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High Temperature Corrosion Problem of Boiler Components in presence of Sulfur and Alkali based Fuels

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Abstract. Material degradation and ageing is of particular concern for fossil fuel fired power plant components. New techniques/approaches have been explored in recent years for Residual Life assessment of aged components and material degradation due to different damage mechanism like creep, fatigue, corrosion and erosion etc. Apart from the creep, the high temperature corrosion problem in a fossil fuel fired boiler is a matter of great concern if the fuel contains sulfur, chlorine sodium, potassium and vanadium etc. This paper discusses the material degradation due to high temperature corrosion in different critical components of boiler like water wall, superheater and reheater tubes and also remedial measures to avoid the premature failure. This paper also high lights the Residual Life Assessment (RLA) methodology of the components based on high temperature fireside corrosion. of different critical components of boiler.

Keywords. Boiler, high temperature corrosion, residual life assessment, water wall, superheater and reheater.

1 Introduction

Residual Life assessment (RLA) and life extension of aging plants is largely concerned with material degradation of high temperature components. Material ageing/degradation of in service components are becoming major issue for techno economical justified Renovation and modernization programme. Ferritic chromium-molybdenum steels (generally referred to as "Cr-Mo" steels) are very much used in the high temperature components of the steam generator/boilers for fossil fuel and nuclear power plant. [1] Generally 1.0 Cr-0.5 Mo steel, 2.25 Cr-1 Mo steel and 9 Cr-1 Mo steels are used for the construction of superheater and reheater tubes in advanced thermal power plant. These steels have good creep resistance as well as oxidation resistance at high temperature. These steel also exhibit good combination of mechanical properties, formability, weldability for manufacturing of pendent tube panels and horizontal tube banks of superheater and reheater. Different damage mechanisms like creep, fatigue, erosion and corrosion are becoming operative during operation and causes material degradation and finally leads to failure [2]. The high temperature corrosion problem in coal-based power plants is prevalent damage mechanism, which finally affects the availability, reliability, and safety of the components. Oxidation is the predominant mode of corrosion in most of the industrial environments. During oxidation, the formation of protective oxide layer resists the further corrosion attack. However this protective layer is non protective due to the presence of sulfur, chlorine, sodium and potassium in the fuel and corrosion takes place through the cracked/spalled unprotective layer [3]. This paper reviews different high temperature corrosion mechanism of critical components of boiler like water wall, superheater, reheater tubes etc. Probable corrective actions are also suggested to minimize the high temperature corrosion rate. This paper also highlights the damage assessment and Residual Life Assessment (RLA) methodology of the boiler tubes due to high temperature corrosion.

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2 High Temperature Corrosion in Boiler Components

The function of boiler is to convert water into superheated steam, which is further delivered to a steam turbine. Coal, oil and natural gas with preheated air is burnt in the furnace. The combustion gases flow up through the furnace and evaporate water into steam inside the furnace waterwall tubes.The gas flow at the roof of the furnace is made horizontal across the banks of superheater and reheater tubes. The gases are then move downward, where it encounters horizontal low temperature superheater and the economizer [4]. The gas flow past the fire side of the waterwall, pendent superheater and reheater, horizontal superheater and reheater and econimiser tube and exists from the boiler.

The high temperature corrosion of the different critical components of the boiler is mainly classified into two broad categories

1. Steam side oxidation at inner side of superheater and reheater tubes.

2. Fire side corrosion of waterwall, superheater and reheater tubes.

2.1 Steamside Oxidation at Inner Side

The superheater and reheater suffer from steam oxidation on the inner surface. It is the formation of oxide scale at higher temperature at the inner side (steam side) of the tubes. The growth of the oxide scales is a function of temperature and time. The steam side oxide scale of a typical superheater tube is shown in Figure 1. Different standard rate laws are used to estimate the tube metal temperature. This tube metal temperature is used in Larson- Miller parameter for estimation of Residual Life of the components. Several expressions have been suggested by and Paterson and Rettig [5] and Rehn and Apblett [6] to describe oxide scale growth kinetics to estimate the mean tube metal temperature. The expressions are given below:

