



BabcockPower

Technical Publication

Furnace Wall Corrosion Problems in Coal Fired Boilers

by

D. N. French

Director

Corporate Quality Assurance

RILEY POWER INC.

a Babcock Power Inc. company
(formerly Riley Stoker Corporation)

Presented at

National Association of Corrosion Engineers

Houston, Texas

March 22-26, 1982

RST-7



BabcockPower

Technical Publication

Furnace Wall Corrosion Problems in Coal Fired Boilers

by

D. N. French

Director

Corporate Quality Assurance

RILEY POWER INC.

a Babcock Power Inc. company
(formerly Riley Stoker Corporation)

Presented at

National Association of Corrosion Engineers

Houston, Texas

Marh 22-26, 1982

RST-7

FURNACE WALL CORROSION PROBLEMS IN COAL FIRED BOILERS

By

D. N. French, Director
Corporate Quality Assurance
RILEY STOKER CORPORATION
WORCESTER, MA 01606

Abstract

Furnace wall corrosion has been a problem in coal fired boilers for many decades. This paper presents a study of several examples of ash corrosion failures of furnace tubes. Common to all samples was the presence of carbon and sulfide corrosion products. EDX scans show only sulfur. However, a low melting point, 650-800°F, constituent of the ash was detected by a differential scanning calorimeter but was present in insufficient quantity to be identified by x-ray diffraction. A possible corrosion mechanism is presented that suggests tube wastage occurs by the formation of iron sulfide. A liquid phase, probably the pyrosulfates of sodium and potassium, is necessary to transport sulfur trioxide to the tube surface and carbon is necessary to reduce sulfur trioxide.

INTRODUCTION

The causes of ash corrosion in the high temperature portions of the superheater and reheater are better understood than ash corrosion of furnace walls. A liquid phase is necessary and the species that form the liquid are different for oil and coal fired boilers. For oil fueled boilers mixtures of vanadium pentoxide (V_2O_5) and sodium oxide (Na_2O) or vanadium pentoxide (V_2O_5) and sodium sulfate (Na_2SO_4) form liquids at superheater metal temperatures. These vanadium salts attack the metal surface by dissolving the normally protective oxide layer and act as an oxygen carrier to facilitate movement of oxygen from the flue gas to the tube metal surface. The lowest melting point in the V_2O_5 - Na_2O system is less than 1000°F at a composition of about 15 weight percent Na_2O ¹. The range of compositions that have melting points below 1100-1150°F is, of course, greater so that liquid ash corrosion may occur over a wider range of ash composition.

Mixtures of V_2O_5 and Na_2SO_4 also have melting points in the temperature range usually encountered in superheater and reheaters. The lowest melting point is below 1000°F at a composition of about 10 weight percent Na_2SO_4 ¹. Regardless of the species that forms the liquid phase, increasing the tube metal temperature to 1100-1150°F opens up the range of ash composition that will form liquids and increases the chances of having this problem.

The conventional understanding of superheater and reheater corrosion by constituents within coal ash centers on the alkali trisulfates ($Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$). Sodium and potassium iron trisulfate melt at about 1150°F and have frequently been identified in corrosion areas²⁻⁴. Mixtures of these two sulfates have melting points as low as about 1030°F. The composition of the mixture of these two will be dependent upon the relative amounts of sodium and potassium in the coal. Again, once the liquid phase forms, the protective iron oxide is dissolved and tube wastage occurs. Corrosion proceeds either by the participation of iron oxide

in the formation of the trisulfate or the ease of transport of oxygen to the tube metal surface by the liquid phase to form iron oxide at the expense of the tube.

While the understanding of high temperature corrosion of superheaters and reheaters by liquid phases within the coal ash is reasonably well understood, no comparable understanding of furnace wall corrosion is available. Furnace tube metal temperatures are about 750-800°F, well below the melting point of either of the trisulfates previously mentioned. Since a liquid phase is presumed necessary, it has been convenient to blame furnace corrosion on sodium or potassium pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$)¹ but no definite evidence has been presented. The melting point of $\text{Na}_2\text{S}_2\text{O}_7$ is 754°F and K_2SO_4 is less than 570°F¹. Mixtures of the two presumably have lower melting points yet.

