BOILER PROBLEMS

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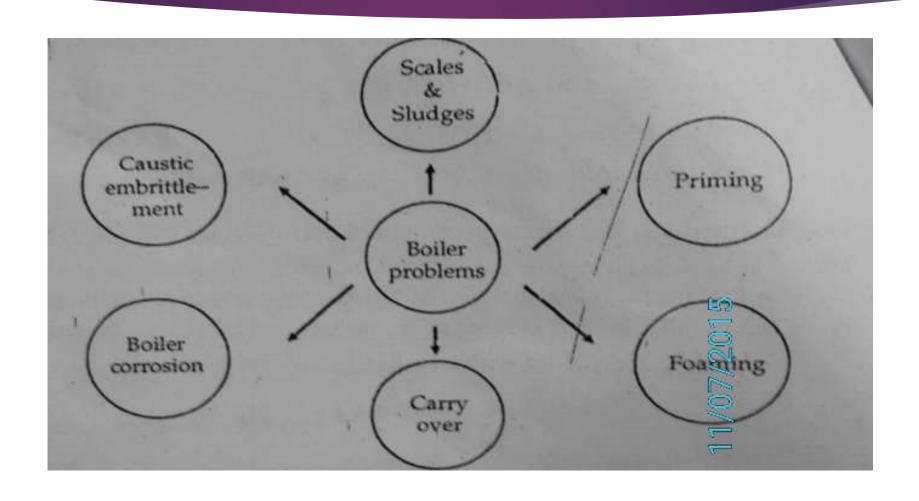
BOILER

- ▶ A boiler is a device for generating steam, which consists of two principal parts: the furnace, which provides heat, usually by burning a fuel, and the boiler proper, a device in which the heat changes water into steam. The steam or hot fluid is then recirculated out of the boiler for use in various processes in heating applications including water heating, central heating, boiler-based power generation, cooking, and sanitation.
- ▶ Proper treatment of boiler feed water is an important part of operating and maintaining a boiler system. As steam is produced, dissolved solids become concentrated and form deposits inside the boiler. This leads to poor heat transfer and reduces the efficiency of the boiler.

BOILER FEED WATER

- ► Feedwater is water that undergoes purification or preheating and is then supplied to boilers for hot water and steam production, or it can remain still. It is typically found in thermal power plants where it is stored and conditioned in tanks, known as boiler feedwater.
- ▶ It should have the following composition:
 - 1. Its hardness should be below 0.2 ppm.
 - 2. Its caustic alkalinity(due to OH⁻)
 - 3. Its soda alkalinity(due to Na₂CO₃)should be 0.45-1ppm.

BOILER PROBLEMS



Sludge and Scale Formation In Boilers

▶ In a boiler, water is continuously evaporated to form steam . This increases the concentration of dissolved salts Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates. If the precipitates formed are soft loose and slimy, these are known as sludges; while if the precipitate is hard and adhering on the inner walls, it is called as scale.

■ Where [A^{y+}] and [B^{x-}] are the ionic concentrations in a saturated solution. Thus, solubility product of an electrolyte may be defined as "the maximum product of the concentrations of its constituent ions (expressed in moles per Litre) in its, solution, when each ionic concentration term being raised to the no. of times the ion occurs in the equation representing the solution of 1 molecule of the electrolyte."

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Let S mole/Litre be the solubility of the electrolyte, then concentration,
                      [A^{y+}] = x S \mod / L and [B^{x-} = y \cdot S \mod / L]
 K_{SP} = [A^{y+}]^x [B^{x-}]^y = [xS]^x [y.S]^y = x^x \cdot y^y \cdot S^{x+y}
For example, in case of BaCl<sub>2</sub> \rightleftharpoons Ba<sup>2+</sup> + 2 Cl<sup>-</sup>; x = 1, y = 2.
                                 K_{SP} = 1^1 \cdot 2^2 \cdot S^{1+2} = 4 \cdot S^3
 Cases:
1. If K_{SP} = [A^{y+}]^x [B^x]^y \implies solution is just saturated
2. If K_{SP} > [A^{y+}]^x [B^{x-}]^y or solubility product > ionic product
⇒ Solution is unsaturated and more salt can be dissolved in it.
3. If K_{SP} < [A^{y+}]^x [B^x]^y or solubility product < ionic product
\Rightarrow Solid A_x B_y will precitipitate out.
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SLUDGE

Sludge is. a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubilities in hot than in cold water, e.g., MgCO₃, MgCl₂, CaCl₂, MgSO₄; etc. They are formed at comparatively in colder portions of the boiler and get collected at places where the flow rate is slow, they can be easily removed. (scrapped off) with a wire brush. If sludges are formed along-with scales, then former gets entrapped in the latter and both get deposited as scales.

Disadvantages of sludge formation

- Sludges are poor conductors, so they tend to waste a portion of heat generated and thus decrease the efficiency of boiler.
- ► Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

Prevention of sludge formation

- ▶ By using softened water.
- ▶ By frequently "blow-down operation', (i.e., partial removal of concentrated water through a tap at the bottom of boiler, when extent of 'hardness in the boiler becomes alarmingly high.)