1. $\log x = -7.1438 + 2.1761 \times 10^{-4} T\ (20 + \log t)$ for 1–3 % steel [7]
2. $\log x = -6.8398 + 2.83 \times 10^{-4} T\ (13.62 + \log t)$ for 2.25 Cr-1 Mo steel [8]

where,
$x =$ Steam side oxide scale thickness in mils,
$T =$ Mean operating temperature $^{0}R = (F + 460)$ and
$t =$ Service time in hours.

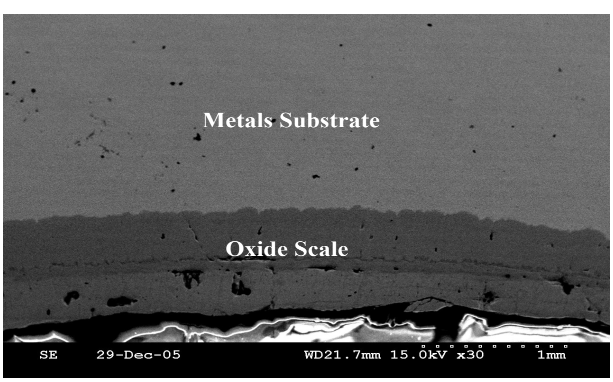

Figure 1. Oxide scales at inner side of superheater tube.

2.2 Fireside Corrosion in Boiler Components

The different critical components of boiler like Water wall, Superheater and Reheater tubes suffer fireside corrosion. Corrosive impurities (i.e. alkali metals, sulfur or vanadium) present in the fuel are responsible for the fireside corrosion of critical components of the boiler. These impurities can lead to the formation of non-protective scales or can disrupt normally protective scales. The principal damage mechanism is oxidation and hot corrosion.

2.2.1 Fireside Corrosion in Water Wall Tubes

The material degradation of the boiler tubes can result from the fireside corrosion that causes wastage of the external metal surface. One possible mode of the fireside corrosion exists due to the incomplete combustion of the fuel near burner zone. The rate of corrosion is drastic in reducing atmosphere. The atmosphere contains high level of carbon monoxide and also delivers unburnt carbon particle of the coal to the tube surface. The incomplete combustion of the coal releases volatile sulfur compounds and chloride compounds (if present) which cause sulfidation and accelerated metal corrosion. Sodium and potassium pyrosulfate compounds (if sodium or potassium is present in the fuel) which have low melting points (below 698 K) are generally responsible for the attack. The characteristics features of the corrosion are formation of thick iron oxide and iron sulfide scales. The tube wall thinning is due to the wastage of external metal from the surface. Tube thinning eventually leads to the premature failure of the tubes.

2.2.2 Fireside Coal Ash Corrosion of Superheater and Reheater Tubes:

Fireside corrosion of superheater and reheater tubes are associated with liquid ash deposits at higher temperature. This type of corrosion can cause wall thinning and contribute to stress rupture failure by increasing the hoop stress. This type of liquid phase corrosion occurs in the temperature range from 868 K to 978 K and is associated with deposit related molten salt attack beneath the surface deposits, if the fuel contains sulfur, sodium and potassium. The low melting salt of the type alkali iron trisulfate [(Na, K) $FeSO_4$] are deposited to the fireside of the tubes and cause the external wastage of the tubes [1]. The fireside deposits in superheater tubes in a typical thermal power plant boiler is shown in Figure 2. The alkali iron trisulfate forms by reaction of alkali sulphates with iron oxide in the presence of SO_3 and have a maximum melting temperature (1 : 1 mixture of sodium and potassium salts) of 825 K, where as melting points of simple sulfates are 1157 K for Na_2SO_4 and 1342 K for K_2SO_4. Although the SO_3 levels in the flue gas are expected to be much lower, catalytic oxidation of SO_2 in the stagnant zones beneath a layer of deposit is believed to generate SO_3 levels sufficiently high to favour the formation of liquid trisulfates at temperature up to 978 K [7]

