(*iv*) **Paper industry** : Calcium and magnesium salts tends to react with chemicals and other materials employed to provide a smooth and glossy (*i.e.*, shining) finish to paper. Moreover, iron salts may even affect the colour of the paper being produced.

(*v*) **Laundry** : Hard water, if used in laundry, causes much of the soap used in washing to go as *waste*. Iron salts may even cause *coloration* of the clothes.

(*vi*) **Concrete making** : Water containing chlorides and sulphates, if used for concrete making, affects the *hydration of cement* and the final *strength* of the hardened concrete.

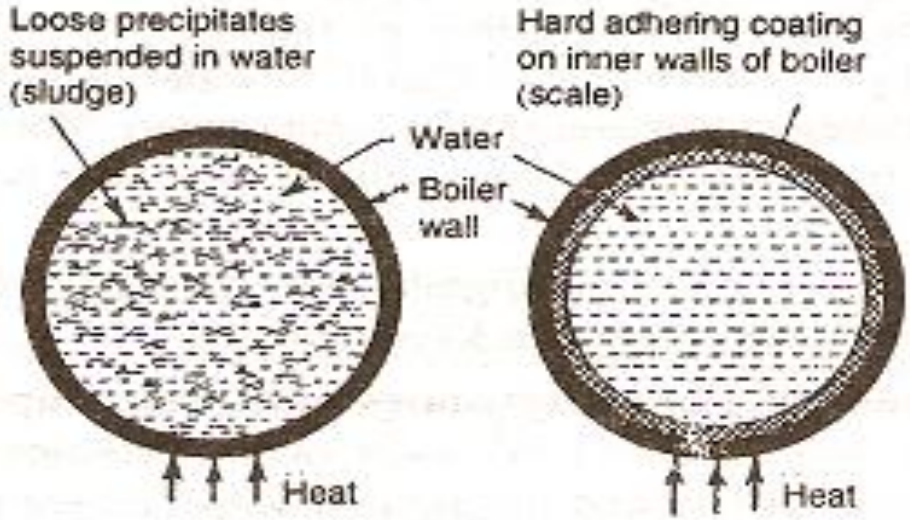
(*vii*) **Pharmaceutical industry** : Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.,) may produce certain *undesirable products* in them.

(3) In steam generation in boilers : For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as : (*i*) *scale and sludge formation*, (*ii*) *corrosion*, (*iii*) *priming and foaming*, and (*iv*) *caustic embrittlement*.

SCALE AND SLUDGE FORMATION IN BOILERS

In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. *When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate,* it is called ***sludge***. On the other hand, *if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler*, it is called ***scale***.

Sludge *is a soft, loose and slimy precipitate formed within the boiler.* Sludge can easily be *scrapped off with a wire brush.* It is formed at comparatively *colder portions of the boiler* and collects in areas of the system, where the *flow rate is slow or at bends. Sludges are formed by substances which have greater solubilities in hot water than in cold water, e.g.,* $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, *etc.*



Scale and sludge in boilers.

Hardness – < 0.2 ppm

Caustic albalinity – 0.15 – 0.45 ppm

Soda alkalinity – 0.15 – 1 ppm

Excess soda ash – 0.3 – 0.55 ppm

If excess of impurities are present in boiler feed water, they cause the following problems.

(*i*) Scale or sludge formation

(*ii*) Corrosion

(*iii*) Priming

(*iv*) Foaming

(*v*) Caustic embrittlement

(*vi*) Scale formation due to presence of silica

Disadvantages of sludge formation : (1) Sludges are poor conductor of heat, so they tend to waste a portion of heat generated. (2) If sludges are formed along-with scales, then former gets entrapped in the latter and both get deposited as scales. (3) 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 : (1) By using well softened water. (2) By frequently *'blow-down operation'*, *i.e.*, drawing off a portion of the concentrated water.