SCALES

- Scales are hard deposits firmly sticking to the inner surfaces of the boiler. They are difficult to remove, even with the help of hammer and chisel, and are the main source of boiler troubles.
- Scales may be formed inside the boiler due to :
- ▶ i) Decomposition of calcium bicarbonate

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$
scale

However, scale composed chiefly of calcium carbonate is soft and is the maincause of scale formation in low-pressure boilers.

But in high—pressure boilers, CaCO₃ is soluble due to the formation of Ca(OH)₂

$$CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2 \uparrow$$
 soluble

Cont....

(ii) Decomposition of calcium sulphate: the solubility of $CaSO_4$ in water decreases with increase in temperature; $CaSO_4$ is soluble in cold water, but almost completely insoluble in superheated water. [It may be due to increased ionization at high temperature so $k_{sp} < k_{ionic\ prod.}$ and less availability of water molecules for solvation at high temperature.

Consequently, CaSO4 gets precipitated as hard scale on the hotter parts, of the boiler. This type of scale causes troubles mainly in high-pressure boilers. Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(iii) Hydrolysis of magnesium salts: Dissolved magnesium salts get hydrolysed (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a soft type of scale, e. g.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 \downarrow + 2HCl$$

(iv) Presence of silica: Even if a small quantity of SiO₂ 'is present, it may deposit as calcium silicate (CaSiO3)"and/ or magnesium silicate (MgSiO₃). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

Disadvantages of Scale formation

- ▶ (1) Wastage of fuel: Scales have a poor thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or overheating is done and this causes increase in fuel consumption.
- ▶ (ii) Lowering of boiler safety: Due to scale formation, over-heating of boiler is done in order to maintain a' steady supply of steam. It makes the boiler material. softer and Weaker. This causes distortion of boiler tube and also makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.
- ▶ (iii) Decrease in efficiency: Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of the boiler.
- ▶ (iv) Danger of explosion: When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in development of sudden high-pressure which may cause explosion of the boiler.

Removal of Scales

- ▶ Scales are removed by mechanical methods (i -iii) and /or by chemical methods (iv).
- (i) If the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush,
- ▶ (ii) If the scales are brittle, it 'can be removed by giving thermal shocks (i .e. heating the boiler and then suddenly cooling with cold water),
- ▶ (iii) If the scales are loosely adhering, they can also be removed by frequent blow-down operation. Blow-down operation is partial removal of hard water through a 'tap' at the bottom of the boiler, when extent of hardness in the boiler becomes alarmingly high. 'Make-up' water is addition of fresh softened water to boiler after blow down operation.
- (iv) if the scales are adherent and hard, they can be removed by dissolving them by adding chemicals e.g., CaCO₃ scales can be dissolved by using 5 10% HCl. Calcium sulphate scales can be removed by adding EDTA, since the Ca EDTA complex is highly soluble in water

Priming

- ▶ When steam is produced rapidly in the boilers, some droplets of water are carried along with the steam. This process of 'wet steam' formation is called priming.
- Priming is caused by :
- ▶ (i) the presence of considerable quantities of dissolved solids (mainly due to suspended impurities and due to dissolved impurities in water).
- (ii) Steam velocities high enough to carry droplets of water into the steam pipe.
- (iii) Sudden boiling .
- ▶ (iv) Faulty design of boiler.

Priming can be avoided by

- ▶ (i) controlling rapid change in steaming velocities.
- ▶ (ii) the proper design of boilers (maintaining low water levels in boilers).
- ► (iii) ensuring efficient softening and
- ▶ (iv) filtration of the boiler-water carried over to the boiler.
- (v) by blowing off sludge or scales from time to time.

Foaming

► Foaming is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. foming is caused by the presence of an oil and alkalis in boiler-feed water. Actually oils and alkalis react to form soaps which greatly lowers the surface tension of water and thus increase the foaming tendency of the liquid.

Foaming can be avoided by

- ▶ (i) the addition of anti-foaming agents, which act by counteracting the reduction in surface tension. For example addition of caster oil (which spreads on the surface of water and therefore) neutralises the surface tension reduction.
- ▶ (ii) The removal of foaming agent (oil) from boiler water.
- ► Traces of oils are generally introduced in boiler feed water through the lubri- cating materials used for pumps etc. Oils can be removed by the addition of aluminium compounds, like sodium alluminate and ' aluminium sulphate which are hydrolysed to form aluminium hydroxide'flocks which entrap oil drops. The flocks of Al(OH)₃ containing oil droplets are removed by filtration through anthrafilt filter bed.

Carry Over

- ► The phenomenon of carrying of water along with impurities by steam is called "carry over". This is mainly due to priming and foaming.
- Priming and foaming, usually occur together. They are objectionable because :
- ▶ (i) dissolved salts or suspended solids in boiler water are carried by the wet steam to superheater and turbine blades, where they get deposited as water evaporates. This deposit decreases the efficiency of boiler.
- ► (ii) dissolved salts may enter the parts of other machinery, thereby decreasing their life;
- ▶ (iii) The maintenance of the boiler pressure becomes difficult because of improper judgement of actual height of water column.

