CONTEMPORARY VIEWS OF CORROSION AND PERFORMANCE RELATED ISSUES IN MODERN COAL FIRED BOILER

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Introduction

Water and coal are the basic consumable raw materials for the continuous, around the clock, production of high purity steam at high temperatures and pressures. Whilst water undergoes a reversible physical trnasformation of state only, the combustion of pulverised coal is a destructive chemical process involving (i) release of thermal energy and of the mineral matter of coal as ash, (ii) formation of the oxides of carbon, hydrogen, sulphur as products of combustion and (iii) the concomittant formation of environment polluting gases, NOX and SOX. Necessarily, heat transfer occurs across metallic interfaces of complex layout. Fluid movement at modern boilers occurs in three distinct paths, each flow being independent of the other:

- o The combustion system includes the path of the flow of combustion gases along with the ash in the so called fire side of the boiler and covering the radiant and convective zones of heat transfer in the waterwalls, superheaters, reheaters and the economisers past fans, through electrostatic precipitators and up the stack; coal mills, pulverised coal carrying pipes and bends are also part of the system.
- o Water and steam paths : the path of the superheater water to the waterwalls (boiler tubes) through the drum; path of the steam from the drum to the turbines through the superheaters and reheater loops and from the turbine to the condenser for the recovery of water to be recycled as feed water;
- o The path of cooling water from its source through the condenser until its discharge.

In actual practice, the material performance scenario is just not innocuous but is rendered complex for two reasons: first, commerical water is not just "H_2O" but contains a host of dissolved and colloidally suspended impurities, dissolved gases, organic wastes and bacteria and second, coal is also more than just carbon as it contains hydrocarbons and mineral matter besides sulphur. Additionally, water reacts with steel.

Corrosion is all pervasive at modern boilers as the three fluid flow paths provide wide and fertile areanas for corrosion to occur. As steam is required at high temperatures and pressures for better thermal efficiency, stresses of high temperature and pressure along with the boiler operational scenario aggravate the material problems through

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the structure degrading influences of creep, fatigue and thermal fatigue. Since the fluids that flow through the boiler system are continuously changing in temperature, pressure, state and composition, corrosion and metallurgical structure related problems in the different zones of the boiler are different from one another.

Corrosion in the Three Paths

Boiler tube failures account for the largest percentage of forced outages at most thermal power stations. A good majority of tube failures is in the highest heat flux area of the waterwalls and many of them are caused by water-side corrosion. The reaction of water with steel is spontaneous and rapid at high boiler temperatures, resulting first in the formation of $Fe(OH)_2$ which is later transformed into magnetitie, (Fe_3O_4). Itself a corrosion product, magnetite thus formed is ordinarily adherent and impervious; it is thus able to effectively stifle further corrosion. The inviobility of the magnetite film during the operational life of the boiler is vitally important and is the only factor responsible for the use of ordinary carbon or low alloy steels in the otherwise corrosion aggressive environment prevalent along the fire side of the boiler.

The basics of the corrosion processes involving water and steel interfaces at ambient and higher temperatures are now well understood to have given rise to science based modern water treatment technology. It is now well appreciated that in order to obtain trouble free performance, the boiler feed water has to conform to rigid standards in terms of the maximum permissble values of its contents of dissolved solids, pH and dissolved oxygen. Any deviation from the prescribed values would cause severe internal corrosion resulting in forced outages and/or scaling causing loss of thermal efficiency. Both result in monetary loss to the power utility. Since the causes of boiler corrosion are now well known as are the means of preventing or reducing the corrosion damage, it would only be a naive power station as would not be fully conscious about them or would not comply with the prescribed operating procedures during start-ups, shut downs and outages to minimise corrosion.

The record of the level of achievement in this regard is high at international level. In a private communication to the author in late 1983, a Danish utility has this to say, "If we should state how many boiler tube failures we have had in the past years we can tell you that Unit 3 from 1980 had 10 including 2 in evaporator area. Some of these were due to faulty hangers so that they will not appear again so in the coming years we do not expect that many".

"Unit 2 which from 1968 have had quite a few failures on the reheater bottom loops in the past because they were very thin from the start and the boiler sufferred from corrosion during outages in long periods due to turbine failures in

1969-70. These loops have all been changed, we have had only two failures. This boiler once had no failures in 27 months, it now has approximately 100,000 service hours".