Scales *are hard deposits, which stick very firmly to the inner surfaces of the boiler.* Scales are difficult to remove, even with the help of hammer and chisel. *Scales are the main source of boiler troubles.* Formation of scales may be due to :

(1) *Decomposition of calcium bicarbonate :*

$$Ca(HCO_3)_2 \longrightarrow \underset{\text{Scale}}{CaCO_3 \downarrow} + H_2O + CO_2 \uparrow$$

However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, $CaCO_3$ is soluble.

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

(2) *Deposition of calcium sulphate :* The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of $CaSO_4$ is 3,200 ppm at 15°C and it reduces to 55 ppm at 230°C and 27 ppm at 320°C. In other words, $CaSO_4$ is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, $CaSO_4$ gets precipitated as *hard scale* on the heated portions of the boiler. *This is the main cause of scales in high-pressure boilers.*

Note : Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

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

$$MgCl_2 + 2H_2O \longrightarrow \underset{\text{Scale}}{Mg(OH)_2} \downarrow + 2HCl \uparrow$$

(4) *Presence of silica* : (SiO_2), even present in small quantities, deposits as calcium silicate ($CaSiO_3$) and / or magnesium silicate ($MgSiO_3$). These deposits stick *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 *low thermal conductivity,* so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, *excessive or over-heating* is done and this causes *increase in fuel consumption.* The wastage of fuel depends upon the thickness and the nature of scale :

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(2) *Lowering of boiler safety* : Due to scale formation, *over-heating* of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material *softer* and *weaker* and this causes *distortion of boiler tube* and makes the boiler *unsafe* to bear the pressure of the steam, especially in high-pressure boilers.

(3) *Decrease in efficiency* : Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially. *This results in decrease in efficiency of the boiler.*

(4) *Danger of explosion* : When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes in formation of *a large amount of steam suddenly.* So sudden high-pressure is developed, which may even cause explosion of the boiler.

Removal of scales : (*i*) With the help of scraper or piece of wood or wire brush, if they are loosely adhering. (*ii*) By giving *thermal shocks* (*i.e.*, heating the boiler and then suddenly cooling with cold water), if they are brittle. (*iii*) By dissolving them by adding them *chemicals*, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5–10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes. (*iv*) By frequent *blow-down operation*, if the scales are loosely adhering.

Prevention of scales formation : (1) ***External treatment*** includes efficient '*softening of water*' (*i.e.*, removing hardness-producing constituents of water). These will be discussed separately.

(2) ***Internal treatment*** : In this process (also called *sequestration*), an ion is prohibited to exhibit its original character by '*complexing*' or converting it into *other more soluble salt* by adding appropriate reagent. *An internal treatment is accomplished by adding a proper chemical to the boiler water either :* (*a*) *to precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down operation,* or (*b*) *to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.*

Notes : (*i*) *Blow down operation* is partial removal of hard water through top at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.

(*ii*) '*Make up*' *water* is addition of fresh softened water to boiler after blow down operation.

Internal treatments methods are, generally, followed by *'blow-down operation'*, so that accumulated sludge is removed. Important internal conditioning/treatment methods are :

(*i*) **Colloidal conditioning** : In *low-pressure boilers*, scale formation can be avoided by adding organic substances like *kerosene, tannin, agar-agar* (a gel), etc., which get coated over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.

(*ii*) **Phosphate conditioning** : In *high-pressure boilers*, scale formation can be avoided by adding *sodium phosphate*, which reacts with hardness of water forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphates, which can be removed by blow-down operation, *e.g.*,

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl$$

The main phosphates employed are : (*a*) NaH_2PO_4, *sodium dihydrogen phosphate* (*acidic*) ; (*b*) Na_2HPO_4, *disodium hydrogen phosphate* (*weakly alkaline*) ; (*c*) Na_3PO_4, *trisodium phosphate* (*alkaline*).

