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BOILER CORROSION - METALLURGICAL ASPECT

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Introduction

Boilers are used to generate steam either to drive a turbine for electric power generation or to run plant and machineries in a process or manufacturing industry. They use fossil fuels or a nuclear reactor as the primary heat source. Our discussion however is mainly concerned with the metallurgical aspect of the fossil fuel fired boilers only. The design of a boiler is based on the principle of heat balance. The heat of combustion of fossil fuel determines the amount and quality of steam generated. Fig.1 gives a schematic view of the various components of a boiler. Within the furnace, flame temperature may approach 1650°C. The furnace wall which is made up of tubes through

which water keeps flowing absorbs the heat and thus reduces the flue gas temperature to 900-1100°C. As a result steam at saturation temperature which is a function of boiler pressure is generated. Heat transfer in this stage is primarily through radiation and convection. The flue gas temperature is further reduced by super-heating or reheating of steam in superheaters and reheaters. To extract more heat and to improve overall efficiency, an economizer preheats the boiler feed water to its boiling point. The flue gas travels through an air preheater which heats the combustion air and then makes its way up the stack. Under steady state condition the typical ranges of heat flux in the various parts of a boiler are given in Table-1.

Table-1

Typical values of heat flux and temperatures of steam/water in various parts of a boiler

Boiler component	Heat Flux W/m ²	Steam/Water Temperature		
Economizer	15,000-32,000	300°C		
Water wall	125,000-400,000	400°C		
Reheater	19,000-38,000	600°C		
Superheater	31,000-63,000	600°C		



Fig. 1 : Schematic view of various components of a boiler



Fig. 2 : Temperature profile across the tube-wall showing the effect of scale formation of metal temperature

Clearly it is at the water wall where the heat flux is maximum, the temperature difference between steam and flue gas is expected to be the highest. The effective resistance to heat transfer is determined by the sum total of the resistance of the ash or soot or scale deposits on the external tube surface, tube wall, internal scale and the thin film of steam on the inner wall. Fig.2 gives a schematic representation of the temperature profile from flue gas temperature (To) to bulk steam temperature (Ts) for clean, as well as internally / externally scaled conditions. Note that formation of internal scale raises tube metal temperature. However formation of ash or shoot deposit or scale formation on the external surface although would reduce efficiency of heat transfer it does not alter the tube wall temperature. To maintain high efficiency removal of ash/soot deposit and periodic cleaning of internal surface is necessary. The steam side heat transfer is a function is of fluid velocity, density and tube bore diameter. Depending on the magnitude of heat flux there is scope of overheating as well (Fig. 3). It is the water wall which is more susceptible to such overheating as there ARE both steam and water & high heat flux.

The boiler components are thus required to withstand high temperature and pressure in an environment of steam/water and flue gases. Steel is the obvious choice for construction of boiler. This is primarily because of its availability in various forms and sizes, low cost, ease of fabrication corrosion resistance and high strength. Steel is primarily an alloy of iron and carbon although most commercial grades contain a host of other elements e.g., Si, Mn, S, P, Cr, Ni etc. Whilst some of them are harmful, many are beneficial as well. By controlling alloy addition, heat treatment and thermomechanical processing a wide range of properties could be developed in steel. Boilers are mostly made up of plain carbon and low alloy steel containing Cr & Mo. The choice of steel depends on the operating condition of the boiler components. For example superheater, reheater tubes or steam pipes where very good high temperature properties and oxidation resistance is required steels having 2.25Cr 1Mo or 1Cr 0.5Mo 0.25V steels are preferred. In boiler generating steam at 650°C or higher even high alloy ferritic or austenitic steels are also being used. However in cases where very high mechanical properties are not essential or where the difficulties of welding make high alloy additions undesirable or uneconomic leaner steels are used. Typical examples are 1Cr 0.5Mo & 0.5Mo steel.