It is a redeeming feature of boiler operation in India that dry corrosion processes in the path of combustion gases do not pose serious problems but erosion-corrosion is becoming a serious problem in pulverised coal transportation pipes and bends as also in the economisers besides the mills themselves. Life of mill parts depends on many factors which vary from plant to plant. Apart from the per se importance of the abrasive characteristics of coal, life of mill parts depends on local conditions of operation, such as mill loading, facilities for the on-line removal of foreign materials, regular maintenance schedules, material procurement policies. Metals and alloys used in the electrostatic precipitators are fast becoming an area of emerging concern with the strict implementation of environment protection laws.

Despite the importance of corrosion occuring at ambient temperatures in the condenser cooling wate path, it would not be discussed in this presentation.

Manifestations of Corrosion

The phenomenon of corrosion manifests in different forms in a boiler plant. These are :

- o Uniform galvanic corrosion causing a wide area of the metal to be corroded. It is predictable, could be easily prevented or circumvented by design changes and solved by regular predetermined replacement of parts:

- o crevice corrosion occurs in spots that are shielded from full exposure to the enviroment, such as under deposits or the junctions of overlapping metal parts. When a fluid stagnates there, its composition, and consequently its electric potential becomes sufficiently different from the rest to set up a corrosion cell in operation.

- o Pitting - a form of localised corrosion. Being unpreditable, it is more dangerous; the pits become deeper and corrosive action becomes more intense with time as the corrosion products get concentrated in the pit.

- o dealloying (cf dezincification) - the preferential corrosion of zinc in brass leaving a copper-rich surface layer or when cast iron corrodes selectively leaving the surface layer richer in cabon.

- o Intergranular corrosion and embrittlement - occurs at grain boundaries which become anodic with respect to the grains (cathodic); a very minimal loss of metal drastically affects the properties.

- o Stress corrosion - a very treacherous form of corrosion failure because the continued presence of stress in the corrosion environment causes the nucleation and growth of cracks. The effects of residual stress are in all respects similar to applied stress in causing stress corrosion failure to occur; residual stresses can be introduced by welding, cold work and by differential stress as in cold preparation of bends, rapid heating and cooling cycles of massive components.

o Creep and creep-fatigue related grain boundary migration, grain fragmentation and recrystallisation, formation of creep voids and wedges etc.

The different principal sites and types of corrosion are the result of the interaction of different metals under differing conditions of temperature and pressure with the local environment.

Corrosion Basics

It is known that iron placed in contact with deaerated water produces an equilibrium pH of about 8.3. Increasing the alkalinity reduces the solubility of the iron corrosion product, $Fe(OH)_2$ or Fe_3O_4. The protective magnetitie is solubilised at pH values below 5.0 or above 13.0; minimum corrosion occurs at pH values between 9.0 to 11.0-pH is usually maintained within this range in boilers.

In case of gross departures in the pH from the prescribed values, corrosion damage could be extensive in the form of genral attack at both depressed and elevated pHs. In the case of the former, loss of protective magnetite layer occurs widely along with metal thinning; the latter may show general pitting beneath internal deposits. Since elemental hydrogen is liberated in both cases, it is immediatly "grabbed" by the metal when it accentuates failures due to hydrogen embrittlement. Metallo-graphic evidence for such failures comes in the form of appearance of randomly distributed hair line cracks. In the case of failures under elevated pHs, additional and distinctive evidence is the loss of pearlitic areas on account of the breakdown of cementite and formation of methane by the inward diffusing hydrogen.

The feed-and boiler-water treatments are designed so as to ensure continued integrity of the protective magnetite film and to protect this film during operation against the aggressive action of impurities which could be introduced into the boiler system with the feed water. Technological adaptation of the scientific understanding of water chemistry has reached a level of maturity and purely water-chemistry related plant outages are relatively rare if due attention is given to maintenance and monitoring schedules and the dissolved gases such as oxygen and hydrogen sulphide are kept at minimum.

In practice, corrosion is "localised" phenomenon and is influenced by concentrations available locally at specific locations on the surfaces of boiler tubes and not by concentrations prevailing in the bulk liquid. Thus corrosive attack may take place beneath deposits where boiler salts, as caustic, can get concentrated enough to react with magnetite in the manner discussed above.

Pitting and localised corrosive attack could also be promoted or aggravated in presence of higher values of stress, operation under low loads and/or variable pressure and by frequent shut downs without prevention of the ingress of oxygen during outages and start-ups.

