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# Ash Corrosion Under Reducing Conditions

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# ASH CORROSION UNDER REDUCING CONDITIONS

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## ABSTRACT

*Observations and examples of both oil and coal ash corrosion under reducing conditions are given. Similarities between corrosion caused by the two types of fuel are:*

1. *Iron sulfide is found in the deposits adjacent to the tube metal.*
2. *Carbon is present in the deposits to give, at least on a microenvironmental level, a reducing atmosphere.*
3. *Some constituent of the ash is present as a liquid to aid in the transport of carbon and sulfur (probably sulfur dioxide) to the metal surface to form iron sulfide and carbon monoxide.*
4. *Severe and rapid tube wastage occurs and leads to premature failure.*

## INTRODUCTION

Observations have been made for 40 years or so on the formation of iron sulfide (FeS) during corrosion and wastage of furnace tubes in coal fired boilers. [1] [2] [3] The usual explanation is that, in large part, the iron sulfide comes from the pyrites in the coal which falls unburned to the hopper slopes. Pyrites provide substantial amounts of FeS in the corrosion deposit and tube wastage by reacting with the tube metal.

$$FeS_2 + Fe = 2\,FeS$$

Iron sulfide is also formed by the direct reaction between the tube metal and the trisulfates ($Na_3Fe(SO_4)_3$) of liquid coal ash.[4] The source of sulfur is obviously the pyrites and other sulfur compounds in the coal, and several chemical reactions have been suggested for the loss of metal and the formation of sulfides in corrosion deposits.

Even after four decades and considerable understanding of the problem, on occasion, coal ash corrosion occurs in the lower portions of the furnace that leads to severe tube metal loss and iron sulfide in oil fired boilers on superheater tubing. The following presents observations on failed (i.e. corroded and ruptured) superheater tubes returned to Riley Stoker Corporation for metallurgical analysis. For comparison similarly failed furnace tubes from a coal fired boiler are given.

### *Oil Fired Boiler Superheater Tubes*

Figure 1 shows a portion of a superheater tube from an oil fired boiler displaying the liquid ash attack and tube wastage. Severe metal loss leads to the failure. Chemical analysis of the scale deposits are given in Table I.

| | |
|---|---|
| V as $V_2O_5$ | 64.2% |
| S as $SO_3$ | 1.5% (average deposit composition) |
| S as $SO_3$ | 6.5% (at metal-deposit interface) |
| Na as $Na_2O$ | 16.9% |
| Ca as CaO | 0.1% |
| Mg as MgO | 4.0% (may use MgO as fuel additive) |
| Cl | 20 ppm |
| C | 0.01-0.25% (2 samples) |

**TABLE I DEPOSIT ANALYSIS, SUPERHEATER TUBE.**

*Figure 1 External Surface Showing of a Superheater Tube From an Oil Fired Boiler Showing Severe Metal Wastage*

Note the large differences in sulfur content between the average deposit composition and the concentration at or near the tube metal-deposit interface.

X-ray diffraction analysis was performed to identify specific compounds in the scale. Table II.

Microstructural analysis shows the penetration of the metal by the corroding species, Figure 2. A sulfur print, Figure 3, of the cross section of the tube showed a high concentration of sulfides at the tube metal-scale deposit interface. [To prepare a sulfur print, dip a piece of photographic paper in 2-3% sulfuric acid solution, drain off the excess acid, press the rough polished (120 grit abrasive) sample surface on to the photographic paper, hold for 2-3 minutes and remove carefully; any sulfides present release $H_2S$ when reaction occurs with the sulfuric acid. $H_2S$ turns the silver salts on the photographic paper black to leave an imprint of the sulfide distribution on the specimen surface.] X-ray diffraction analysis confirmed the presence of iron sulfide, FeS, on the superheater tube, Table II.

FeS
$Fe_2O_3$
$Na_2SO_4$
$Mg_2SiO_4$ or $MgSiO_3$
$Fe_3O_4$
$FeCl_2$ or $FeCl_3$
$V_2O_5$