Commercial steels invariably contain residual or tramp elements. Those universally present are S & P, coming from the ores, fuel or slags used to refine steel. Some ores contain significant amounts of As, Sb, Bi and Sn. Besides Sn and Cu may come from scrap. The effect of these elements without exception is damaging. When present in steel they migrate to grain R.N. GHOSH



Fig. 3 : Variation of steam/water and metal temperature at different levels of heat flux

(a) and (b) : The effect of scale thickness on the temperature gradient across the scale; (c) and (d) : The effect of Scale thickness on the temperature of the metal at the outer surface of the tube. Th graphs are based on a continuous, uniform scale, with a thermal conductivity of 14.4 W/m . K (10Btu . in./h . ft^2 . ^oF) on tubes in the film-boiling regrino of 690-kPa (100-psi) system (saturation temperature 285°C, or 545°F).

boundaries and markedly reduce their resistance to fracture. These have been identified as the main cause of embrittlement. Embrittled steels exhibit intergranular fracture. This tendency is promoted by certain alloy additions viz., C, Mn, Si and Ni but retarded by Mo. Embrittlement can be minimised by reducing the content of content of residual elements from levels of about 0.01% to 0.001% by careful choice of scrap and slagging.

The types of steel used in various parts of a boiler are given in Fig.1. Possibly the best way to describe the metallurgical aspect of boiler design is to discuss why in spite of judicious selection of material some of the components fail in service. A survey conducted by one laboratory over a period of 12 years based on 413 investigations indicate overheating as the main cause of failure. Table-2 gives a summary of this survey. However defective material does not always cause a component to fail soon after being put into service. Even massive defects were found to be present in some areas without causing fracture to occur until after considerable period of service. This is because boiler design is inherently conservative.

Overheating Failure

Overheating results from restriction of flow within a heated tube or from localized heating of the tube wall. Mild restriction of flow favours a small degree of overheating. This leads to failure by stress rupture. Such failures are characterized by thick tip rupture with little ductility (Fig. 4).

Rapid overheating is most likely to occur at start up or during periods of rapid fluctuation in steam demand or during full power operation it may be caused by sudden loss of circulation for example feed pump failure or local loss of circulation. This leads to failure by tensile fracture which is transgranular in nature. Such failures are accompanied by extensive tube swelling and thinning down of tube wall (Fig.5).

During operation a wide variety of deposits can form on either sides of the tubes. This can also cause overheating failure by changing the heat transfer

Cause of failure	Frequency	%
Overheating	201	48.7
Fatigue + Corrosion Fatigue	89	21.5
Corrosion, SCC, Hydrogen Embrittlement	68	16.5
Defective Material	55	13.3

Table-2							
Sample	failure	statistics	of	boiler	components		



Fig. 4 : Characteristic thin-lip rapture and associated microstructural features

Type 321 stainless steel (ASME SA-213, Grade TP321H) superheater tube that failed by thick-ip stress rupture (a) Overall view showing a typical fishmouth rupture. Approximately ¹/₂ x. (b) Unetched section fro location between arrows in (a) showing extensive transverse cracking adjacent to the main fracture (at right). Approximately 4¹/₂ x. (c) Specimen etched electrolytically in 60% HNO₃ (nitric acid) showing intergranular nature of cracking. 100x



Fig. 5 : Characteristic thin-lip rapture Thin-lip rupture in a 64-mm (2¹/₂-in.) outside-diameter x 2.7-mm (0.105-in.) wall thickness carbon steel furnace-wall tube that was caused by rapid overheating Knve-edge wall thinning at longitudinal main rupture is shown in corss section in the inset. Note secondary circumferential fracture at left end of the longitudinal main rupture.

R.N. GHOSH

characteristics of a tube bank or of an individual tube. Fire side deposits either insulate portions of the heat transfer surface or in cases these are thick enough the flow pattern of flue gases through a tube bank is altered. In both cases the metal wall temperature of regions devoid of deposits will be higher than in regions where deposits are present.

When waterside deposits are presents tube wall temperature increases in the region of deposits. Figure 3 shows the effect of scale thickness on metal wall temperature. The increase is more pronounced in case tubes of smaller diameter. It can even go beyond the recommended limit for the steel. Therefore it is necessary to keep the water side surface free of adherent scale particularly in the regions of high flux.

Such overheating significantly alters the structure and properties of the steel tube. Prolonged overheating at temperatures below AC₁ (the temperature at which austenite begins to form) in carbon and low alloy steel causes decomposition of pearlite (or Bainite) into ferrite and spheroidal carbides. This weakens the tube material. If continued overheating persists it could cause formation of voids at grain boundaries and eventual grain separation, resulting in stress rupture failure.