The coal ash corrosion is temperature dependent. Stringer [8] shows that the corrosion increases with the increase of temperature reaches up to a certain temperature and then decreases with temperature for low alloy ferritic steel (SA 213 T22) and austenetic stainless steel (321 grade). The rate of corrosion is less in case of 321 stainless steel grade in comparison to low alloy ferritic steel (T22 grade) [8] This is due to the higher Cr content of stainless

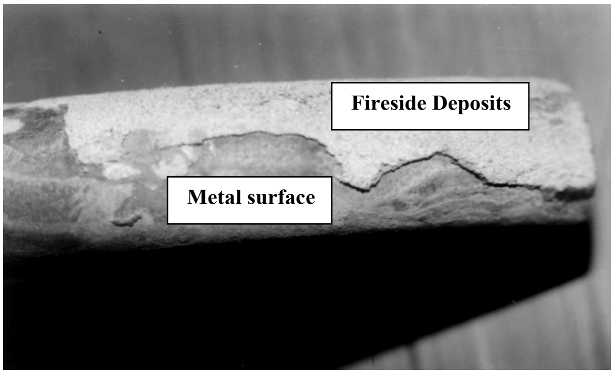

Figure 2. Fireside ash deposits on the super heater tube.

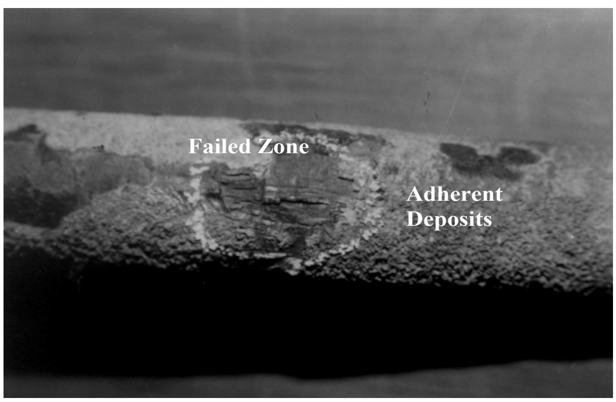

Figure 3. Typical premature high temperature corrosion failure of superheater tube.

steel (321 grade) in comparison to the T22. The higher Cr content will minimize the corrosion rate. The maximum corrosion attack is found at 923 K. The rate of corrosion increases with the increase of temperature due to the formation of molten sulfate phase and reaches a maximum around 923 K. The corrosion rate then decreases as a result of dissociation of sulfate phase into solid deposits due to insufficient pressure of SO_3.

The high temperature coal ash corrosion of superheater and reheater tubes is associated with tube wall thinning from the external surface and premature failure occurs due to tube wall thinning. The premature failure of the superheater tube of a thermal power plant boiler is shown in Figure 3. Grain boundary sulfide attack around the failure zone is observed in metal- deposits interface as a result of drastic corrosion (sulfidation) as shown in Figure 4.

2.2.3 Fireside oil ash corrosion of Superheater and Reheater tubes:

The corrosion in different oil fired boiler occurs when molten slag of the oil contains vanadium compounds. Accelerated corrosion occurs by fluxing action of molten sodium-vanadium compounds on the protective oxide scale

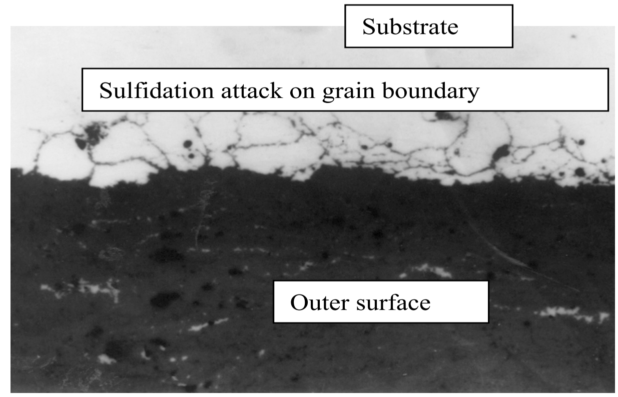

Figure 4. Grain boundary sulfide attack on eh outer surface of the superheater tube.