**TABLE II COMPOUNDS PRESENT IN SUPERHEATER TUBE DEPOSIT.**

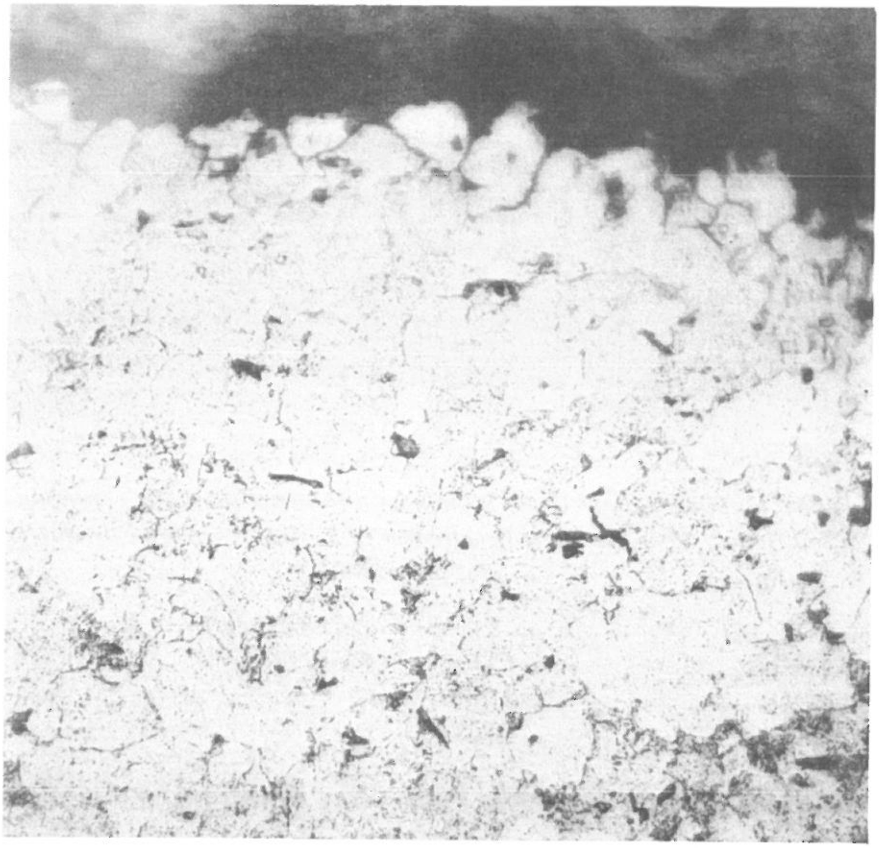

*Figure 2 Microstructure of the Superheater Tube From Figure 1, Note the Intergranular Penetration of the Sulfide Corrosion Product. 250X*

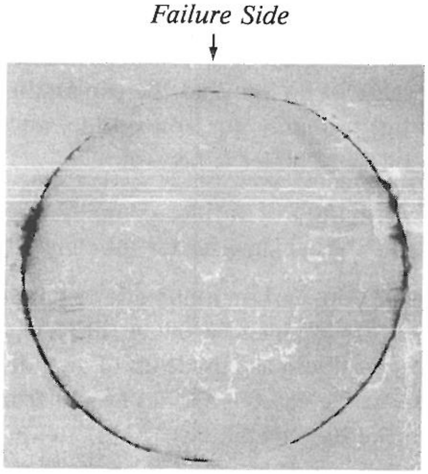

*Figure 3 Sulfur Print of the Cross Section of Superheater Tube From Figure 1. Note the Heavy Concentration of Sulfides Around the Perimeter of the Tube.*

*Coal Fired Boiler Furnace Tube*

Figure 4 shows a longitudinal section of a failed furnace tube of a coal fired boiler. Table III lists the composition of the scale deposit.

The compounds identified by X-ray diffraction analysis are $Fe_3O_4$, $Fe_2O$, FeS

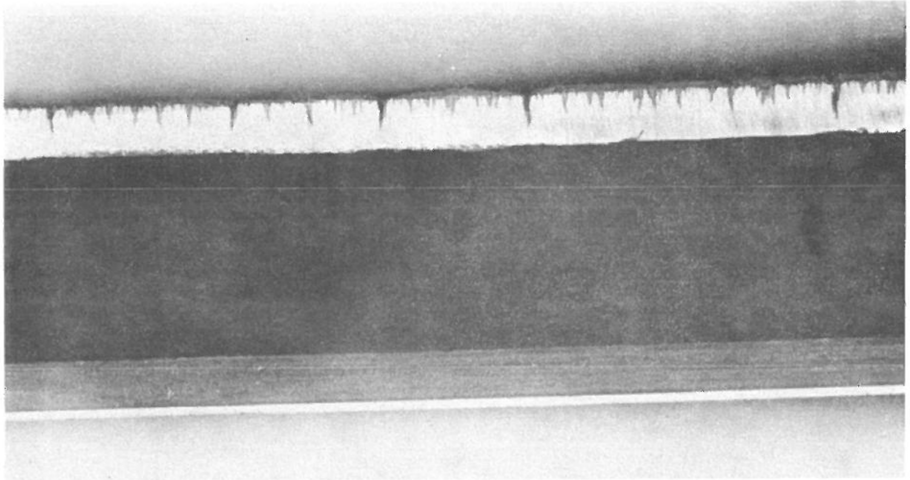

*Figure 4 Longitudinal Cross Section of a Furnace Wall Tube From a Coal Fired Boiler. Note the Deep Penetration of Sulfide Corrosion Products Into the Tube Wall.*

| | | | |
|---|---|---|---|
| Si as $SiO_2$ | 8.6% | CaO and MgO | 0.4% |
| Fe as $Fe_2O_3$ | 67.6% | $Na_2O + K_2O$ | 0.8% |
| Al as $Al_2O_3$ | 11.8% | Cl | 0.2% |
| S as $SO_3$ | 2.3% | C | 1.2% |

