CAUSTIC GOUGING IN BED TUBES OF HIGH PRESSURE AFBC BOILERS

SYNOPSIS

This article is about water side corrosion due to a mistake in design of boiler. Corrosion in the boiler is prevented by maintaining a boiler water condition in such a way that the magnetite layer is retained. Boiler water has to be at a pH of 9 to 10.2 in order to preserve the magnetite layer of steel. This is done by dosing sodium phosphate in boiler water through HP dosing system. In case there is a mechanism of concentration of the alkalinity of boiler water anywhere in the evaporative circuit, caustic gouging / caustic attack occur. This is what happened in the some of the high pressure AFBC installations that came up in the last year.

A RECALL OF THE PAST

I had come across the first failure in the year 1990 in 30 TPH AFBC boiler. The bed evaporator tubes failed in 4th compartment within six months after the boiler was commissioned. I happened to analyze the failure cause at that time. I had seen gross deviations in water chemistry. The alkalinity level was very high and there was clear indication of free OH presence in boiler water. Since the load on the boiler was less, the 4th compartment was always kept under shut down. Circulation is a function of heat flux in the evaporator tube. When the heat input is less the steam generation is less. The velocity of the water in such tubes is expected to be too low, resulting in film boiling. Film boiling would lead to concentration of boiler water. The local water alkalinity could reach very high level thus resulting in break down of magnetite layer. The iron gets dissolved as $Fe(OH)2$. The failed tubes had a groove mark as shown in photo 1. The leakage develops through a pin hole in the groove portion where the material is continuously removed by the caustic action. See the Photo -1.

IN THIS YEAR,

In the recent past 12 months, I came across the same failure in several FBC boilers which were designed for high pressure. In AFBC Boilers the heat flux is the highest in bed evaporator tubes. It is in the order of 390 to 400 kW/m2 expressed on tube inside area basis. As the pressure of the boiler goes to 88 kg/cm2 & above, the circulation ratio comes down. This could be 8 to 10 depending the circulation system design. The flow through the bed tubes may not be a fully mixed flow. It is a subject of flow pattern inside tubes, when the steam fraction increases in the boiler tubes.

FLOW PATTERNS

Steam and water have different densities at different pressure. At the critical pressure, the water and steam have practically the same density. At the lower circulation ratios, the steam and water can exist in several flow patterns inside the tubes. Flow pattern means distribution of the steam with respect to water. The important physical parameters which determine the flow pattern are

- Surface tension – which keep the pipe always wet and which tends to make small water droplets and less diameter spherical steam bubbles.
- Gravity – which tends to pull the water to bottom of pipe and push the steam to the top of pipe – specifically in inclined tube.

There are various patterns of flow that exist inside tubes. The patterns are defined with respect to orientation of tubes.

FLOW PATTERN IN VERTICALLY ORIENTED TUBE

The common flow patterns for vertical upward flow, which is when the boiler tube is oriented vertical, are as shown in figure 1. As the quality, that is steam to water ratio increases, the flow patterns change from bubbly to wispy annular flow. In the boiler the steam / water ratio that is prevailing in the particular circuit along with the mass flux would have decided the flow pattern inside tube. Undoubtedly, the flow has to be bubbly flow so that the water / steam flow well mixed inside tube without any steam blanketing inside the tube. Otherwise the metal temperature would go up resulting in tube bursts.

Bubbly flow: the steam / water bubbles are uniform in size.

Slug / Plug flow: the steam flows as large bullet shaped bubble. Also the steam bubbles prevail as small bubbles in water. This flow pattern is also called plug flow.

Churn flow: Highly unstable flow of oscillatory in nature. The water near the tube walls continuously pulses up and down.

Annular flow: The liquid travels partly as annular film on the walls of the tube and partly as small drops distributed in the steam which flows in the centre of the tubes.

Wispy- annular flow: As the water flow rate is increased in annular flow, the concentration of drops in the steam core increases. Ultimately the droplet concentration in the core leads to large lumps or streaks / wisps of water in the steam core. The flow pattern is the characteristic of high mass flux.

FLOW PATTERN IN HORIZONTALLY ORIENTED TUBE

The phases tend to separate due to density difference causing a form of stratified flow to be very common. This makes the heavier water phase to accumulate at the bottom of tube. When the tube is inclined at an angle the pattern the slug / plug flow is common. The common flow patterns in horizontal tubes are illustrated in figure 2.