on the tube steel. This corrosion is particularly aggressive when fuel contains vanadium, sulfur and sodium. Greater wastage material is observed when the tube metal operates at temperature above 863 K. The severity of oil ash corrosion is affected by temperature, the amount of vanadium, sulfur and sodium, the amount of excess air available for the formation of V_2O_5. The highest corrosion occurs when the ratio of sodium oxide (Na_2O) to vanadium oxide (V_2O_5) is about 1 : 5. Increases in the tube metal temperature due to steamside oxidation can also lead to the premature failure due oil ash corrosion.

3 Corrective Actions to Minimize the High Temperature Fireside Corrosion

Several corrective actions are adopted to minimize the high temperature fireside corrosion [1]. These include

1. shielding the tubes with clamp-on tube protectors,
2. using thicker tubes of the same material,
3. coating the tube with thermal sprayed corrosion resistant material,
4. blending coals to reduce corrosive constituents in the ash,
5. replacing the tubes with higher grade alloy (high Cr content alloy),
6. co-extruded tube steel,
7. lowering the metal temperature by lowering the final steam outlet temperature,
8. redesigning the superheater or reheater to modify the heat transfer rates and lower the metal temperature.

Using thicker tubes of the same material and shielding tubes with clamp-on tube protectors have limited application because of continued and/or additional cost. Lowering the final steam outlet temperature limits the lower unit capacity which is not economic to the cost of generation of electricity. Coating tubes with thermal sprayed corrosion resistant materials provides only short-term protections and recoating is necessary time to time during unit shut down for continued operation without premature failure of the tube.

Increasing the chromium content of the steel at the outside surface improves its resistance to high temperature corrosion, but Cr alone will not give high temperature creep strength alone. The other alloying element like Mo will improve creep properties, oxidation resistance is not good as chromium. Co-extruded tubing with a creep resistant inner layer and corrosion resistant outer layer has been successfully used in different countries. A substrate of 310 H austenitic stainless steel over an outer layer of 25 Cr-20 Ni Steel can be used. The initial cost of the co-extruded tube material is estimated to be four to five times greater than that of single layer austenitic stainless steel, so that application of co-extruded tubes may depend on life cycle cost including additional outage cost.

The use of magnesium compound to minimize the oil ash corrosion is found to be economically feasible. Addition of magnesium compounds results in the formation of magnesium vanadate complex (MgO_6V_2). The melting point of the compound is high enough to prevent the existence of the liquid phase in superheater and reheater section. The oil soluble form of magnesium, magnesium based additives, combination of other metals in oil soluble form and dry powder have been found to be effective in reducing oil ash corrosion. The use of high grade alloy containing Cr and co extruded tubing of creep resistant inner layer and corrosion resistant outer layer is much more effective to minimize the oil ash corrosion.

4 Residual Life Assesment Approach Based on High Temperature Fire Side Corrosion

In case of superheater/reheater tubes, fireside corrosion can lead to decrease in wall thickness and consequence increase in stress and decrease in rupture life. Moles and Westwood have proposed model for estimation of residual life under wall thinning due to high temperature fireside corrosion [9]. The model for estimation of residual life is given as follows.

$$t_{\mathrm{nr}} = \frac{1}{K'}\left\{1 - [1 + K'(n-1)t_{\mathrm{r}}]\frac{1}{(1-n)}\right\} \tag{1}$$

where K' is wall thinning rate,

$n =$ is stress sensitivity (Nortons law exponent),

$t_{\mathrm{r}} =$ time to rupture for a tube of no wall thinning,

$t_{\mathrm{nr}} =$ service rupture life under wall thinning condition.

