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# FIRESIDE CORROSION IN BOILERS

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## *Introduction*

Corrosion is a significant problem facing all industries including the electric power industry. Besides being costly, corrosion can have other important consequences on power plant operations. Corrosion damage can result in costly replacements to equipment. Severe corrosion problems can cause forced shut downs and these forced shut downs cannot be tolerated.$^{(1)}$ Corrosion would also cause overall loss in power plant efficiency which depends upon smooth and uninterrupted functioning of the boiler unit along with other units. The frequent tube failure in boilers is a threat to power generation and is to be combated and overcome.$^{(2)}$

During operation, a wide variety of deposits can form on both sides of heat transfer surfaces. These deposits can cause aqueous corrosion on the waterside and high temperature corrosion on the fire side. On the water side the reaction between water, deposits and the pipe material gets accelerated due to high temperature and if the inclusions are present in the pipe material they may provide the preferable areas of attack due to formation of anodic and cathodic sites leading to pitting type corrosion which is more dangerous than the uniform corrosion.

The deposits on water side may also act as insulator thereby leading to generation of hot spots where the dry as well as salt corrosion will be accelerated due to generation of high temperatures.

On fireside, there can be attack by fly ash, salt deposits, flue gases containing sulphur on the plate material. $Na_2SO_4$, NaCl, $V_2O_5$ and other compounds are formed by reaction between the various elements present in the environment. $Na_2SO_4$ itself is not very aggressive at the temperatures at which boilers are run, where as, the presence of small amount of chloride of $V_2O_5$ forms a low temperature eutectic. In the external corrosion and occurrence of deposits, the factors involved are the temperature of the metal and the flue gas stream, the composition of the substances in contact with the material surface and the particle size of the deposited material. High temperature corrosion by flue gases can occur in a variety of forms at many locations of the boilers like furnace wall tubes, superheaters, reheaters economisers where ever gas temperature is more than 500°C. In many cases these deposits contain sulphates of Na, Mg, Ca and $V_2O_5$, etc., depending upon the type of fuel used.(4) These deposits modified high temperature corrosion in fire side of boiler is frequently called hot corrosion.(5)

Many research papers describe the mechanism by which the hot corrosion of boiler tubes occurs. There is no complete agreement between investigators on the details of the hot corrosion process but the general features are more or less accepted. For example, hot corrosion can be divided into initiation and propogation stages. The liquid nature of the deposit transports the reactants in the corrosion reaction as well as it affects the oxide scales development on the surface. The reaction between scale and the deposit may be acidic or basic. More work is required to understand the mechanism by which the degradation of alloys occurs.(6)

This degradation of alloys can be minimised by using recently developed materials like Fe, Ni and Co base superalloys with suitable additives and incorporating rare/reactive metals in the alloy by resisting high temperatures, stresses and corrosion in aggressive environments.

### *Occurrence of Corrosion*

Corrosion from combustion gases occurs in a variety of form and in many locations in boilers. Generally corrosion of furnace wall tube, superheaters and economisers is a high temperature hot corrosion as the temperature in the these parts is more than 500°C. Where the temperature is less than 500°C, as with air heaters and in stacks, metal loss occurs by low temperature hot corrosion.(4)

In the lower part of the boiler at the grate, the temperature is more than 1000°C with free burning coal up to about 900°C, coal ash acts as a solid and is chemically inert. The iron pyrite, $FeS_2$ is about half the sulphur in the coal. They dissociate to form FeS. This FeS, in turn can lead to rapid corrosion of iron at quite moderate temperatures. The important point is that the iron can react with FeS to form an eutectic melting at bout 900°C, and FeO and FeS eutectic melts at 850°C. Both of these eutectics are liquids in the range of metal temperatures of grate bars and of tuyeres with blocked airflow and free burning fuel beds.(7)

Deposits on the surfaces of boiler and superheater tubes are very common. Such deposits often collect on the alkali matrix base by volatilisation of Na and K in the flame, condense on relatively cool tube surfaces and react with $SO_2$ and $O_2$ or with $SO_3$ to form sticky surface. Usually this matrix base contains alkali sulphates and is largely soluble in water. This matrix base provides the surface to which particles of ash suspended in the flue gas can get bonded to form an adherent deposit commonly known as Soot.(7)

Phosphate-type deposit occures when coal is burned in fuel beds. Phosphorous compounds in coal such as $CaF_2.3Ca_3P_2O_8$ lose flourine at relatively low temperatures but resulting calcium phosphate is stable in air even up to 1600°C.[(4)]

### *Corrosion of Wall Tubes*

The surface deposits mainly consist of $Fe_2O_3$, $Na_2O$, $K_2O$, $SiO_2$, $Al_2O_3$, CaO, MgO and others. This deposit has two layers, the outer layer is at high temperature and is moving whereas the inner layer is stationary and is at low temperature.[(4)]