Rapid overheating of boiler tubes made of carbon and low alloy steel usually results in failure because of decrease in yield strength. If failure takes place below recrystallization temperature microstructure near fracture would exhibit elongated grains. Rupture that occurs at temperatures greater than AC₁ may exhibit pearlitic/bainitic areas formed as a result of quenching effect of escaping water or steam on partly austenitic structure existing at the time of rupture.

Microstructural evidence as described above may not always be taken as conclusive proof of overheating. Such features may have been present at the time of installation. To confirm it is therefore necessary to examine microstructures of either adjacent tube or unused tube of the same lot. Careful examination of microstructures along with hardness and oxide scale thickness measurement nevertheless can give a very good estimate of the extent of overheating. Such estimates could prove extremely helpful in calculating the remaining life of various components of a boiler. To facilitate such computation a computer software called RELIEF has been developed at NML. A demonstration could be arranged for those who may be interested.

Austenitic steel however exhibits different kinds of microstructural instability. These are carbide or ferrite or σ phase precipitation. All these may shorten the stress rupture life of stainless steels and can enhance the probability of tube failure with prolonged overheating.

Embrittlement ~

Metallurgical changes within the

tube metal are responsible for ruptures caused by embrittlement. The main mechanisms are hydrogen damage and graphitization.

Hydrogen damage takes place primarily in steel components. Discontinuous intergranular cracking and decarburization are its characteristic features. Such cracking results from precipitation of hydrogen or methane. Tubes that have undergone such damage often exhibit window type fracture.

Hydrogen is one of the normal product of corrosion reaction between iron and water in both acidic or basic conditions.

 $2 H^+ + Fe = Fe^{2+} + 2 H$ (acidic conditions) $2 OH^- + Fe = FeO_2^{2-} + 2 H$ (basic cond.)

Hydrogen damage is usually associated with thick internal deposits. The metal temperature under this deposit is usually higher. Hydroxide ion concentration is therefore more in these regions (because of local boiling). Corrosion rate increases with pH (Fig.6). Similarly if all internal deposits are not removed during chemical cleaning, the porous deposits will retain the cleaning acid. During start up the low pH will also lead to rapid corrosion.

Most of the dissolved hydrogen migrate through the tube wall and gets carried away by the flue gases. However some of the dissolved hydrogen may react with carbide.

 $4 H + Fe_3 C = 3 Fe + CH_4.$

Methane is a large molecule and cannot diffuse out of steel. It collects at grain boundaries and when the pressure is high enough, leaves cracks behind.

Steels embrittled by hydrogen can be restored to its original ductility only if grain boundary cracks have not developed or decarburization has not occurred. A low temperature baking for 2-3 hours at 175-200°C is enough to drive out dissolved hydrogen and restore ductility. However damage involving internal cracking is irreversible, materials embrittled in this manner must be replaced.

Graphitization is a microstructural change that takes place in carbon or low alloy steels subjected to moderate temperatures for long periods of time. Graphitization results from the decomposition of cementite in to firrite pearlite and graphite. This can embrittle steel parts especially when the graphite particles form along a continuous zone through a load carrying member. Randomly distributed graphite particles throughout the microstructure cause only moderate loss of strength.

Graphitization and sulpheroidization are two competing mechanisms of pearlite decomposition. Below 550°C graphitization is the usual mode of pearlite decomposition whereas above 550°C it is spheroidization that predominates (Fig. 7). Since graphitization requires prolonged exposure at temperatures lower that 550°C, it seldom occurs in boiling surface







Fig. 7 : Kinetics of graphitization and spheroidization

trace of spheroidized carbon remaining. Etched

with nital. (500 x)

tubings. Economizers, steam pipes and other components subjected to 425-550°C for several thousand hours are more likely to be embrittled by graphitization. The heat affected zones (HAZ) adjacent to welds are among the more likely locations for graphitization to occur.