Thus, corrosion related failures do continue to occur at thermal power stations. This prsentation makes an attempt to discuss some less known/ appreciated factors including the effects of variations of metallurgical structures, fluid flow heat flux and heat transfer related issues as their individual or cumulative effects on localised corrosion are neither fully understood nor appreciated. A discussion of these aspects is considered important as the brunt of the wrath of the management for corrosion related failures is often passed on to the water treatment section of the power station without as much as a second thought.

Scale Formation - Oxygen Pitting in a Boiler System

Most materials that form boiler deposits or the heat transfer deterrant scale originate from the pre-boiler system where they may be present as (i) contaminants in the make-up water, (ii) corrosion products formed outside the boiler and introduced into the Unit with the feed water (iii) contaminants from the process equipment introduced into the condensate returned to the boiler (iv) solids present in condenser leakage. Since the solubility of most scale forming substances decreases with increase of temperature, the formation of the heat transfer obstructing scale is enhanced at higher temperatures - localised or otherwide, or with increased heat flux. Further the thermal conductivity of the scale being low, even a paper thin scale layer is potentially disastrous as the boiler tube temperature thereby rises to produce creep damage and structural damge to accelerate the failure.

It is known that localised pitting corrosion is most severe when a deposit covers a small area on account of the creation of a differential aeration cell about and beneath the deposit. The metal beneath the deposit is lower in oxygen than the surrounding, becomes anodic and is attacked. Pitting mostly occurs in stressed sections of the boiler tubing such as welds, cold worked sections and at surface discontinuities in the metal. Presence of oxygen being pre-emptive for corrosion to occur, both the boiler design and operation must prevent oxygen infiltration. Oxygen leakage into the boiler system in conjunction with condenser leakage is sure to give rise to corrosion related problems. To achieve low residual (0.005 ppm) oxygen, it is necessary to:(i) exclude air leakage into the condenser, (ii) judiciously control the addition of undeaerated water to the condensate feed water, (iii) prevent the addition of aerated heater drips into the condensate and (iv) assure exclusion of air into the feed water cycle during short outages of the boiler.

The following quote from Combustion Engineering Handbook summarises the complexity of situation best; "One major problem in curtailing corrosion from oxygen is the exclusion of air upon boiler start-up. Normally, pressure in a deaerator is not attained until steam is admitted to the turbine and the bleed steam is available for heating. It is possible to introduce more oxygen into the boiler at this time than in several months of regular operation. Admitting auxilliary steam to a deaerator to pressurise the unit to 3-5 psig can prevent much of the problem. In this condition air is excluded and feed water delivered to the boiler is low in oxygen during start-up operation".

Hydrazine is added to reduce the dissolved oxygen content, but its oxygen scavenging effect is both time and temperature dependent. Nitrogen blanketing (displacing oxygen above the water surface is another way to reduce oxygen content. It is most effective when a plant is being shut down.

Deposit Corrosion of Copper

Since the presence of copper in steel causes adverse influence on the stress-tupture properties, stringent limits are imposed on the quality of water/steam with respect to the concentration of copper which must be less than 2 ppb. At a copper concentration of 0.02 ppm, - a level not uncommon in boiler feed waters, - and in aboiler evaporating 1000 tonnes of water per hour, the boiler will receive the equivalent of about 15 kg of copper in the course of a year. Copper may also be derived from the copper based alloys used in the condensers or low pressure heaters. When alkalinity is maintained by the additions of sodium phosphate, copper circulates around the boiler as a phosphate. In modern all volatile treatment of feed water, where hydrazing/ammonia/morpholine are used, copper may be circulating in the boiler in some complex form. Irrespective of its precise chemical nature, it is readily converted into cuprous oxide. If there is a temperature rise to 600-650°C, the cuprous oxide may be reduced to metallic copper. Copper deposited on the steel surface, promotes rapid galvanic corrosion of steel. When boiler tube temperatures exceed 850°C and are prevalent for longer periods, a hot tensile type of failure with typical thin edged burst, may occur. If a temperature excursion beyond the melting point of copper is sustained even for a short duration, copper can melt and cause liquid metal embrittlement through intergranular penetration of copper in steel.

Even if extensive corrosion damage has not occurred, the presence copper/compounds in the protective magnetite layers can cause serious damage to the tubes whenever and wherever high temperatures are and wherever high temperatures are encountered. One of the tasks in the routine repair of power boilers is the changing of burst tubes through welding or the localised repair of minor punctures. Under such conditions copper may enter the steel through any of the above mechanisms and cause intercrystalline cracks in the heat affected zone; such cracks would be disposed circumferentially across the tube.