Flow patterns vary from that of vertical tubes due to gravitational forces which act perpendicular to the direction of flow. As the steam fraction increases, the flow pattern changes from Plug to annular flow.

Plug flow: The individual steam bubbles have coalesced to produce long plugs. The steam bubbles tend to flow along the top of the tube.

Stratified flow: the steam to water interface is smooth.

Wavy flow: the stratified flow may not remain smooth for long as the steam fraction increases, the flow becomes wavy.

Slug flow: the wave amplitude is so large that the wave touches the top of the tube.

Dispersed bubble flow: many small steam bubbles are distributed uniformly across the entire tube cross section when the steam and water velocities are high.

Figure 3 is the very well known representation of the steam bubble behavior inside a horizontally oriented tube. It is the designer’s job to design the evaporation circuit with proper downcomer and riser arrangements, evaporator tube arrangements to ensure the nucleate boiling prevails in each part of the boiling circuit.

WHAT CAN HAPPEN INSIDE THE BED TUBE UNDER VERY LESS HEAT INPUT?

When the velocity inside the tube is less, the steam bubble may rise to the top and form a bubble adhering to tube wall at 12^o clock position. In vertically oriented tube the steam bubble would get in to the water phase. As the steam bubble sticks to the top, the water begins to concentrate in alkalinity. The tubes may not fail due to steam blanketing because the gas side temperature may be low. But corrosion mechanism begins and results in a gouged tube as seen in photo 2.

WHAT CAN HAPPEN INSIDE BED TUBE UNDER SITUATION OF HIGH HEAT INPUT, HORIZONTAL / LOW SLOPED ORIENTATION / LESS VELOCITY?

High heat input would help in forming more steam bubbles to facilitate the growth of the bubble. As the bubble size increases, it would raise to the top of the tube in the absence of sufficient horizontal velocity or when the tube is horizontal or inclined to very low angle. Now the steam forms a blanket inside the tube, may be for a moment, before being washed away by water.

SO WHAT IF THE STEAM BLANKETS THE TUBE?

When the blanket is heavy and in the absence of horizontal velocity component, the steam would get superheated and tube would have failed due to high metal temperature. The failure would have been instantaneous. This is called dry out and the heat flux is called critical heat flux.

When there is a horizontal velocity component the steam bubbles and water wetting alternately take place at the top of the tube. This is described as slug flow / intermittent flow. Now we have a mechanism of local concentration of solids due to evaporative boiling. The water going along the top of the tubes has a different velocity as compared to the stream of water going along bottom of tubes. This boiler water sample, upon which the control is based, represents an average of all the water within the boiler and as such it contains water subjected to both the most severe and the least severe conditions within the boiler. Hence water chemistry except for presence of corroded iron at drum internals, does not indicate concentration of solids / chemicals inside the low sloped bed tubes. The low slope tubes may prevent adequate mixing with the bulk liquid phase and over time, a concentration gradient will develop between the bulk boiler water and the localized solution in contact with the magnetite surface. Localized concentrations for some species may be two or more orders of magnitude higher than in the bulk boiler water (Cohen et al., 1962). Under these conditions, species, such as NaOH and NaCl, with relatively high solubilities tend to stay in solution, while those of more limited solubility, such as those incorporating phosphate species, may exceed their solubility limits, and undergo precipitation. In general wherever the tubes had failed due to gouging, the analysis indicated phosphate salts.

APPEARANCES OF FAILED BED TUBES

The gouging type failures (as in photo 1) have been seen in at least six installations where the slope of the bed tube happened to be less than 5 deg. The steam to water fraction happened to be higher and the overall circulation ratio was estimated as 8-12. Depending upon the water outlet temperature at economiser, the water inside the bed tubes begin to boil at a distance from the wall. The gouging mark was seen inside the tube after the steaming point. At one unit where the economiser outlet water temperature was very less, the gouging was seen in the upper portion of hairpin bed coil.

WHAT NEEDS TO BE DONE TO DELAY THE FAILURE?

When it happened, the immediate concern was to how to keep the boiler on line before any remedial measures could be taken.

1. Operating at lower loads / lower pressure will lead to delayed failure. This is mainly due to the reason that the steam to water ratio is more at rated load & rated pressure.

