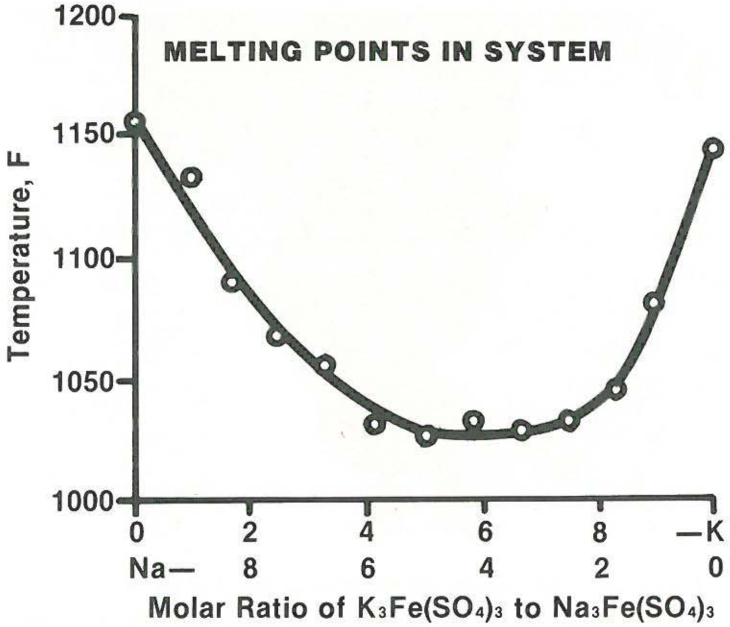


Figure 12 Melting Points in System $Na_3Fe(SO_4)_3 - K_3Fe(SO_4)_3^2$

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 are mixtures of vanadium pentoxide, V_2O_5, sodium oxide, Na_2O or sodium sulfate, Na_2SO_4. These vanadium compounds attack the tube metal in similar ways to the alkali iron trisulfates. They dissolve the protective oxide and/or act as an oxygen carrier. Figure 13 shows the phase diagram for V_2O_5 and Na_2O. The lowest melting point occurs at a composition of about 35 mol % Na_2O (or about 16 wt% Na_2O) and has a melting point below 1000°F.

Melting point curves are shown in Figure 14 for mixtures of Na_2SO_4 and V_2O_5. Again, the lowest melting point is below 1000°F at a composition of about 10 wt% Na_2SO_4. Regardless of the species that causes the liquid ash phase, increasing the tube metal temperature opens up the range of ash composition that will form liquids and cause rapid tube wastage. The most severe case from our files is 321H stainless steel reheater that corroded to the point of replacement in less than six months from oil ash attack.

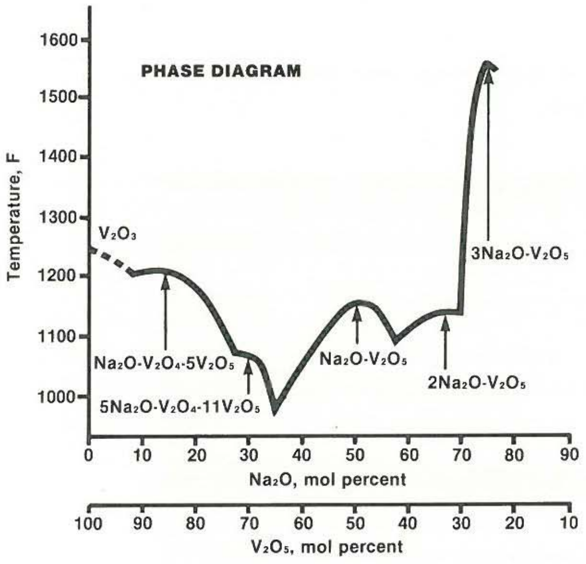


Figure 13 Phase Diagram for $Na_2O - V_2O_5$ System[2]