### *Corrosion of Superheater Tubes*

Corrosion of superheater and reheater tubes is a serious probelm. This corrosion remains as a major difficulty in the operation of coal and oil fired boilers. At lower temperatures, the compounds are solids and non reactive but at temperatures above 600°C, the compounds melt and cause rapid loss of metal. Alexander et. al.[(9)] show that the deposits on the tubes were mainly $Na_2SO_4$, even though the fuel oil being burned contained less than 20 ppm $Na_2O$. There is a great importance of temperature in the corrosion of superheaters. When steam temperature is up to 500°C, no corrosion occurs but at temperatures of steam above this, excessive corrosion occurs.

This deposit of superheater tubes may be classified into three main types: (1) Sintered and Fused, (2) Alkali Matrix, and (3) Phosphatic. Sintered and fused deposits consist essentially of coal ash carried by the flue gas in the fom of small particles. They form slag deposits and they produce "birdnest" on superheater and reheater surfaces. Coal ash made up of complex mixture of silicates, alumina, iron oxide, lime, mangesia and alkalies is relatively inert below 900°C. However, even at temperatures down to about 600°C, sintering can occur, binding loose ash particles into a moderately strong mass. Alkali matrix deposits form largely because alkali sulphates, such as $Na_2SO_4$, are present in the mass of fly ash collected on a tube surface. If alkali sulphates occur in any reasonably high proportions, they can serve as the bonding material for the remainder of the ash at temperatures as low as 750°C, that is, the minimum melting point of $Na_2SO_4$-$K_2SO_4$ system. Phosphatic deposits are bonded like alkali-matrix type, but the bonding agent is phosphorous compound rather than a sulphate. Phosphatic deposits seldom occur in pulverized-coal-fired boilers.[(4, 10)]

### *Air Heaters*

Oxidation of metal components by flue gas at air heater temperatures is significant, but the presence of a liquid film of $H_2SO_4$ can cause a catastrophic corrosion failure.[(11)]

### *Oilfired Furnaces*

The nature of the ash in fuel oil in its quantity and composition, leads to problems in corrosion and deposits generally unlike those caused by the ash in solid fuels. The ash content is about 1% of that in the solid fuels. It does not contribute to flue gas steam. Because of its composition, vanadium in some fuels causes unique problems in corrosion, while the high concentration of sodium in most fuels leads to problems with alkali sulphates. The composition of the furnace deposits with oil firing varies widely depending on the ash of the fuel. They consist of varying amount of $V_2O_5$, $Na_2SO_4$, $NaHSO_4$, $MgSO_4$, $Fe_2O_3$, $SiO_2$ etc. The deposit consists of two distinct layers. Fourfifths of the inner black layer is $V_2O_5$ and $Na_2SO_4$ with $NaHSO_4$ as the major remaining material.(4, 12, 13,14)

An occasionally troublesome factor in burning residual oil is the formation of acidsmuts in the cold end of a boiler, resulting from the condensation of $H_2SO_4$ on small particles of carbon resulting from incomplete combustion. These acidic nuclie coal-esce to form fakes of soot, which settle in the viscinity of the stack and cause serious annoyance because of their acidic nature.(8)

Makipaa(15)et. al. have concluded that the accelerated corrosion occurs when the chlorides are enriched on the heating surfaces in the boiler when fired with pulverized coal. Malik et. al.(16) have studie Fe-base alloys with varying carbon content in boiler atmospheres. They concluded that hot corrosion is function of temperature and carbon content. Carbides of the alloys provide a convenient route for internal penetration of salt into the alloy.

### *Mechanism of Corrosion*

Metal loss in boilers may occur in many different ways. Chemical attack, however, is more common. Corrosion may occur by gas phase oxidation, by removal of the protective scale on metals through chemical reaction with a corrodent formed within an overlying deposit, by reaction of the protective scale with constituents in the flue gas and the overlying deposit, or by direct attack of the metal surface.

There is no concensus on which of these mechanisms is mainly reponsible for high temperature corrosion. The point generally accepted is that a liquid phase is necessary for corrosion reactions to take place at an appreciable rate. Fire side corrosion is the result of many mechanisms and not exclusively of one set of chemical reactions.

### *Gas Phase Oxidation*

Exposure to air and particularly to hot flue gas rapidly provides an oxide film on metal surfaces that may be protective or that may be shed eventually to expose fresh metal to oxidation. Alloys intended for high temperature service have tightly adherent oxide coatings. These minimise metal loss either by slowing down the diffusion of metal atoms outwards to where they can be oxidised by surrounding atmospheres, or by decreasing the rate of oxygen diffusion through the scale.