Water Side Corrosion

This is one of the main cause of forced outages of steam generators. Corrosion in boiler takes places by a variety of mechanisms. It is most common in water walls and economizers. These are usually made of plain carbon steel although in a few cases low chromium ferritic steels have been used. The metal wall temperature is less than 400°C.

A thin film of Fe₃O₄ that forms on the water side of the tube acts as a protective layer. This forms as a result of the following reaction.

 $3 \text{ Fe} + 4 \text{ H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4 \text{ H}_2.$

The oxide consists of two layers. In practice the outer layer is seldom formed, because as the iron diffuses outward the Fe₃O₄ formed at the outer interface usually becomes entrained in the boiler water flow and then deposits in another region of the boiler. The protective nature of this layer depends on pH of the water and on the amount of contaminants.

Fig. 6, gives the effect of pH on rate of corrosion of steel by water. Magnetite is unstable and soluble at pH <5 and at pH >12.

The significant categories of water side corrosion failure mechanisms are caustic corrosion, hydrogen damage (already discussed) and pitting (localized corrosion). In all these cases the amount of corrosion product deposited on the tube wall plays an important role. Caustic corrosion & hydrogen damage result from the break down of the protective Fe3O4 layer by the concentration of corrosive chemicals within a wall deposit. Caustic corrosion develops as the concentration of NaOH in the deposit builds up to raise the pH. At high pH, Fe3O4 layer becomes soluble and rapid corrosion takes place.

Caustic corrosion is caused by the selective deposition of corrosion products and NaOH at locations of high flux. Porous deposits accumulating in high heat input areas promote concentration of NaOH by a process known as wick boiling. As a result caustic level could go up from 200 ppm in bulk water to over 200,000 ppm adjacent to the tube surface.

Susceptibility of caustic corrosion can be minimized by restricting the entry of deposit forming materials and periodic removal of waterside deposit by chemical cleaning. Careful monitoring and control of water chemistry is necessary to prevent accumulation of NaOH.

Pitting or localized corrosion results from oxygen attack or acidic conditions on the internal surface of the boiler tubes. This can lead to perforation of the tube wall particuarly when a small area becomes anodic with respect to the rest of the tube surface. This condition can develop from an exposure of the tubes to water with high acid or oxygen concentrations or at crevices.

The oxygen in water reacts with and rapidly removes the hydrogen produced at the cathode, thus promotes cathodic reaction. The oxygen will also oxidize the Fe^{2+} ion to produce Hematite (Fe_2O_3) as the corrosion product which covers crater like perforations in the tube wall.

Pitting failure can occur anywhere in the boiler, particularly in economizer, superheater, reheater and the non-heated portion of the water wall tubes. For full protection against pitting during shut down it is necessary to keep the boiler filled with hydrazine treated water and blanketed or capped with nitrogen. Oxygen pitting of economizer can be minimized by proper operation of deaerators and their heaters; by elimination of air leakage and by injection of oxygen scavenger.

Superheaters and reheaters unlike economizers and water wall tubes are designed for a finite life. This is based on a conservative creep failure criterion. To produce steam at 540°C or beyond, the tube wall temperature could exceed 600°C especially in the last stages of superheat and reheat sections. Depending on the temperature/design tube material could vary from carbon to low alloy ferritic to austenitic steels.

Chromium containing steels when exposed to 500°C-650°C develops spinel type oxides consisting of two layers. Their relative thicknesses depend on the Cr content of the steel. In superheater & reheaters the outer layer is invariably Fe₃O₄ and the inner layer is an Fe-Cr spinel type oxide containing the alloying elements of steel. Such layers normally protects further oxidation. However there are two ways in which this protection can breakdown (i) excessive growth & exfoliation, (ii) stress corrosion cracking (SCC).

For ferritic steel corrosion initially follows a parabolic law. However depending on temperature at a latter stage it might change over to linear kinetics. This is associated with formation of multiple layers of oxide. As a result of the difference in thermal expansion between the scale and the tube exfoliation occurs. when oxide exfoliates and travels into the turbine components it may cause serious solid particle erosion problem.

Austenitic stainless steels because of higher Cr content corrode more slowly than ferritic steels under the same steam conditions. However here as well exfoliation could take place due to either breakdown of the inner layer or void formation at oxide/oxide interface. Nevertheless in comparison to ferritic steel the problem of exfoliation in this case is much less.