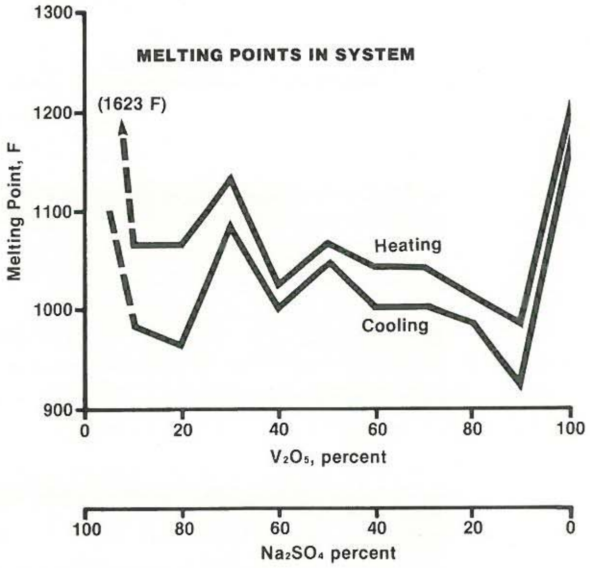


Figure 14 Melting Points in System $V_2O_5 - Na_2SO_4$[2]

Within these ash deposits, there are similarities, regardless of whether the fuel is coal or oil. In both cases, the ash contains carbon and metallic sulfides. The suspicion is that carbon is necessary to preserve, at least on a microenvironmental scale, reducing conditions necessary to stabilize the metallic sulfides found.[9], [11]

A couple of examples to illustrate the kinds of problems that may occur.

Metallurgical Investigation of Reheater Tube Failures

Boiler Statistics:

Size:	1,600,000 lbs. steam/hr.
Steam Temperature:	1005°/1005°F
Steam Pressure:	1980 psig
Fuel:	Pulverized Coal
Length of Service:	13 years

The investigation covers several reheater tube samples including a tube that failed, Figures 15 and 16 show the samples. The tubes are 1 3/4″ OD x 0.148 inch min. wall SA213-T22 material. Visual examination revealed the following:

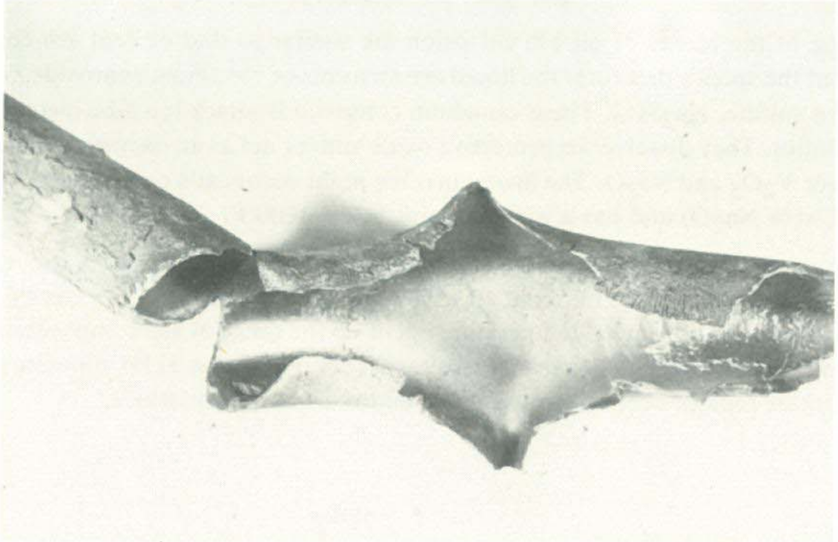


Figure 15 Failed Reheater Tube. Note the ID Scale and Thin Knife Edge Failure.