Post Operation Cleaning of Boilers

Experience has shown that boiler evaporators (water wall tubes) should be acid-cleaned when the deposit amount has grown to 50 mg/cm^2 corresponding to a thickness of 100-150 μm. The somewhat diffuse marginal value based on measurement of thickness is due to the varity of oxide deposits. A compact oxide deposit will result in a ratio of 1:2 between the mg/cm^2 value and the μm value. More voluminous deposits will change the ratio to 1:3.

The growth of scales on the inner surface is a combination of several events : oxidation of the steel on site influenced by thermal considerations only, alkali corrosion or deposition of iron oxides carried by the feed water or transported from other areas in the boiler. In a few cases, cleaning could be determined by heavy salt ingressions into boilers due to condensor leakages under unfortunate condensate purification conditions. Copper build up in scales could also provide an indication for the tube cleaning operation. Presence of thick deposits of oxide often result in hydrogen embrittlement causing tube bursts.

The above marginal value covers deposit examinations of test pieces from the 60° tube section from the furnace side. As the amount of deposit matter increases when measuring away from this area, the marginal value obtained from deposit examinations of the 180° tube section from furnace side should be reduced by approximately 30% i.e., about 35 mg/cm^2.

Sometimes, the right time of acid cleaning is decided by means of wall temperature measurements or by hydrogen measurements on saturated steam as forewarning for an acid-cleaning operation.

It is necessary to execute acid cleaning at regular intervals; scale deposit volume is increased after 20-30,000 hours of operation, but record of acid cleaning operations indicates a wide range of periods ranging from 8,000 to 80,000 hours, depending upon the efficacy of the feed water treatment plants. Optimal cleaning chemicals are chosen after trials in laboratories, where the cleaning process may be simulated.

Material Selection

The desire to obtain high thermal efficiency has brought about a progressive increase in the steam temperature, the metal temperature being still higher. The inter-related parameters which determine the metal temperatures, (and temperature gradients across the tube wall thickness), such as heat flux, gas temperature, steam temperature and flow rate are usually assessed by the designer in determining the tube operating temperature. The accepted design codes neither specify the maximum design stress for any temperature nor steam pressures in different parts nor indeed the material of construction. Individual boiler makers use their own expertise and experience in designing the most economic tube layout and operating conditions, to decide the limits of pressures and temperatures on the premise that the average life of the pressure element should be of the order of 10^5–$2x10^5$ hours. There is thus scope of considerable differences in the approaches of different boiler makers and even more so, amongst the metallurgists. The ensuing discussion should therefore be viewed in broader prespective.

Boiler materials for service at high temperatures are selected on collective considerations of their creep rupture strength, oxidation resistance, corrosion resistance, weldability and structural stability for prolonged periods. High temperature strength is an especially important factor in selecting materials in the ASME and other boiler codes and allowable stress for respective materials is specified on the basis of creep-rupture strength of 10^5 hours.

Acceptance of the tubes/pipes is further governed by their meeting the requirement of several other tests involving bending, flattening, flaring and hydrostatic pressure tests as specified in the various standards such as those of the ASTM/BSS/ DIN/ISI/ISO.

Further, high temperature creep resistivity steels are known to undergo structural deterioration on account of a number of other factors, notable amongst them may be the following:

- water hammer
- thermal fatigue
- corrosion fatigue
- erosion
- fouling
- vibration
- maldistribution of flow

Steels for Boiler Tubes/Pipes

Table-I lists some of the important ASTM specifications of ferritic steels used in the manufacture of tubes and pipes and Table-II summarises important aspects of their compsition, tube manufacture and heat treatment (the corresponding ASME Boiler and Pressure Vessel Code specification number can be obtained merely by replacing the prefix with the letters "SA". It may be useful to reiterate the metallurgical dictum that composition alone is grossly inadequate to define the properties of any steel and, therefore, does not provide any indication about its performance under any defined conditions of service.

Depending on the zone of applicacation of the tubes in boiler,the specifications provide that the tube can be made by the electric resistance welding of strip steel, or by the seamless process of tube making and could in the latter case, be either hot finished or cold drawn. In order to eliminate the welding stresses and the heat affected zone, all electric resistance welded tubes are supplied after normalising heat treatment which involves heating of the ferritic tubes to temperatures high enough in the austenitic range (1650°F), followed by cooling in air or in the cooling chamber of a controlled atmosphere furnace. When austenite transforms into a ferritic structure during cooling in the normalising treatment, the resulting structure possesses good tensile and stress-rupture properties.