The wall thinning rate (K') can be derived from the following equation

$$K' = \frac{W_{\mathrm{i}} - W_{\mathrm{f}}}{W_{\mathrm{i}} * t_{\mathrm{op}}}$$

where W_{i} is initial tube wall thickness,

$W_{\mathrm{f}} =$ Final tube wall thickness,

$t_{\mathrm{op}} =$ Operating time in hours.

K' is assumed to be constant and the stress sensitivity (n) is taken as 4. This value has little effect on service life predictions, where high wall thinning rate is encountered.

5 Conclusion

High temperature corrosion is one of the predominant damage mechanism in different critical components of boiler like waterwall, superheater and reheater components. This type of corrosion results wastage of material from the external surface and finally causes the premature failure of the boiler tubes. The corrosion rate is severe in reducing environment in comparison to the oxidizing environment. The reducing environment exists due to the incomplete combustion of the coal in the furnace. The corrosion is also much more severe if he fuel contains sulfur, chlorine and alkali metals. The formation of low melting alkali tri iron sulfate leads to the drastic corrosion on the external surface of the tube metal. This type of corrosion is temperature dependent and corrosion increases with the increase of temperature up to the certain extent and then decreases with the increase of temperature. The corrosion is oil fired boiler exists if the fuel contains vanadium and sodium. The formation of vanadium-sodium compounds destroys the protective scale and corrodes the external surface in high temperature.

There are so many corrosion protection methods like coating, use of thicker material, higher grade of alloy with more Cr content and co extruded tubing to minimize the high temperature corrosion in boiler. But none methods as mentioned are effective for control of high temperature corrosion for long term in thermal power plants. The problem is much more severe when the fuel contains alkali metals, sulfur and chlorine. The combustion of biomass, baggase, wood waste generates sulfur, alkali metals and chlorine and further causes drastic corrosion of the conventional material to the power plants. So there is a challenge to the corrosion engineers to study the extent of corrosion and finally develop suitable material and also corrosion protection method to minimize the extent of high temperature corrosion and finally to avoid premature failure of the boiler tubes.

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References

[1] R. Viswanathan, *Damage mechanism and Life assessment of high temperature components.* ASM International, Metals Park, Ohio, USA (1989), pp. 194–196.

[2] G. A. Lamping and R. M. Arrowwood, Jr., *Manual for investigation and correction of boiler tube failures'* Report CS 3945, Electric Power Research Institute, Palo Alto, CA, April (1985).

[3] G. Y. Lai, *High Temperature Corrosion of Engineering Alloys.* ASM International, USA (1990), p. 117.

[4] *Steam/its generation and use*, 40th edition, The Babcock & Wilcox Company (1992).

[5] S. R. Paterson and T. W. Rettig, "*Remaining Life Estimation of Boiler Pressure Parts-in 2*1/2 *Cr-1 Mo Superheater and Reheater Tubes*", Project RP 2253–5, Final Report EPRI, Palo Alto, CA (1987).

[6] I. M. Rehn and W. Apblett, "*Corrosion problems in Coal Fired Fossil Boiler Superheater and Reheater Tubes*" Report: CS 1811, EPRI, Palo Alto, CA (1981).

[7] W. Nelson and C. Cain, *J., Trans ASME, J. of Engg for power*, *Series A*, 82 (1960), 194.

[8] J. Stringer, "*High temperature corrosion problems in the Electric Power Industry and their Solutions" In high temperature corrosion* NACE-6 (1983), pp. 389–397.

[9] M. D. C. Moles and H. J. Westwood, "*Residual Life Estimation of High Temperature Super Heater and Reheater tubing*", CEA RP 78–66. Final Report of Ontario Hydro Research Div. Toronto, for the Canadian Electrical Assn. Montreal, March (1982), pp. 67–82.