2. Operation of the boiler within narrow range of phosphate offers a time delay against unavoidable failure.

WHAT IS TO BE DONE TO PREVENT THE FAILURES IN FUTURE?

When it was zeroed down that the angle of slope of the bed coil was the prime cause for failure, the next question was how to rectify the design defect.

1. To prevent failure the slope of the tube has to be raised. In many cases the increase in angle would have resulted in less bed HTA. Alternate configurations have to be thought of to avoid lower slopes. While replacement of bed tubes increased slopes shall be considered. This conclusion was based on one boiler operating with 10 deg slope at 110 kg/cm2 pressure.
2. The circulation ratio can be improved by adopting better designed downcomer riser layout. We can not adopt a common downcomer system for two circuits which have different heat flux. This mistake is seen in some units: the downcomer is common for water walls that were having less steaming rates. In such circuits there will be poor flow rates. This also reduces the mass flow rate in bed tubes depending upon how the branching is done.
3. Rifle bore / internally ribbed tubes are to be used to enhance mixing of steam and water. In the installations where the tubes had already failed this was the only solution. Rifle bore tubes have spiral ribs which impart swirling motion to steam-water mixture flowing through the tubes. The mixing of steam & water ensures the constituents of water inside the tube are the same as that of bulk water. Rifle bore / internally ribbed tubes are being used in once-through boilers. In future for 88 kg/cm2 and beyond, rifle bore tubes are to be used.

A REVIEW OF CAUSTIC GOUGING MECHANISMS

Caustic gouging is a form of corrosion of steel. It generally results from fouled heating surface and the active corrodent (sodium hydroxide) in the boiler water. Concentrated solutions of alkali occur in situations where the normal water washing of tube metal is restricted after the steam bubble release. The concentrations of corrosive solutions occur at the heat transfer surfaces as the result of fouling by porous deposits such as iron and copper oxides. These deposits are typically formed from particles suspended in boiler water. Once the corrosive concentration mechanism is started, the additional corrosion products are generated from porous deposits. Boiling under the deposits is often referred as Wick boiling. Boiler water permeates the porous deposit by capillary action through small pores like a liquid permeating a wick. Steam then escapes through the larger pores (channels) leaving non volatile solutes behind. These new deposits then concentrate beneath deposits.

Feedwater solids concentrate in the boiler relative to blow down rates. Boiler water solids may concentrate an additional 2000 times at the heat transfer surface as a result of a concentrating film produced from non boiling equilibrium. The formation of a steam bubble further concentrates boiler solids. These conditions are most likely reached in the presence of porous deposit.

Once the local caustic concentrations are reached such that caustic attack occurs, the corrosion can proceed to failure in a very short time. Caustic corrosion is an irregular thinning or gouging of the tube water side surface. Areas subject to caustic attack typically show smooth round rolling contours surrounded by encrusted boiler water solids and crystalline dense oxides. The oxides however are not protective. Particles of metallic copper may also be embedded in the deposit layer.

Failures due to caustic attack are caused by metal loss. The damage progresses to failure when the tube wall thins to a point where rupture occurs locally. The microstructure does not change and the tube metal retains ductility.

Caustic attack can also lead to other type of failures. One form is the hydrogen damage which results from hydrogen liberated in the corrosion process diffusing in to the metal. The hydrogen can then react with iron carbides in the metal to produce methane which develops pressure leading to the formation of inter-crystalline cracks. Stress corrosion cracking can also occur due to hydrogen diffusion along the grain boundaries.

DETAILED CORROSION MECHANISM

FORMATION OF MAGNETITE LAYER

The control of corrosion in boiler environment is based on maintaining conditions which enhance passive film formation. Magnetite, Fe_3O_4 is the preferred high temperature iron oxide form. Well crystallized (unhydrated) magnetite forms a dense layer resulting in excellent passivation. The formation of magnetite takes place as shown below.

Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric Ion
FeO	Ferrous oxide – Iron II oxide
Fe_2O_3	Ferric oxide – Iron III oxide
Fe_3O_4	Ferrous ferric oxide – Iron II, III oxide
$FeOH_2$	Iron II hydroxide
FeO(OH)	Iron II oxide hydroxide
$Fe(OH)_3$	Iron III hydroxide

(Reaction -1) $Fe + 2H_2O \leftrightarrow Fe^{+2} + 2OH^- + H_2$

(Reaction -2) $Fe^{+2} + 2OH^- \leftrightarrow Fe(OH)_2$

(Reaction -3) $3Fe(OH)_2 \leftrightarrow Fe_3O_4 + 2H_2O + H_2$

It is seen from reaction 2, that the hydroxyl ions are to help in continuous formation of $Fe(OH)_2$ – that is soluble iron II oxide. Fe_3O_4 forms over the inner surface of tube offering a continuous protection. On the whole it is a passivation process is basically due to an active surface of Fe being corroded to a relatively inactive state of Fe_3O_4.

Under good operating condition, the oxidation of iron to magnetite at the metal surface is slow because the magnetite forms a fine, tight adherent layer with good protective properties. The film generally displays good adhesive strength in part because thermal coefficients of liner expansion for magnetite and layer are very similar. Therefore varying heat load and surface temperature do not cause undue stress between the film and the underlying metal surface.

DETERIORATION OF MAGNETITE LAYER IN HIGHLY ALKALINE ENVIRONMENT

Magnetite is considered to be a co polymer of the iron (II) hydroxide –FeO and iron (III) oxide – Fe2O3. In this system the bonds of divalent iron are more easily hydrolyzed. That is FeO can become FeO.OH by the following equation. The iron (II) hydroxide system (aqueous) is considered to be in solution equilibrium with magnetite as follows.

(Reaction -4) - $Fe_3O_4 + 2H_2O \leftrightarrow Fe(OH)_2 + 2FeO.OH$

The solubility of magnetite layer in highly alkaline atmosphere (OH^-) is explained as below. Under highly alkaline conditions the ferrous hydroxide in solution may react as follows.

(Reaction -5) - $Fe(OH)_2 + OH- \leftrightarrow Fe(OH)_3 \leftrightarrow HFeO_2 + 2H_2O$

(Reaction -6) - $Fe(OH)_2 + 2OH- \leftrightarrow Fe(OH)_4 \leftrightarrow FeO_2^{-2} + 2H_2O$

Caustic attack occurs in this manner through activation of the carbon steel surface by removal of passive oxide layer inhibiting its formation. These conditions lead to the formation of a velvet black, finely crystalline, reactive magnetite. It has low adherence and practically no protective effect.

As a result the magnetite layer is dissolved in the form soluble ferrate ions as the equilibrium in reaction 4 is driven to the right via removal of ferrous oxide. In addition further formation of magnetite layer is inhibited as the equilibrium in reaction 2 is driven to favor soluble ferrate ion formation instead of magnetite as illustrated in reaction 3.

The distortion of equilibrium illustrated in reactions 2 and 4 following the reactions 5 and 6 requires the presence of very high concentration of hydroxyl ions. Concentration of hydroxyl ions can be found at boiler heating surfaces where normal washing of surfaces by boiler water is restricted due to either presence of deposits or the development of a film of superheated steam at the surface of tube.

CONCLUSION

To summarize, steam blanketing can also lead to caustic gouging. This occurs when stratification of the steam water mixture produces high concentration of caustic. Steam blanketing can occur when the fluid velocity is insufficient to maintain turbulence and produce phase mixing. Steam blanketing can also occur in low sloped tubes where the heat flux is high.

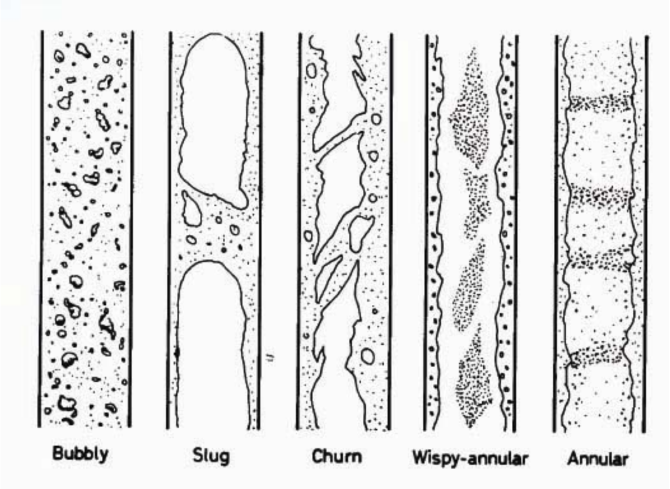

Figure 1: flow patterns in vertical oriented tube.