Hot finished tubes and pipes are produced when the entire tube piercing operation is completed in the austenitic range of temperature so that air cooling of the tube, after the completion of the tube making operation, still in the austenitic range, results in simultaneous normalising; occasionally tempering of the normalised structures at 1200°F and above, is additionally recommended as in A 209. If the tube making operation continues to temperatures below the lower critical temperatures of the steel (the so called A_1 temperature), the steel transforms into ferritic structures whilst it is concurrently undergoing plastic deformation when both the ferritic and the pearlitic areas of the structure are mechanically elongated in the direction of metal flow. Whereas the deformed ferritic areas are almost instantaneously recrystallised, as the temperature is still above the recrystallisation temperature of ferrite, the pearlitic areas are not and provide a banded appearance when examined under a microscope. Such tubes would in all probability, pass the short term mechanical acceptance tests prescribed for the hot finished tubes, they are not strictly so. These 'psudo' hot finished tubes posses inferior corrosion and stress-rupture properties which could be easily restored if a full normalising treatment were given.

As far as the cold drawn seamless tubes are concerned, the specifications provide that they may be given a sub-critical anneal, a full anneal or a normalising heat treatment. The subcritical annealing treatment would require heating of the tubes to temperatures below the lower critical temperature (A1) so that only the cold worked ferrite grains are recrstallised into strain-free polygonal ferrite grains and the pearlitic areas remain elongated or deformed. Full annealing and normalising heat treatment would involve heating to 1650°F, and above, and cooling at rates appropriate to the heat treatment. These strucutres are mutually closely similar and also with that of the hot finished tube.

Failures at Bends

None of the specifications, unambiguously define methods for the production of bends, but taking a cue from various specifications for tubes, it can be inferred that for reliable service for extended periods, their structural condition must be closely similar to that of the normalised and tempered structures of the tubes; any cold work or residual stress reduces creep life and creep ductility. In order to avoid the development of cold worked structure, the bending operation should be done after heating the sand filled tube to a temperature high enough in the austentic range. When heating is done outside a furnace, with the help of a flame on the shop floor, utmost care must be exercised in ensuring that neither local overheating norunderheating occurs. Many of the frequent failures of the bends could be metallurgically attributed to the presence of cold work/residual stress or even to the process annealed structures; such failures are characterised by narrow opening with little or no plastic flow or the pitting corrosion occurring from within.

Functional Classification of Boiler Steels

Tubes and pipes used in thermal power stations can broadly be classified into two categoeis : (i) those where heat transfer occurs across the tube wall under conditions of high temperature and pressure and (ii) where the tube/pipe operates under high temperature and pressure but without any heat transfer and is thus used for the purpose of transporting steam. The metal temperatures in latter category remain more or less steady because the temperature of the steam is additionally regulated through the use of attemperator water; in the case of the former type of tubes, the metal temperatures often exceed the maximum of the designed limits and depending on the vagaries of the combustion system, the amount of excess air used and the extent of leakages, load fluctuations, changes in fuel quality, steam starvation etc., the increase in temperature could be upto several hundred degrees Celcius.

In order to optimise the cost of construction of thermal power plants, it is necessary to use cheaper steels, commensurate with long life and continuity of operation. The selection of steels is, therefore, based on the service temperatures and as the thermal conditions inside any boiler vary widely in different locations, a number of steel grades are necessarily used. In those zones, where the temperatures do not exceed about 450°Cs, proof stress at the service temperature need only be taken into account as under these conditions the contribution of creep deformation is minimal; but where the service temperatures exceed 450°C, the contribution of creep deformation assumes importance in determining the service life of the component - the design under these conditions is then based on the values of the stress required to cause rupture in 10^5 hours.

Both the tensile and stress-rupture properties are strongly dependent upon temperature. The seriousness of the problems arising out of the temperature dependence of the stressrupture properties can be appreciated from the fact that a mere 20°C rise in service temperature, for same values of stress, can effectively reduce the rupture life to a third of its life at the lower temperature. When higher temperature excursions occur periodically for shorter durations, the damage is cumulative and the service life is proportinionately shortened.

Since there is no possibility of their temperatures even exceeding the temperature of the steam, cold drawn seamless steel tubes in subcritically annealed or process annealed condition can be used for tubes/pipes meant for transporting high pressure, high temperature steam, in preference to the fully normalised tubes of the same composition because of considerations of cost and surface quality. In this case, the choice between the simple carbon and the chromium-molybdenum steels is based on the temperature of steam - the alloy steels being preferred when steam temperatures exceed 500°C. The tube must be in fully normalised or normalised and tempered condition for all other applications where heat transfer occurs and is the most important functional requirement of the tube. This is true for all grades of steel, including the simple carbon-steels.