For the past 25 years, the Metallurgy Laboratory of Riley Stoker Corporation has been investigating boiler component failures. Recently, the past decade or so, several furnace wall tube failures caused by coal ash corrosion have been studied. The perspective of the following paper is that of failure analyses done over a number of years. The information provided with the tube samples is usually sketchy and incomplete. However, what information is provided and what is learned from the failures does follow a consistent pattern.

TUBE FAILURES

The examples illustrate the features common to all of the samples studied. The failures exhibit the following:

- 1) The circumferential penetration of the corrosion products on the fireside of the furnace tube is displayed. Figure 1 shows the tube fireside surface with the ash deposit and scale removed, Figures 2 and 3 show longitudinal cross sections. Note, the deep fingerlike penetrations into the tube surface.
- 2) Sulfur prints show the corrosion deposits within the tube wall penetrations and on the tube surface to contain sulfides. Figure 4 shows a circumferential and longitudinal sulfur print.
- 3) The O.D. ash deposit appears to be in two layers, a reddish brown outer layer and a dark black glassy appearing inner layer.
- 4) The ash deposits contain carbon as well as the usual oxides associated with coal ash, see Table I.

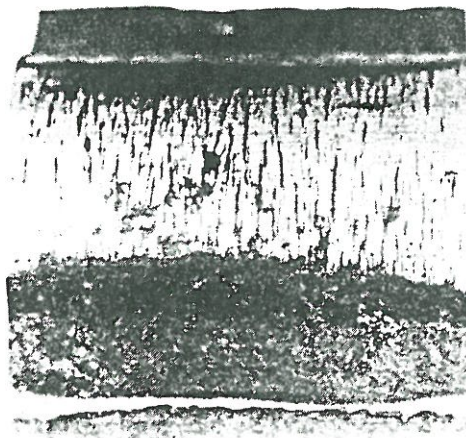


Figure 1 Surface of a Furnace Wall Tube That Shows the Circumferential Sulfide Wall Penetrations, About 4x.

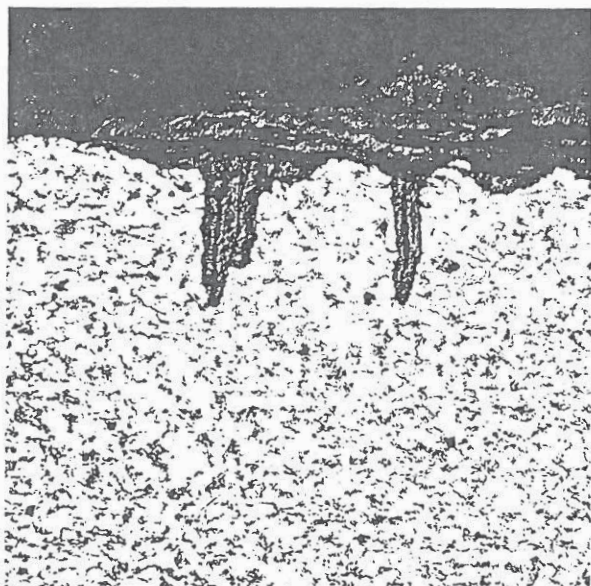


Figure 2 Longitudinal Cross Section of the Tube in Figure 1, 2% Nital Etch 100x.

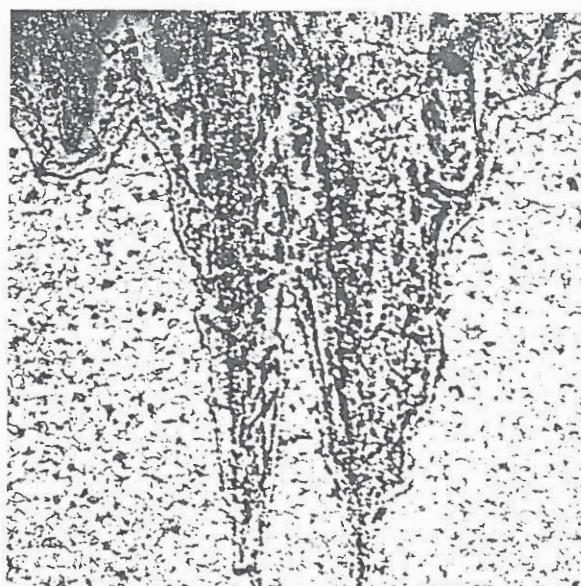


Figure 3 Another Example of the Deep, Finger-like Penetrations Into the Tube Surface, 2% Nital Etch, 100x.