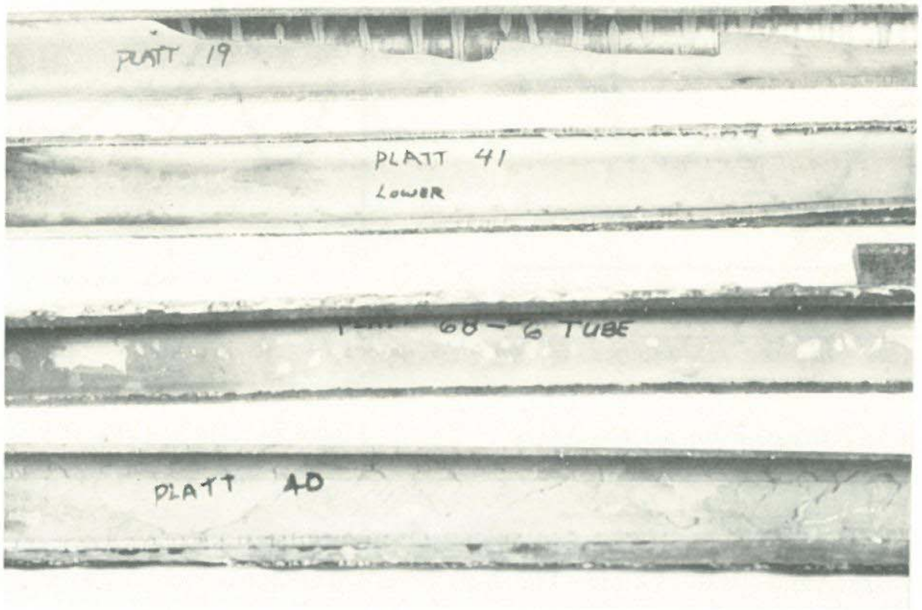


Figure 16 As-received Reheater Tubes. Note the Heavy Internal Oxide Scale.

A. The rupture was a wide open burst with the tube wall drawn to a knife edge at the failure.
B. The OD scale measured 0.011 inch and the deposit from the products of combustion was more than 0.04 inch thick.
C. Internal scale measured from 0.015 to 0.027 inch thick depending on the location.
D. The tube wall thickness 12 inches away from the failure and in the same plane measured 0.127 inch, 180° from this point measured 0.171 inch.
E. The remaining reheater tube sections showed ID scale varying from 0.018 to 0.012 inch thick and OD scale and deposits more than 0.04 inch thick.
F. Wall thickness measurements of these unfailed tubes varied from 0.170 to 0.127 inch depending on the sample and location.

Microstructural analysis of all these tubes showed complete spheroidization of the carbides indicating exposure to elevated temperatures for an extended period of time, Figure 17. For comparison, Figure 18, shows the microstructure of a new tube of the same alloy. Scale affects the tube metal temperature, as already noted several times, but wall thinning caused by ash corrosion increases the stress in the tube. Figure 19 shows the stress for 1% creep deformation in 10,000 and 100,000 hours for three temperatures for T-22 material.

1.)The ID scale raises the tube metal temperature by about 40°F, see Figure 3.

2.)Since the wall thickness has been reduced from specified 0.150 inch to 0.127 inch, about 15%, the hoop stress in the tube will be correspondingly increased.

The design stress for T-22 at 1050°F is 5800 psi[8]. Actual operating conditions at the time of rupture will be about 1100°F and a stress of 6700 psi. As can be seen from Figure 19, the time to give 1% creep deformation falls from 100,000 hours for the design conditions to about 10,000 hours for 1100°F and 6700 psi. The inescapable conclusion is that the cause of this reheater tube rupture is a combination of higher temperature caused by internal scale and wall thinning caused by ash corrosion caused by the higher temperature. Creep deformation and corrosion thin down the tube wall until the final rupture is caused by high temperature tensile failure.

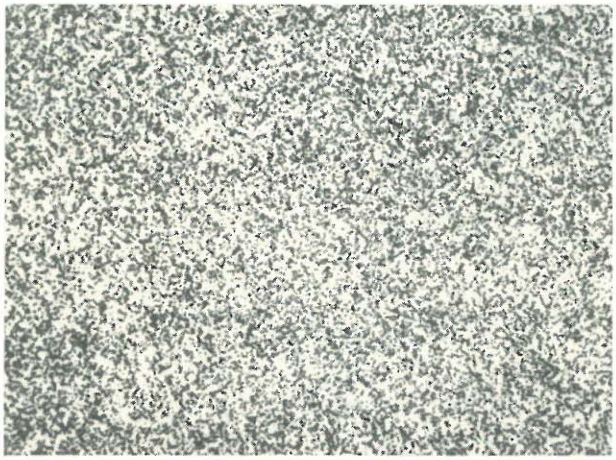


Figure 17 Microstructure Representative of All T-22 Reheater Tube Samples. The Structure is of Spheroidized Carbides and Ferrite. Typical of Long Term Exposure to Elevated Temperatures. (350X, Nital Etch)