**TABLE III SCALE DEPOSIT ANALYSIS, COAL FIRED BOILER FURNACE TUBE.**

## DISCUSSION

In both cases severe liquid ash corrosion lead to tube metal wastage and wall thinning until rupture occurred. In both cases small amounts of carbon were present in the ash deposits so, at least on a microenvironmental scale, reducing conditions existed. Since coal contains some iron sulfide, $FeS_2$, it would seem likely that the observations of 40 years or so ago and the explanation of Reid hold true in this case also. However, since oil contains sulfur but probably not iron sulfide, another explanation for the formation of FeS on superheater tubes from an oil fired boiler is necessary.

Table IV lists the free energy of formation of various compounds likely to be formed on the superheater tube at 900°K (about 1100°F, typical external superheater tube metal temperature).

Several possible reactions among carbon, carbon monoxide or dioxide, sulfur dioxide, iron, iron oxide are conceptually possible to give iron sulfide as an end product. In all cases the iron comes from the tube metal and leads to metal loss. The presence of liquid ash made up of vanadium pentoxide, sodium oxide or sulfate mixtures may be necessary to transport the gaseous species to and from the reaction sites and to dissolve the protective oxide films that form on the tube metal.

| COMPOUND | $F^0$ (900°K) |
|---|---|
| CO | -45,800 |
| $CO_2$ | -94,600 |
| $SO_2$ | -70,800 |
| $Fe_2O_3$ | -140,300 |
| FeS | -25,500 |

**TABLE IV FREE ENERGY OF FORMATION OF SEVERAL COMPOUNDS.**

Several possible reactions among carbon, carbon monoxide or dioxide, sulfur dioxide, iron, iron oxide are conceptually possible to give iron sulfide as an end product. In all cases the iron comes from the tube metal and leads to metal loss. The presence of liquid ash made up of vanadium pentoxide, sodium oxide or sulfate mixtures may be necessary to transport the gaseous species to and from the reaction sites and to dissolve the protective oxide films that form on the tube metal.

1. $2C + SO_2 + Fe = FeS + 2CO$ $\Delta F^{0}$ (900°K) -45,300 cals
2. $7C + 2SO_2 + Fe_2O_3 = 2FeS + 7CO$ $\Delta F^{0}$ (900°K) -89,700 cals

Reaction 1 may occur if the liquid ash dissolves the iron oxide exposing fresh metal for corrosion. Reaction 2 shows that removal of iron oxide is not necessary if carbon is present to reduce both iron and sulfur oxides. The fact that the free energy of formation, $\Delta F^{0}$, is negative for these reactions does not mean that the reaction will occur, only that it can occur.

3. $2CO + SO_2 + Fe = FeS + 2CO_2$ $\Delta F^{0}$ (900°K) -52,300 cals
4. $7CO + 2SO_2 + Fe_2O_3 = 2FeS + 7CO_2$ $\Delta F^{0}$ (900°K) -110,700 cals

Since small amounts of CO are usually present in the vicinity of the lower portion of the superheater and FeS does not form, it appears likely that the presence of both carbon, to give reducing conditions at the corrosion site, and the liquid slags (made up of $V_2O_5 + Na_2O$ or $V_2O_5 + Na_2SO_4$) for ease of gaseous transport and oxide solution, are necessary for the formation of iron sulfide that can form by Reaction 1 or 2 above.

It seems probable that reducing conditions are necessary for the formation of FeS, otherwise $Fe_2O_3$ and $SO_2$ will form. The presence of carbon in these ash deposits assures that, on a microenvironmental scale where the chemical reactions are proceeding, reducing conditions are maintained. Also needed is a liquid component of the ash, pyrosulfates ($Na_2S_2O_7$) or trisulfates ($Na_3Fe(SO_4)_3$) in the case of coal fired boilers and mixtures of vanadium pentoxide, sodium oxide, and/or sodium sulfate, in the case of oil fired boilers. Reducing conditions may exist within the ash deposit even though measuring devices used by the boiler operator indicate, overall, proper and complete combustion has occurred.

## CONCLUSION

Similar to observations made many years ago on furnace tubes of coal fired boilers, superheater tubes of oil fired boilers may contain FeS as a corrosion product if conditions are suitable. Such conditions include the presence of carbon to give reducing conditions at the corrosion site and a liquid ash species to facilitate the transport of gaseous reactant to the corrosion site and the solution of protective oxide films.

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