Figure 4 Sulfur Print That Shows Sulfide Distribution in the Longitudinal and Circumferential Cross Sections.

Sodium as Na ₂ O	0.4%	0.4%
Silicon as SiO ₂	33.6	8.6
Aluminum as Al ₂ O ₃	19.0	11.8
Sulfur as SO ₃	1.9	2.3
Calcium and Magnesium as CaO	1.1	0.4
Iron as Fe ₂ O ₃	36.2	67.6
Potassium as K ₂ O	1.6	0.4
Carbon	0.64	1.23
Melting Point (DSC measurement)	770°	635° & 730°F

Table I Ash Deposit Analyses

ANALYSIS

Several samples were submitted for detailed examination of the corrosion deposits attacking the tube surface. The analyses were performed by Energy Dispersive X-Ray (EDX) Spectroscopy in conjunction with a scanning electron microscope (SEM). Figure 5 shows the corrosion penetration area scanned and Figure 6 shows the x-ray map for sulfur. The only other elements detected were silicon, chromium and iron. No sodium, potassium, or chlorine was observed. The amounts of sodium and potassium are below the limits of detectability, from Table I, 0.29%Na and 1.3% and 0.33%K. Even though none of these elements was found, the presence of both in the ash suggests that pyrosulfates are possible.



Figure 5 The Corrosion Penetration Scanned by EDX for S, 52x.

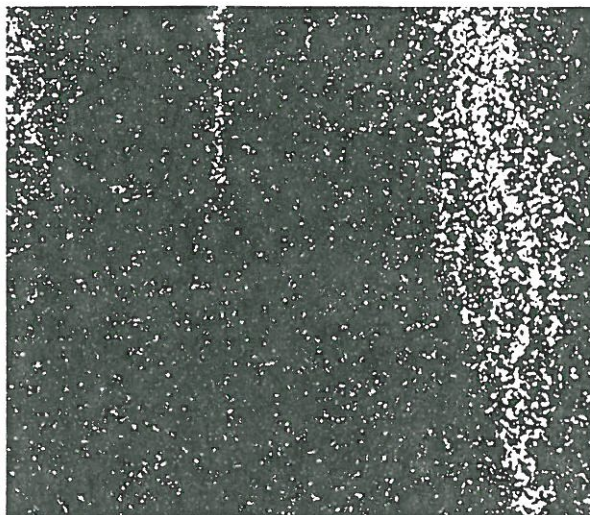


Figure 6 EDX Scan for Sulfur, Note the Concentration of Sulfur in the Corrosion Products, 52x.

A Differential Scanning Calorimeter (DSC) was used to determine melting points that may occur. Melting points were observed between 630 and 770°F. X-ray diffraction was performed but the only lines that were detected were attributable to the iron oxides. The conclusion is that low melting point phases are present but in such low quantity as to be unidentifiable by the methods of analyses used.

DISCUSSION

All of the coal ashes studied contain carbon and the sulfur is present as a sulfide as noted from sulfur prints. The suggestion is a corrosion attack occurs that requires strongly reducing conditions at the tube surface but less so where SO₃ and pyrosulfates exist. Carbon is required so the sulfides that form are stable. Carbon can enter the ash deposit either as unburned coal or the deposition from carbon monoxide.



Low temperatures favor the reaction as given above.

Table II lists the free energy of formation at 800°F of several species that may participate in the corrosion attack. Table III lists possible reactions and the associated free energy change at 800°F. It should be noted that a negative free energy does not mean that the reaction will occur, only that it can occur.

CO	- 41,500	cal/mol
CO ₂	- 94,500	
FeS	- 27,100	
SO ₂	- 74,300	
SO ₃	- 82,100	
Fe ₂ O ₃	- 152,200	

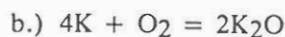
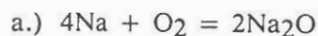
Table II Free Energy of Formation at 800°F