Figure 18 Microstructure of As-received New T-22 Tubing. Compare the Changes in Carbide Morphology. (350X, Nital Etch)

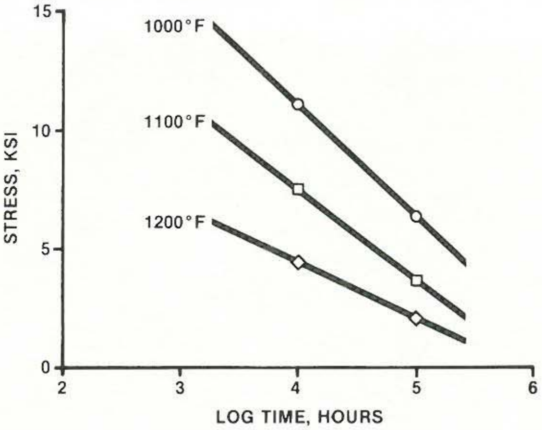


Figure 19 Stress for 1% Creep in SA 213-T22 Alloys

The second example is of a reheater tube from an oil fired boiler, SA213-T22, 2 inch OD x 0.148 min. wall.

Boiler Statistics:

Size:	550,000 lbs. steam/hr.
Steam Temperature:	1005°/1005°F
Steam Pressure:	1875 psig
Fuel:	No. 6 Oil
Length of Service	8 years

Visual examination of the tube revealed the following:

A. The tube is heavily coated with a thick scale and ash deposit.
B. The ID scale is 0.015 inch thick.
C. The tube is thinned for a significant portion of its circumference, Figure 20.
D. Micrometer measurements on a cleaned portion of the tube showed the wall thickness under the lug to be 0.152 inch and 180° away, the thinnest place, 0.020 inch.

Figure 20 Cross-sectional View of an As-received T-22 Reheater Tube. Note the Extensive Metal Wastage in the Lower Portion of the Photograph.

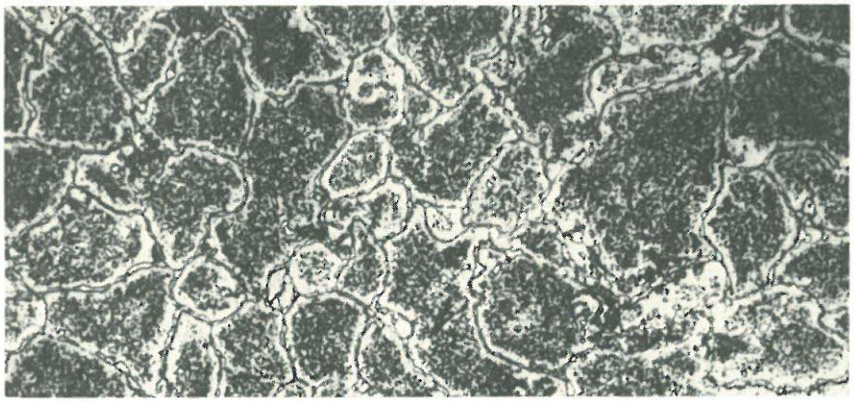


Figure 21 Microstructure Of the Tube Sample. Observe the Spheroidized Carbides and the Carbide Network Surrounding Each Ferrite Crystal. (500X, Nital Etch)

The microstructure shows that the sample is completely spheroidized with a carbide network around the ferrite grains, see Figure 21. Extensive tube wastage indicates a severe OD oil ash corrosion attack. Yet, this unit successfully operated for several years "without any corrosion problems". Chemical analysis of the deposit confirms the presence of V_2O_5, Na_2O and SO_3 in the ash, see Table III.