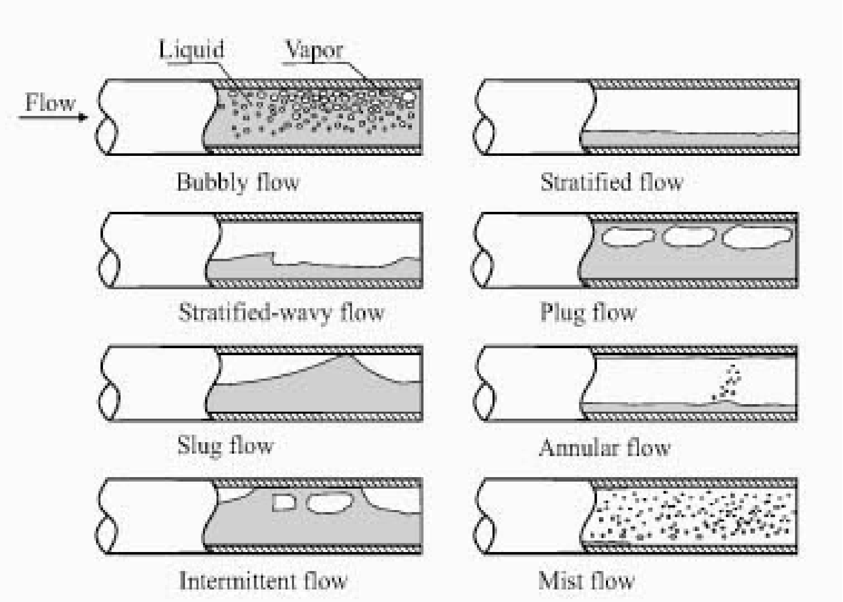

Figure 2. Flow patterns in horizontal tubes.

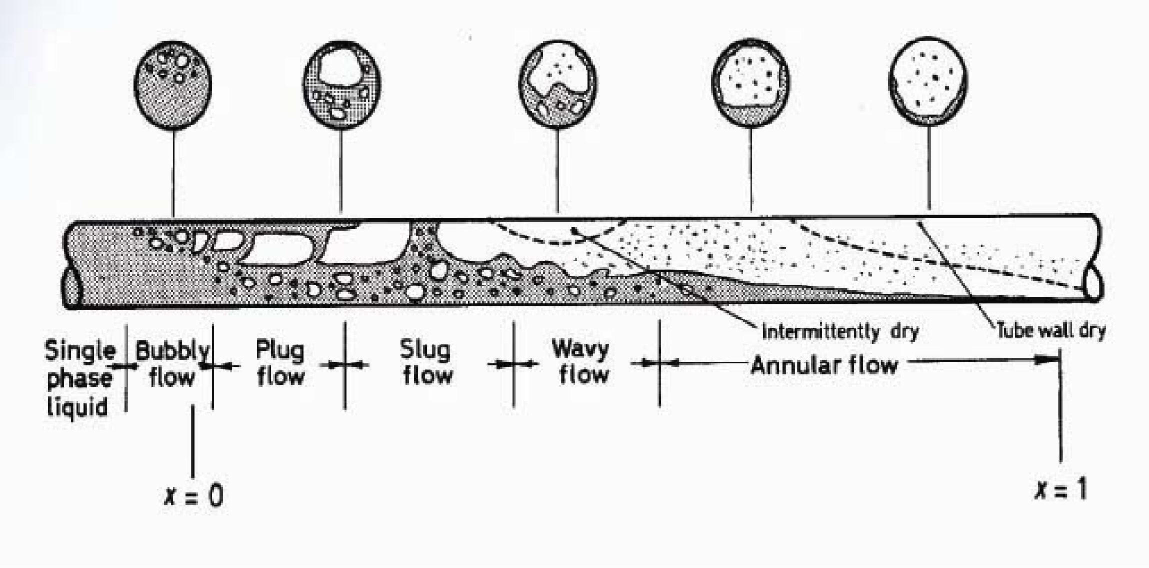

Figure 3. Boiling phenomenon in horizontal tubes for various steam fraction.

Photo 1- shows the deposition of chemical at top portion of bed tube.

Photo 2- shows the material loss at top portion of bed tube.

Photo 3- shows the internally ribbed tube / also known as rifle bore tube.