It is, therefore, necessary to specify both the steel composition and the heat-treatment. A Japanese paper confirms this point of view. Of the 117 cases of investigations, failures in 76 cases (65%) of evaporator and heater tubes could be attributed to excessive heat phenomena, resulting in "troubles of microstructure change, breaking and swelling due to temperature rising."

BHEL has clarified that all cold drawn tubes used by BHEL are bought from tube supplier's works in the heat treated condition only as per the Technical Delivery Conditions of the purchase of a cold drawn tube being used for manufacture without heat treatment. However, utilities are advised to be careful in drawing up of their purchase specifications for replacements etc.

Premature Water-Wall Tube Failures

During the course of several investigations of the failures of water wall tubes from more than one thermal power station, we have found that many a failures have occurred in those tubes where the structural condition is that of either the subcritically annealed, also called procees annealed, cold drawn tubes, or that characteristic of the psuedo-hot finished tubes. Such structures are grossly inadequate to withstand the vigours of the thermal conditions prevalent in boilers under the Indian conditions where many boilers are not operating as base load units and load fluctuations are a common affair. In such cases the metal temperatures may often be entering the creep range, though the designed conditions of temperature and pressure in the water walls are considerably below the temperature range of creep deformation. The occurrence of thermal fluctuations further aggravates the structural instability of the process annealed steels.

Need for Caution in Interpretation of Specifications

Any material specification is necessarily broad based specially when a range of mechanical pro-perties can be obtained from a particular grade of steel through changes in the heat treatment; in such cases, the steel and its heat treatment. There is need to exercise consider-able caution, not only at the time of ordering, but also during storage and installation specially when one grade of steel, in its differently heat treated conditions can be used in various sectors of a boiler. This aspect has been illustrated above with the help of actual incidences of premature failures when it was shown that the cold drawn seamless tubes in sub-critically or process annealed condition are inadequate for those regions of the boiler where heat transfer is the most important functional requirement, though the sub-critically annealed tubes could give satisfactory long-term perfor-mance in tubes/pipes carrying steam (but without any heat transfer) at relatively higher temperatures and pressures. Under the prevalent conditions of heat transfer, seamless steel tubes of the same composition but in normalised and tempered condition are more desirable.

Tube Failure : Overheating -Heat Flux

The operational scenario may be summarised as follows :

1. Boiler drum in sub-critical circulation boilers receives water from the feed heaters via the economiser where its temperature is raised to near its saturation temperature.

2. Water enters the water wall tubes through downcomers where no heat transfer occurs. Ideally there should be no steam entrapment in the downcomers as any entrapment lowers the available head for natural circulation under the thermo-siphon effect.

3. Heat input pattern varies widely along the length of the heat absorbing path but the design perhaps is based on integrated values of average flux.

4. Upward flow in the riser water wall circuits is basically a two-phase flow with the gaseous steam phase continuoulsy increasing along the upward movement of the fluid (water and steam).

5. Water wall tubes are usually of carbon or low alloy ferritic steel and may be having bends and different diameters along their leingths in the heat transfer zones.

6. The cooling action of the circulating fluids in the tubes effectively prevents burn-out failures due to gross overheating.

7. Ideally, heat transfer should occur through "nucleate boiling" as any departures from nucleate boiling (DNB) would raise the tube wall temperature instantly; the tube temperature returns to normal the moment the vapour

film blanket is ruptured. When this occurs repeatedly at the same location, the metal is additionally subjected to thermal fatigue. Conditions under which the DNB could occur under the same heat flux are not known.

8. DNB occurs readily if the heat flux increases. Though theoretical models for such a situation are not available, the situation of gross rise of temperature is confirmed through experimental studies.

As boiler water is converted to steam, the dissolved solids concentrate in a residual laminar film. The concentration of solids in this film increases until the boiling point of the solution is elevated to the temperature at the wall in accordance with the "concentrating film" theory; specially high concentrations are reached when the deposits are porous, otherwide the turbulent flow around would level out the concentration. On one hand, the deposit raises the metal temperature and on the other, could additionally promote corrosion.