Oxidation of metals take place at rates based on linear, parabolic, logrithmic or cubic relationships but the parabolic law Y = K t is most common, where Y is the thickness of the oxidized layer, k is a constant and t is time. Hence the rate at which scale forms decreases as the scale becomes thicker. The rate never becomes zero, but as thickness continues to increase, the rate of doxidation can become so small as to be insignificant. A form of "accelerated oxidation" can occur with alloys containing elements that form low melting oxides.

### *Liquid Phase Corrosion*

As noted earlier, the presence of a liquid phase on the surface of a metal is usually necessary for corrosion reactions to occur at high rate. Most of the researchers are trying to find out reactions leading at some stage to the formation of a liquid film. There are two principal reasons for this:(1) Chemical reactions are invariably faster when a liquid phase is present than when only solid-solid reactions are possible, and (2) A liquid phase provides an electrolyte for electrochemical attack reaction with oxide scale.

Steps in this process are as follows(4):

a. An oxide film forms on the metal surface,

b. Alkali sulphates, originating from the alkalies in the fuel ash and the sulphur oxides in the furnace atmosphere are deposited on this oxide layer e.g., $K_2SO_4$.

c. The outer surface of the $K_2SO_4$ layer becomes sticky because of the increasing temperature gradient so that particles of fly ash are captured. The temperature of this fly ash increases to the point where $SO_3$ is released by the thermal dissociation of sulphur compounds in the ash and this $SO_3$ migrates towards the cooler metal surface. A layer of slag forms on the outer surface.

d. As more ash is collected, reaching an equilibrium thickness, the temperature falls in the $K_2SO_4$ layer and reaction with the oxide scale and the $SO_3$ occurs to form $K_3Fe(SO_4)_3$, with this removal of the oxide scale, the metal oxidises further.

e. Deslagging occurs because of normal temperature excursions in the furnace exposing the $K_3Fe(SO_4)$ layer to the temperatures high enough to dissociate it in part, releasing some $SO_3$. Part of this $SO_3$ moves towards the cooler part of the deposit, where it reacts with $K_2SO_3$ still present and the oxide scale on the tube to form additional amount of $K_3Fe(SO_4)$. Further oxidation of the metal occurs to provide the normal equilibrium thickness of the scale.

### *Formation within the Ash Deposits*

a. Loose unbonded fly ash accumulates on a tube surface.

b. Alkalies in this deposit begin to form sulphates by reactions with the $SO_3$ originally in the gas stream and that formed by oxidation of $SO_2$.

c. The deposit nearest to the tube metal continues to react with $SO_3$ to convert a major part of the alkalies in this inner layer to sulphates.

d. Iron oxides in the ash and $SO_3$ react with these sulphates to form alkali iron trisulphates immediately next to the tube.

e. Alkali iron and an alkali aluminium sulphates form low melting phases that bond firmly to the tube metal.

f. Both in inner and the outer layer of deposit increase in thickness so that the temperature of the outer layer is higher and the sintering occurs.

g. The surface temperature eventually becomes high enough that fly ash sticks to the deposit and the rate of build up of deposit accelerates.

### *Sulphide formation*

The mechanism proposed by Corey et. al.(18) is based on the finding that black brittle scale present occasionally in corrosion areas may consist largely of FeS with small amount of trisulphates. They have concluded that the FeS must have come from the fuel as discrete particles of unburnt pyrites. The mechanism to account for massive amounts of FeS in corroded areas is as follows:

a. Alkalies from the fuel condense on the oxidised tube surface as alkali sulphates.

b. Unburned coal particles of pyrites adhere to the tube surface and form a thick deposit.

c. The pyrites gradually oxidise to FeS and $Fe_3O_4$ with the sulphur evolved forming $SO_2$ and $SO_3$ within the deposit.

d. These sulphur dioxides then form trisulphates in small quantities, leading to loss of metal.

### *Vanadium Compounds*

Vanadium is particularly a serious cause of fire side corrosion because it forms many low-melting compounds that are molten at the temperatures of superheaters. There is a general agreement that sodium vanadates are more corrosive than vanadium oxides alone. All the sodium vanadates melt at lower temperatures than $V_2O_5$. The possible mechanism has been described to explain how molten vanadium salts attack a metal surface:

1. Vanadates act as an oxygen carrier.

2. Vandates distort the normal stable lattice of the metal oxide.
3. Molten vanadates dissolve the normally protective oxide layer.