Note : The choice of salt depends upon the *alkalinity* of the boiler-feed water. Calcium cannot be precipitated properly *below a pH of* 9.5, so select a phosphate that adjusts pH to optimum value (9.5–10.5). Trisodium phosphate is most suitable for treatment, when the alkalinity of boiler water is low, as it is most alkaline in nature. If boiler water's alkalinity is sufficient, then disodium phosphate is more preferred. But if the alkalinity of boiler water is too high and requires to be reduced, then monosodium phosphate, being acidic in nature, is preferred.

(*iii*) **Carbonate conditioning :** In *low-pressure boilers,* scale-formation can be avoided by adding *sodium carbonate* to boiler water, when $CaSO_4$ is converted into calcium carbonate *in equilibrium.*

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$$

Consequently, *deposition of $CaSO_4$ as scale does not take place and calcium is precipitated as loose sludge of $CaCO_3$,* which can be removed by *blow-down operation.*

(*iv*) **Calgon conditioning** involves in adding *calgon* [sodium hexa meta phosphate $(NaPO_3)_6$ to boiler water. It prevents the scale and sludge formation by forming *soluble complex compound* with $CaSO_4$.

$$\underset{\text{Calgon}}{Na_2[Na_4(PO_3)_6]} \rightleftharpoons 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{2-} \longrightarrow \underset{\text{Soluble complex ion}}{[Ca_2P_6O_{18}]^{2-}} + 2Na_2SO_4$$

(*v*) **Treatment with sodium aluminate ($NaAlO_2$)** : Sodium aluminate gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminium hydroxide. Thus :

$$\underset{\text{Sod. meta-aluminate}}{NaAlO_2} + 2H_2O \longrightarrow NaOH + \underset{\text{(Gelatinous ppt.)}}{Al[OH]_3 \downarrow}$$

The sodium hydroxide, so-formed, precipitates some of the magnesium as $Mg(OH)_2$, *i.e.,*

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 \downarrow + 2NaCl$$

The *flocculent precipitate of $Mg(OH)_2$ plus $Al(OH)_3$*, produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitate can be removed by pre-determined blow-down operation.

Note : Sodium aluminate in thick solution form is available in plenty and at a cheap rate from bauxite refining units and this can be used as such for boiler-water treatment.

(*vi*) **Electrical conditioning** : *Sealed glass bulbs*, containing mercury connected to a battery, are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, which *prevents scale forming particles to ahdere/stick together to form scale.*

(*vii*) **Radioactive conditioning** : Tablets containing radioactive salts are placed inside the boiler water at a few points. *The energy radiations emitted by these salts prevent scale formation.*

(*vii*) **Complexometric method** involves adding 1.5% alkaline (pH = 8.5) solution of EDTA to feed-water. The EDTA binds the scale-forming cations to form *stable and soluble complex*. As a result, the sludge and scale formation in boiler is prevented. Moreover, this treatment : (*i*) prevents the deposition of iron oxides in the boiler, (*ii*) reduces the carry over of oxides with steam, and (*iii*) protects the boiler units from corrosion by wet steam (steam containing liquid water).

PRIMING AND FOAMING

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation, is called **priming**. Priming is caused by : (*i*) the presence of large amount of dissolved solids ; (*ii*) high steam velocities ; (*iii*) sudden boiling ; (*iv*) improper boiler design, and (*v*) sudden increase in steam-production rate.

Foaming *is the production of persistent foam or bubbles in boilers, which do not break easily*. Foaming is due to presence of substances like *oils* (which greatly reduce the surface tension of water).

Priming and foaming, usually, occur *together. They are objectionable because :* (*i*) dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency ; (*ii*) dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery ; (*iii*) actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

Priming can be avoided by : (*i*) fitting mechanical steam purifiers ; (*ii*) avoiding rapid change in steaming rate ; (*iii*) maintaining low water levels in boilers, and (*iv*) efficient softening and filtration of the boiler-feed water.

Foaming can be avoided by : (*i*) adding anti-foaming chemicals like castor oil, or (*ii*) removing oil from boiler water by adding compounds like sodium aluminate.

SOFTENING METHODS

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. It should, therefore, be freed from hardness-producing salts

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