Internal Deposits and Formation of Blisters

A blister may form when the internal deposit increases tube metal temperature until creep occurs. As the heated area swells, the internal deposit cracks off and the tube metal temperature returns to normal. The process may be repeated several times before the blister ruptures. Commonly a large number of tubes are blistered and not noticed until one of the blister cracks open. Since blistering is associated with internal deposits, they are more likely to occur in boilers operated with high percentage of feed water; it should be noted that internal deposit may not be noticed at all on the tube surfaces as it is dislodged by the very process of blistering and carried away to the drum.

Does "Cavitation" Occur?

Apart from the possibility of raising the tube wall temperature in sustained or intermittent manner and promoting a tendency for blister formation in presence of internal deposits or causing degeneration of metallurgical structure through accumulation of creep or thermal fatigue damage, heat transfer under conditions of high heat flux could give rise to the complicating situation in the following manner: When heat flux is great enough, some water in contact with the tube is evaporated, but as the bulk of the liquid is yet below the boiling temperature, steam bubbles migrating from the surface to the interior condense in the main body of the liquid. When the steam bubble collapses, it gives rise to high local pressures and the situation becomes analogous to the phenomenon of "cavitation". Pressure waves similar to those encountered in "water hammer" are created. Under such conditions fluid flow could be considerably affected. The complete phenomenon of cavitation viz., formation of vapour bubbles, their growth and movement into colder regions and their final collapse may take place in a few thousandths of a second. The boundary surface is thus alternately stressed and relieved thereby subjecting the metal to fatigue.

Corrosion in the Combustion Gas Path

Fouling and Fire Side Corrosion

The temperature of the furnace and of the combustion gases decreases progressively through the boiler path. On account of the intense cooling effect of water, the metal temperature in the water wall can be kept in the range 400-450°C though the skin temperature on the fireside can be considerably higher i.e., upto 1200°C on account of the deposition of fine particles of insulating ash on the surface exposed to receive radiant heat. The highest metal temperatures occur in the superheater and reheater sections, not only because steam is required to be superheated, but also because the cooling effect of steam is lower. Since both the creep strength and the corrosion resistance are seriously impaired above 600°C, metal temperatures must not be allowed to have excursions in the forbidden range, otherwise disastrous consequences would follow. Maintenance of oxidising conditions with about 10% excess air in the furnaces ensures stability of the protective magnetite layers on the outer surface.

If, by any chance, mixing of air and pulverised fuel particles is not uniform, reducing conditins could prevail in the furnace locally and cause damage to the protective magnetite film through its reduction. Most damaging reducing conditions occur when incompletely burnt cool particles or carbon-monoxide gas impinge on tube surfaces, or when corrosive and fusible slag forms on the tube surface as a result of complex reactions occurring between the oxides of iron and volatile compounds of sulphur, sodium and other alkali metals and which are further complicated by the presence of vanadium oxide in the furnace oil.

Usually the morphology of corrosive damage on the superheater and reheater tubes in coal fired boilers is different from that on the water wall tubes due to corrosion caused by ash deposits. During ash build up on the tube, the sulphates of sodium, potassium and calcium formed upstream in the furnace section gradually accumulate at the base of the porous ash deposit. This mixed sulphate deposit remains molten at the tube surface temperature around 600-650°C and forms a thin layer of extremely corrosive liquid next to the protective oxide layer. The molten sulphate layer offer "boarding" to free SO_3 which attacks the protective oxide layer and thus enhances the rate of metal wastage.

Copper in Coal Ash - A Unique Situation

It may at this stage be appropriate to make a general remark with regard to the ash of coal. The ash is gnerally regarded as non-corrosive and is perhaps so unless it is vitiated by trace impurities present in the ash or furnace oil as stated above. Coal ash is known to contain trace of metallic impurities and some may contain harmful metals like copper and arsenic besides alkalies. The following data can be taken as illustrative of the situation only :

Element	UK Coal ppm	Indian Coal ppm	Indian Ash ppm
Arsenic	1-100	Trace	Nil
Boron	5-140	-	-
Chronium	-	1-2	400-700
Copper	5-50	-	16-40
iron	5-500	10-15	-
Gallium	3-10	Upto 20	-
Germanium	8-10	Upto 12	3-30
Tin	-	Trace	-
Vanadium	1-60	100-400	-
Zinc	5-60	14	110-2600

Aggressive vanadium deposit may not be formed in the absence of alkali and sulphate which are very low in Indian coals. Further, the alkali present in Indian coal may not be released for the purpose of formation of deposits because the high temperature required for their release is high enough to simultaneously form a glassy phase, thus consuming the alkali which is thus not available in free state to form corrosive, low melting phase with vanadium. It has been found that the aggressiveness of vanadium deposits is minimized by addition of zinc compounds - zinc alkali vanado sulphate thus formed is less aggressive than alkali vanado sulphate to cause corrosion. Indian coals do contain zinc and this is their welcome feature.