Replacement of superheater/ reheater rubes with chromate treated chromized or stainless steels (for the existing ferritic steel tube) is an effective method of overcoming scale exfoliation problem.

SCC failures in a boiler usually occurs in stainless tubes used for superheaters/reheaters, although some ferritic steels are prone to such failures in caustic environment. Contamination of boiler water or steam and presence of high residual tensile stresses due to fabrication/assembly promote such failures. Common contaminants are chlorides and caustic. These result in transgranular cracks whereas sulfur which might come from chemical cleaning results in intergranular cracking.

In short steel has sufficiently good corrosion resistance against steam/ water in the usual range of operating conditions. However in order to exploit its full potential it is necessary to maintain a close control over the quality of water/ steam flowing through different parts of a boiler.

Fire Side Corrosion

Impurities present in fuel are mainly responsible for fire side corrosion. Harmful elements present in coal are S, Na, K and Cl. Whereas those in oil are Na, V and S. As a result of combustion these impurities melt or vaporize and deposit on relatively cool surfaces. This promotes accumulation of fly ash deposits.

Fire side corrosion of water wall

tubes is more pronounced in areas around the burners. The thick, hard scale deposits could be quite smooth but often exhibit cracks and grooves. Such cracking is more common in areas of high heat flux and is primarily due to super imposed thermal stresses.

In presence of S as an impurity the scale is a mixture of iron sulfide and iron oxide. The Cr from the alloy is dispersed in the inner layer. Reducing atmosphere is primarily responsible for corrosion. This is further promoted by molten salt and slag related attack as the normal oxide scale dissolves. Besides under reducing condition H2S is present in the flue gas. This is more corrosive than SO₂ which predominates in oxidizing conditions. In addition under reducing condition scale consists of FeS through which Fe⁺⁺ could move much faster than in oxides. However unlike iron oxide Cr2O3 is a very good protective layer. It is stable even in reducing conditions. High Cr steels having protective layers of Cr2O3 are therefore more resistant to fire side corrosion.

Slag related attacks are of several types. Local disruption of the normal oxide film on the tube wall by intrusion of molten slag leads to accelerated corrosion. In coal fired boilers alkali sulfates deposited on the water walls may react with SO₂ or SO₃ to form pyrosulfates (K₂S₂O₇) or complex alkali iron trisulfates. The K₂SO₄ - K₂S₂O₇ forms a low melting mixture (407°C) in presence of 150 ppm of SO₃. The corresponding Na salts require about 2500 ppm of SO₃ which is less likely to be present in the furnace atmosphere. Therefore molten salt attack by $K_2S_2O_7$ is more likely. This occurs according to the following reaction;

 $K_2S_2O_7 + 3 Fe$ = FeS + Fe₂O₃ + K₂SO₄.

Differential scanning calorimetry of such deposits indicates melting point in the range 335-410°C.

Role of chlorine of fire side corrosion is rather difficult to define. However under reducing conditions HCl or NaCl can render oxide scale less effective for corrosion protection either through blister or crack formation or through reactions with oxides to form volatile products.

Molten salt related corrosion of water wall tubes seldom occurs in oil fired boilers. This is because of low ash content and absence of chlorine in the oil. Therefore the deposits formed in oil fired boiler tubes are very thin and do not provide conditions for formation of pyrosulfates. Moreover the chance of local overheating due to formation of deposits is much less. The metal wall temperature in the water wall is usually below 400°C which is lower than the melting points of any possible compounds between Na and V oxides.

Problems of fire side corrosion can be overcome either by changing the operating conditions or the tube material. Where corrosion results from the reducing conditions near the tube wall adjustment of burners and proper fuel & air distribution can be helpful. An alternate method could be to introduce a flow of air along the walls through openings in the membrane between water wall tubes. This is often referred to as air curtain. This can be implemented in conjunction with local monitoring of the gas composition.

Removal of chemical species responsible for corrosion from the fuel is an another alternative to combat fire side corrosion. Standard coal washing technique can remove half of the sulfur and alkali metal content from the coal. However washing generally does not remove chlorine. Blending of coal to reduce average content of corrosive species is an alternative strategy. However all these would certainly involve additional fuel cost.