1. $\text{Fe} + 3\text{C} + \text{SO}_3 = \text{FeS} + 3\text{CO}$	$F^\circ = - 69,500$
2. $\text{Fe}_2\text{O}_3 + 9\text{C} + 2\text{SO}_3 = 2\text{FeS} + 9\text{CO}$	$F^\circ = - 111,300$
3. $2\text{Fe} + 3\text{C} + 2\text{SO}_3 = 2\text{FeS} + 3\text{CO}_2$	$F^\circ = - 91,400$
4. $2\text{Fe}_2\text{O}_3 + 9\text{C} + 4\text{SO}_3 = 4\text{FeS} + 9\text{CO}_2$	$F^\circ = - 326,100$
5. $2\text{CO} = \text{CO}_2 + \text{C}$	$F^\circ = - 11,500$
6. $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$	$F^\circ = - 7,800$

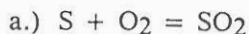
Table III Potential Reactions and Free Energy Change at 800°F

The corrosion probably proceeds in several stages:

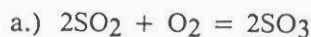
1) Na and K in the coal become oxides - in the flame.



2) Sulfur in the coal becomes sulfur dioxide - in the flame.



3) Sulfur dioxide becomes the trioxide - catalyzed on the tube surface or occurs in the low temperatures near the furnace wall.



4) Pyrosulfates form on the tube surface.

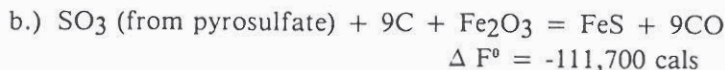
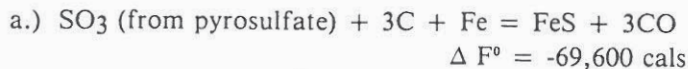


5) Carbon deposits within the ash either by:

a.) unburned coal



6) Tube wastage occurs by either:



An alternate scheme involves chlorides that would form low melting point iron chloride or mixtures with other metals. Once these liquids form at the tube surface, the corrosion proceeds in a similar fashion, SO_3 is transported by the liquid to the ash-metal interface where tube wastage occurs by the same reactions as given in item 6 above.

The necessary conditions are:

- 1) The temperatures at the tube surface must be high enough so mixtures of $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$ are molten. The exact temperatures depend on the relative amounts of sodium and potassium in the coal. Tube metal temperatures increase as internal scale and/or deposits form. Scale deposits on the I.D. of the tube reduces heat transfer from the flue gas to the steam-water emulsion and thus, raise the tube metal temperature.
- 2) Carbon is required to maintain, on a micro-environmental scale at least, reducing conditions. Since not all furnace tubes show this type of corrosion, it appears that carbon from unburned coal is unlikely to be sufficiently active or well dispersed to give the needed reducing conditions at the tube metal-deposit interface. The deposition of carbon by carbon monoxide decomposition would give a finer, more uniform and perhaps a more "active" form of carbon within the deposit. It may be that carbon is formed only at the tube metal surface and thus, the pyrosulfates can be maintained in the bulk and sulfides at the tube interface where corrosion occurs. The suspicion is that CO is transported by the liquid ash constituent to decompose to carbon and CO_2 and the CO_2 is transported away.
- 3) Liquid is necessary to transport reactants to and the gaseous corrosion products away from the metal surface as it corrodes. Without the liquid present, reaction proceeds too slowly to be troublesome.
- 4) Na_2O and K_2O circulate within the deposit as the transport vehicle for the sulfur as SO_3 in the pyrosulfates. This suggests that the low melting phase actively participates in the corrosion mechanism in four ways:
 - a.) As the necessary liquid.
 - b.) As the carrier for sulfur as the trioxide to the metal surface to give the sulfides as a corrosion product.
 - c.) As the carrier for carbon, the needed reducing agent to turn SO_3 into sulfide corrosion products.
 - d.) As a liquid necessary to dissolve or penetrate the protective oxide film.

ACKNOWLEDGEMENTS

I should like to thank Mr. J. H. Bauer of Riley Stoker for the metallography, Mr. A. Connors of Manlabs, Inc. for the DSC studies, and Mr. D. Shaw of Mass. Materials Research for the EDX analysis.

REFERENCES

1. W.T. Reid, "External Corrosion and Deposits, Boiler and Gas Turbines," American Elsevier Publishing Company, Inc., New York, 1971.
2. W.T. Reid, R.C. Corey, and B.J. Cross, Trans ASME, May, 1945, p. 279-288.
3. R.C. Corey, B.J. Cross, and W.T. Reid, Trans ASME, May 1945, p.289-302.
4. R.C. Corey, H.A. Grabowski, and B.J. Cross, Trans ASME, November, 1949, p. 951-963.