Many failures caused by external corrosion at Korba were found to have been aggravated by the presence of copper which was traced to its minor presence in coal/ash.

Table - I

Specifications Having Relevance for the Boiler Industry

ASTM NO.	Description	COMPOSITION %					
		Grade	C	Mn	Cr	Mo	Si
106-68	Seamless carbon steel pipe for high temperature service and for use in central stations having steam service pressures of 400 psi and over and high temperatures	Grade A	0.25 max.	0.27-0.93	-	-	-
		Grade B	0.30 max.	0.29-1.06	-	-	
		Grade C	0.35 max.	0.29-1.06	-	-	-
178-69	Electric Resistance welded carbon steel boiler tubes intended for use as boiler tubes, boiler flues, superheater flues.	Grade A Low carbon steel	0.06-0.18	0.27-0.63	-	-	-
		Grade C medium-carbon	0.35 max.	0.80 max.	-	-	-
179-66	Seamless cold drawn low-carbon steel heat exchanger and condenser tubes for appplications covered		0.06-0.18	0.27-0.63	-	-	-
192-62	Seamless carbon steel boiler tubes for high pressure service		0.06-0.18	0.27-0.63	-	-	-
199-69	Seamless cold drawn intermediate alloy steel heat edxchanger and condenser tubes	Grade 3B					-
		T3b	0.15 max.	-	1.65-2.35	0.44-0.65	-
		T4	0.15 max.	-	2.15-2.85	0.44-0.65	-
		T5	0.15 max.	-	4.00-6.00	0.45-0.65	-
		T7	0.15 max.	-	6.00-8.00	0.44-0.65	-
		T9	0.15 max.	-	8.00-10.0	0.90-1.10	-
		T11	0.15 max.	-	1.00-1.50	0.44-0.65	-
		T21	0.15 max.	-	2.65-2.25	0.80-1.06	
		T22	0.15 max.	-	1.90-2.60	0.87-1.13	

ASTM NO.	Description	COMPOSITION %					
		Grade	C	Mn	Cr	Mo	Si
209-69	Seamless carbon-molybdenum alloy steel boiler and superheater tubes	Grade T1	0.10-0.20	-	-	0.44-0.65	-
		Grade T1a	0.15-0.25	-	-	0.44-0.65	-
		Grade T1b	0.14 max.	-	-	0.44-0.65	-
210-69	Seamless medium-carbon steel boiler and superheater tubes	Grade A-1	0.27 max.	0.93 max.	-	-	-
		Grade C	0.35 max.	0.29-1.06	-	-	-
213-66	Seamless ferritic and austenitic alloy steel boiler superheater and heat exchanger tubes	T2	0.10-0.20	-	0.50-0.81	0.44-0.65	-
		T5b	0.15	-	4.00-6.00 with silicon	0.44-0.65 0.50 max. 1.00-2.00	-
		T5c	0.12 max.	-	4.00-6.00 with silicon	0.44-0.65 0.50 max.	-
		T12	0.15 max.	-	0.80-1.25	0.44-0.65	-
		T17	0.15-0.25 max.	-	0.80-1.25 with 0.15 vanadium		-
-250	Electric resistance-welded carbon-molybdenum alloy steel boiler and superheater tubes			(same as 209)			
335-65	Seamless ferritic alloy pipe for high temperature service	P1	0.11-0.20	-	-	0.44-0.65	0.1-0.5
		P15	0.15 max.	-	-	0.44-0.65	1.15-1.65
		Also grades P2, P5, P5b, P5c, P7, P9, P11, P21, P22 where the composition is identical with corresponding tube grades in A-199 and A-213 above.					

Whereas the amount and nature of ash can partly be changed by coal-washing operations (studies for the optimisation of which are required), it is a moot question, if steam conditions could be reduced where the use of coals with aggressive ash is unavoidable. The entry of copper in steel of boiler tubes is facilitated by the tube running at higher the tube running at higher temperatures; such failures at Korba may not have occurred if the temperatures were in range estimated in their design.

Since thermal fluctuations are unavoidable, an element of flexibility must be introduced in boiler design and material selection. ❑