Material solutions to fire side corrosion problems involve either replacement of the tubes with more corrosion resistant material or by application of protective coatings. In cases where tube wall thinning rate is only slightly greater than allowable, replacement of tubes with same material and regular monitoring of wall thickness is recommended. For severe wall thinning conditions steel containing upto 9% Cr exhibit similar performance. In this case possibly thicker plains carbon steel tubes or composite coextruded tubes with an outer layer of austenitic stainless steel could be used.

R.N. GHOSH



Typical microstructures of 0.18% C steel boiler tubes that ruptured as a result of rapid overheating (a) Elongated grains near tensile rupture resulting from rapid overheating below the recrystallization temperature. (b) Mixed structure near rupture resulting from rapid overheating between Ac₁, and Ac₃ amd sinseqiemt qienching by escaping water or steam. Both etched with 2% nital, (250x).

Fig. 8 : Typical microstructural change as a result of rapid over heating



Micrograph of an etched specimen from a carbon steel boiler tube. Decarburization and discontinuous intergranular cracking resulted from hydrogen damage ((250x) speheroidization (light, globular), both of which are characteristic of tertiary creep, (250x) (b) Intergranular separation adjacent to facture surface (top). 50x Moltled areas in both specimens are regions where pearlite has decomposed into ferrite and spheroidal carbides. Both etched with 2% nital

(a) Voids (black) in grain boundaries and

Fig. 9 : Typical microstructural change as a result of prolonged overheating below critical temperature



A Window Fracture :Typical results from hydrogen damage in carbon or low-alloy steel boiler tubes

Fig. 10 : *Typical microstructural changes and nature of tube rupture as a result of hydrogen damage* Enrichment of the surface by Al or Cr can also improve corrosion resistance. This can be attained by a number of methods. Diffusion coating, flame or plasma spraying has been used to apply high Cr, high Al, or Fe-Al-Cr alloy coatings on water wall tubes. Although such alloys exhibit excellent corrosion resistance in laboratory testing, there are many technical problems concerning reproducibility, ease of fabrication and joining are required to be tackled before their commercial use.

Concluding Remarks

A short overview of the material related problems of a boiler has been presented. Steel being the most commonly use material our discussion has been mostly centered around steel. The fact that many of the steel components in a boiler are known to have survived more than 50 years of service life without any appreciable

deposit corrosion. Moreover, the fuel contaminants can form ash/sal deposits on meal surfaces during high-temperature exposure which play significant role in the corrosion process. For example, supplur from the fuel and NaCl from the ingosted and may react during combustion to form salt vapour, such as Na, SO, which at lower temperatures, deposits on the metal surfaces resulting in accelerated corrosion, caused by the chemical reaction between the protective oxide scale and the salt deposit, leading to the breakdown of the scale. Such a corrosion process occurring in the presence of salt deposites termed as "Hor Corrosion". The presence of large particles of quartz, FeS, provide and the scale of the protective presence of large particles of quartz, FeS, provide an in the scale of the protective provide scale such as "Hor Corrosion". The loss of strength, toughness and section size goes to show that majority of the problems could be solved by having closer control on the operating condition, the quality of water and the quality of fuel. Nevertheless there is ample scope for improving the efficiency of boiler by proper choice of steel, better design and possibly by introducing special material at critical locations. In spite of the best effort on the part of designers, fabricators, and operators, component failures often take place. A proper analysis of these not only helps identify the cause of failure but also suggests remedial measures to overcome them. A number of case studies concerning failure of boiler components will be discussed in subsequent lectures. In majority of the cases corrosion either directly or indirectly responsible for failure. The points discussed here will possibly help you appreciate that.

materiais for construction of industrial equipments. The principal modes of high-temperature corrosion, frequently responsible for component failure are oxidation, sulphidation, nitridation, carburization, hot corrosion and flyash erosion. Oxidation most often participates in the high-temperature corrosion process, regardless of the predominan mode of corrosion. In fact, alleys often a protective exide scale to resist various high-temperature corrosion Environin coal of based power plants contain several corrosive species which may result in "oxidizing" (very high oxygen activity) or "reducing" (very low oxygen