Vanadium as V_2O_5	**39.2%**
Sulfur as SO_3	**13.9%**
Sodium as Na_2O	**12.2%**
Iron as Fe_2O_3	**31.2%**
Carbon	**0.4%**

Table III Oil Ash Analysis

From the ash analysis, the amounts of V_2O_5 and Na_2O suggest that the melting point of this mixture is around 1100°F [52 mol% V_2O_5, 48 mol% Na_2O, and Figure 13]. The oxidation limit for T-22 is 1075°F. From the thermal analysis and Figure 3, the metal temperature increase is estimated to be nearly 50°F as a result of the 0.015 inch thick ID scale. Since the unit ran for several years without trouble, the tube OD temperature finally reached the melting point of the V_2O_5-Na_2O mixture in the oil ash, rapid corrosion, wastage, and failure followed.

CONTROL OF ASH CORROSION

In severe cases of superheater and reheater corrosion by coal ash, it has been found that shields added to the tube surface offer good results in preventing further metal loss. The trisulfates decompose at 1250° to 1300°F and cease to be liquids. By the use of high alloy shields, the effective tube metal temperature is raised above the range of stability of the trisulfates and rapid liquid ash corrosion can no longer continue. Figure 22 shows the corrosion rate of 321 stainless steel by molten trisulfate[9], note the sharp drop in corrosion rate above 1300°F.

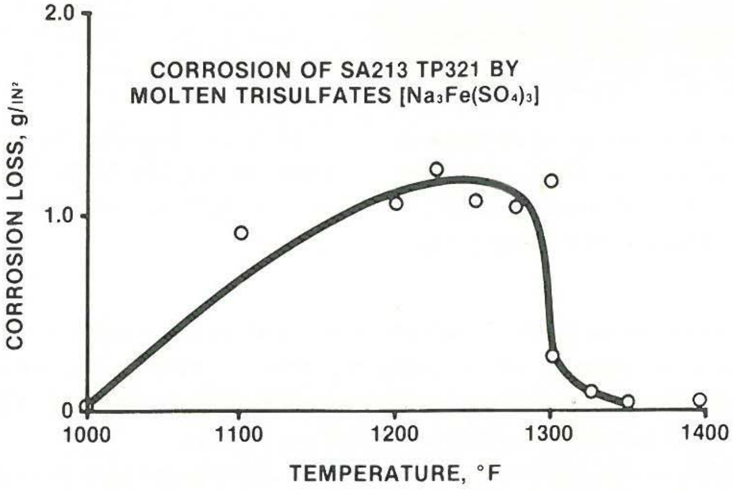


Figure 22 Corrosion Rate Versus Temperature for SA 213-TP321 in a Coal Ash Environment, from Reference 4.

The formation of complex sulfates with calcium and magnesium can occur and the melting points of these are higher than normal superheater and reheater tube temperature. Even simple $CaSO_4$ and $MgSO_4$ tie up the sulfur oxides in an innocuous form. Regardless of the exact chemistry, the presence of particular compounds of calcium and magnesium do reduce the corrosion. However, the use of additives has not been a great success in coal fired boilers as the volume of ash is so great and the chemistry so variable.

Magnesium oxide or hydroxide additives have been successful in the control of oil ash corrosion. The volume of oil ash, about 0.1% (a couple of pounds per ton of fuel) is small enough to make additive use a viable method of control. Magnesium oxide forms a sulfate with sulfur trioxide, a sulfite with sulfur dioxide, and a vanadate with vanadium pentoxide; all of the compounds have melting points out of range of normal temperatures of superheater or reheater tubes. Shields are not useful in the control of oil ash corrosion as none of the troublesome compounds decompose at temperatures low enough.

DESIGN ALTERNATIVES

There are several changes that can be made at the time a boiler is designed to reduce exfoliation in the high temperature steam lines.