Boiler Corrosion

- ▶ Boiler corrosion is "decay" or "disintegration" of boiler body material either due to chemical or electrochemical reaction with its environment.
- ► The disadvanatages of corrosion are :
- ► (i) Shortening of boiler life.
- (ii) leakages of the joints and rivets.
- ▶ (iii) increased cost of repairs and maintenance.

Corrosion in boilers is due to the following reasons

▶ (1) Dissolved oxygen :

This is the most usual corrosion causing factor. In boilers, oxygen is introduced through the raw water supply. Water usually contains about 8 ppm of dissolved oxygen at room temp. As the water is heated; the dissolved oxygen is set free and the boiler starts corroding. Dissolved oxygen reacts with the iron of boiler in presence of water and under prevailing high temp. to form ferric oxide (rust).

$$4\text{Fe}+4\text{ H}_2\text{O}+2\text{O}_2 \rightarrow 4\text{Fe}(\text{OH})_2$$

$$4Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O]$$

Ferrous hydroxide Rust

Removal of dissolved oxgyen

(i) By adding hydrazine or sodium sulphite or sodium sulphide.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

- Hydrazine is an ideal chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Consequently, hydrazine removes oxygen without increasing the conc. of dissolved solids/ salts.
- (i) Pure hydrazine is not used in water treatment because it is an explosive inflammable liquid so 40% Aqueous solution of hydrazine is used which is quite safe.
- (ii) Excess hydrazine must not be used because excess of it decomposes to give NH₃, which causes corrosion of some alloys like brass etc. used in condenser tubes.

$$3 N_2 H_4 \longrightarrow 4 N H_3 + N_2$$

- On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate is formed. Under high pressure it decomposes giving SO₂. The SO₂ enters the steam pipes and appears as corrosive sulphurous acid'(H₂SO₃) in steam condensate. So as a rule a very low concentration of 5-10 ppm of Na₂SO₃ in the boiler is maintained, rather adding it intermittently.
- (ii) By mechanical deaeration: This process consists of spraying water over preheated perforated plates stacked in a tower. Removal of dissolved 02 is ensured by applying high temperature and vacuum.

(2) Carbon dioxide.

► There are two sources of CO₂ in boiler water, viz. dissolved CO₂ in raw water and CO₂ formed by decomposition of bicarbonates in H₂O according to the equation :

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$

Carbon dioxide presence of water forms carbonic acid which has a corrosive effect on the boiler material like any other acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$
Carbonic acid

- CO₂ can be removed by:
 - (i) mechanical de-aeration along with O_2 .
 - (ii) filtering water through limestone

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

But this method increases hardness

iii) addition of appropriate quantity of ammonium hydroxide

$$CO_2 + 2NH_4OH \longrightarrow (NH_4)_2 CO_3 + H_2O$$

(3) Mineral acids.

Magnesium chloride, if present in boiler feed water, can undergo hydrolysis producing HCl

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 \downarrow + 2HCl \uparrow$$
scale

The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust in the following way:

Fe + 2HCl
$$\longrightarrow$$
 FeCl₂ + H₂

FeCl₂ + 2H₂O \longrightarrow Fe(OH)₂ + 2HCl

2Fe(OH)₂ + O₂ \longrightarrow Fe₂O₃ . H₂O

- Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Consequently, presence of even a small amount of MgCl₂ cause corrosion of iron to a large extent.
- As the boiler water is generally alkaline and hence the acid is usually neutralized. In case, the amount of acid is more, calculated quantity of alkali is added from outside to neutralize the acid for preventing this corrosion.

Caustic Embrittlement

- Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.
- During softening by lime-soda process, it is likely that some residual Na₂CO₃ is still present in the softened water. In high pressure boilers Na₂CO₃ decomposes to give sodium hydroxide and CO₂, and sodium hydroxide thus produced makes the boiler water "caustic".

$$Na_2CO_3 + H_2O \rightarrow 2 NaOH + CO_2$$

- ► This caustic water flows into the minute hair-cracks, present in the inner side of boiler, by capillary action. On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, thereby dissolving iron of boiler as sodium ferrate. This causes embrittlement of boiler walls more particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.
- Mechanistically embrittlement arises due to the setting up of a concentration all. With the iron surrounded by dil. NaOH acting as the Cathode, while the iron surrounded by conc. NaOH acting as the anode. The iron in the anodic part gets dissolved or corroded.

Caustic embrittlement can be prevented

- (i) by using sodium phosphate as softening reagent, instead of sodium carbonate in external treatment of boiler water.
- (ii) by adding tannin or lignin to boiler water which blocks the hair cracks ' in the boiler walls thereby preventing infiltration of caustic soda solution into these areas.
- (iii) by adding sodium sulphate to boiler Water: Na₂SO₄ also blocks hair-cracks, thereby preventing infiltration cf caustic soda solution in these. it has been observed that caustic cracking can be prevented, if Na₂SO₄ is added to boiler water so that the ratio:

[Na₂SO₄ conc.] / [NaOH conc.] is kept as I: 1, 2: I and 3: 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

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