### *Chlorides*

Chlorine present in the fuels can contribute appreciably to metal loss at high temperatures, either directly through the formation of volatile chlorides or synergistically in combination with complex sulphates.[4,15]

Smith and Marder[19] conclude that circumferential cracking of water wall boiler tubes is an important problem in coal fired boilers. Analysis of the problem indicated that the crack mechanism had two components, thermal stress and corrosion. The *corrosion* component was found to be localised sulfidation corrosion. The sulphidation mechanism occurs beneath a previously existing oxide layer and attack the fire side surface grain boundaries. These corroded grain boundaries act as surface notches, which concentrate the thermal stresses at the grain boundaries, leading to crack initiation. The corrosion mechanism also contributes to circumferential crack growth by attacking the tube steel in front of the crack tip.

Detailed examination of deposits of boiler tubes was made by Tapping et. al[20]. Deposition on to tube surfaces is a two-step process, and spalling occurs at the interface between the passive film and the corrosion product film. The deposition surface can strongly affect deposit adherence and removal. The deposits are quite porous and show evidence for wick boiling.

Hargrave[21] has concluded that copper rich deposits on the boiler tube surfaces can aggravate boiler tube failure mechanism. Metal in deposit can lead to severe intergranular cracking via liquid metal embrittlement during a high temperature overheating incident. Thick accumulation of Cu alloy corrosion products on boiler heat transfer surfaces concentrate metal temperature and thus promote overheating damage to boiler tubes.

### *Prevention of Corrosion*

Fireside corrosion can rarely be eliminated altogether. Obviously, if alkali and sulphur could be removed from coal, fireside corrosion would largely disappear. Reduction of fireside corrosion can be accomplished by one or more of the following methods[10]:

1. Fuel selection : use of ashless or sulphur free fuel is perhaps the most direct means of minimising fireside corrosion. Most natural and manufactured gaseous fuels are ashle, whereas most oils, coals, cokes, vegetation residues and waste gases have some ash content. Any type of fuel may contain sulphur, few coals, oils, tars or burnable wastes are sulphur free, whereas

gases are more likely to be sulphur free.

2. Combustion control : adjustment of firing rate, amount of excess air, air temperature and amount of recirculated flue gas can be very effective in controlling the amount and composition of ash deposit.

3. Boiler design and construction: including pipe size and spacing, furnace configuration size and directing of flue gas passages can help control ash deposition.

4. Periodic ash removal: although less effective in controlling fireside corrosion than procedures that reduce ash deposition, is nevertheless an important aspect of boiler operation. Ash removal prevents development of conditions that alter the distribution of metal temperatures on heat transfer surfaces, which can lead to problems such as failure by overheating.

The tubes should be swept daily with the tube brushes provided, or as often as necessary to clear them of soot.(8)

Paul and Seeley(12) have suggested that limiting tube metal temperatures will prevent ash deposits from becoming molten, thereby avoiding the onset of oil ash corrosion. Tube metal temperatures are limited by the use of parallel flow and by limiting steam outlet temperatures.

5. Additives: additives are used to control both coal-ash and oil-ash corrosion. Sometimes additives are mixed with fuel oil prior to combustion. Additives promote the formation of ash deposits that are easily removed.(10)

Reid(4) explains the advantages of additives that are added to change the physical or chemical characteristics of the deposits. They may be solid, liquid or gaseous. The reasons for using additives are:

i. To minimise catalytic formation of $SO_3$ on hot surfaces.

ii. To prevent formation of corrosive substances on heat receiving surfaces.

iii. To decrease the sintering tendency of high temperature deposits.

iv. To neutralise acids normally condensing on cool surfaces. The commonly used additives are $Al_2O_3$, $SiO_2$ (Solid), CaO and MgO (Liquid) coating and water vapours or amonia to reduce $SO_3$ formation.

6. *Low Excess Air* : Paul and Seeley(12) suggest that operating a boiler with low excess air has helped avoid oil ash corrosion by altering the corrosive combustion products. High Cr alloys and coatings form more stable protective scales on tubing surfaces which result in

lower oil-ash corrosion rates. Reid[4] concluded that of all the practical methods of controlling corrosion in boilers, low excess air (LEA) appears most promising. This minimises effectively to superheater and air preheater deposits and prevents high temperature metal wastage by forming high-melting, lower oxides of vanadium in place of $V_2O_5$.

### *Economic Aspect*

The cost of fireside corrosion are difficult to estimate Even direct out-of-pocket costs are not readily determined for materials and for repair crews to replace badly corroded wall tubes, superheater elements, air heater baskets etc. lowered efficiency in boilers through limited superheater temperature and higher stack-gas temperature also is difficult to evaluate on cost basis. Additional power requirements to move combustion products through partially plugged tube banks likewise add to operating costs. A further addition is the cost of energy that can be obtained from some other source because of a corrosion-caused unscheduled outage.

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