1.) The most obvious is to reduce the oxidation limits of ferritic steels, or put another way, use more austerritic steels, stainless and Incoloy® materials. From measurements made on 321H stainless steel and T-22 less than 12 inches apart across a dissimilar weld, the stainless had about 40% of the internal scale that T-22 had. The actual measurements are 0.013 inch on T-22 and 0.005 inch on 321 after nearly 15 years of service. Figures 23 and 24 show the morphology of these oxides. Note the smooth oxide-metal interface on the T-22 and the wavy interface on 321. While the use of higher alloys will not completely prevent exfoliation, the condition will be reduced.

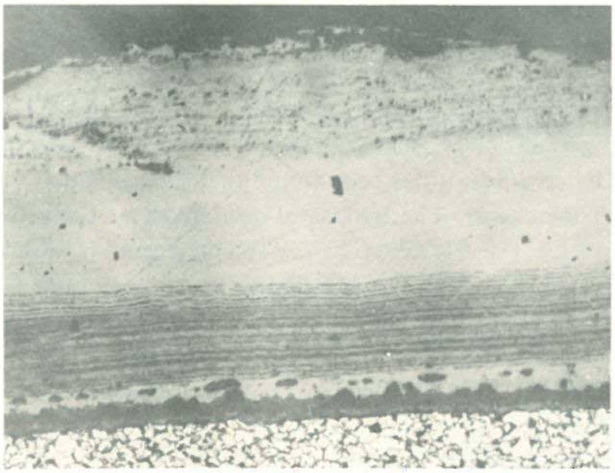


Figure 23 Interface Morphology of Steam Side Oxide on SA 213-T22 Tubing. The Scale/Metal Boundary is Planar With No Grain Boundary Penetration of the Oxide. (70X, Nital Etch)

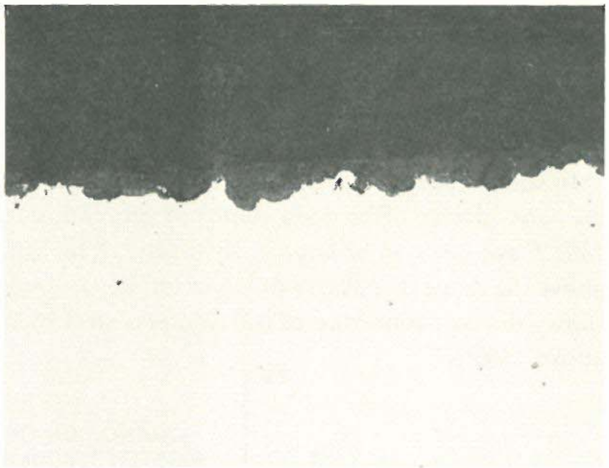


Figure 24 Interface Morphology of Steam Side Oxide on SA 213-TP321 Tubing. Note the Unevenness to the Scale/Metal Interface. (70X, Unetched)

2.) Since most of the oxide particles spall off from the ID of these high temperature steam lines during rapid temperature changes, either during cool down or start-up, the use of by-pass arrangements to reroute the first steam during start-up around the turbine will help. The oxide particles will be flushed out and harmlessly by-passed around the turbine.

3.) Thermal shock of the superheater and especially the reheater may be avoided during start-up by using drum steam through these portions of the boiler. The first steam back from the turbine to the reheater may be as cold as 300°F and a significant quench will occur from metal temperatures around 1100°F (or higher).

4.) Scale removal during the normal life by suitable chemical cleaning methods will return tube metal temperatures to their lower design value. Superheaters and reheaters should be designed as drainable type to facilitate chemical cleaning.

5.) Finally - don't abuse the boiler!

However, since we all work and sell in a very competitive market, these days especially, any of the above design improvements will increase our tender price. Unless Riley Stoker receives credit for reduced long term maintenance or extended superheater and reheater life, or the specifications require them, our offerings will not likely include any of them. At the time of purchase of a new boiler or when the specifications are written, more attention should be given to the operational and maintenance items of the unit you will live with over the next three or four decades. The lowest first cost is not necessarily the lowest life cost.

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