

WATER TREATMENT

In industries water is used for steam generation & as coolant mainly. Other uses are drinking, bathing, washing, sanitation irrigation etc.

Sources of water:

A) Surface water- available as

- Rain water
- River water
- Lake water
- Sea water

Such water contains suspended impurities & pathogenic bacteria, so unfit for human consumption.

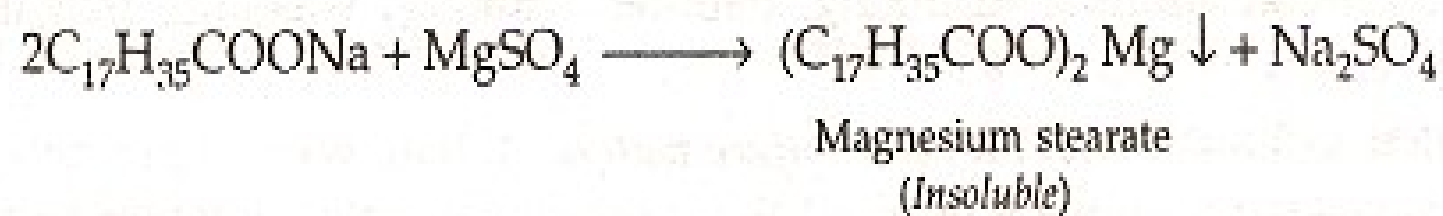
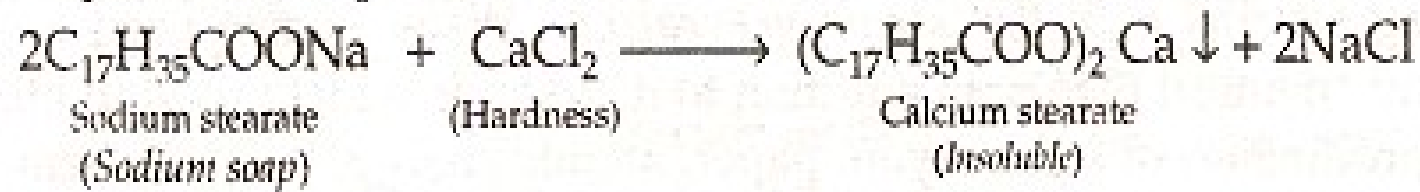
B) Underground Water- available as

- springs
- well water

It is clear due to filtering action (percolation) of soil but contains more of dissolved salts & organic impurities.

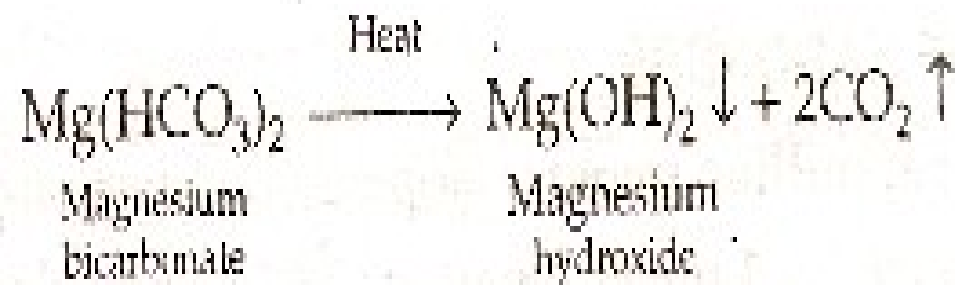
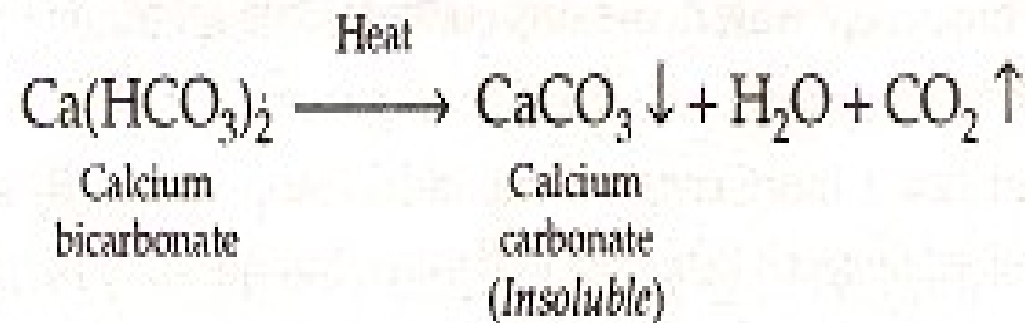
HARDNESS OF WATER

Hardness in water is that characteristic, which "prevents the lathering of soap". This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms a white scum or precipitate. This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are depicted as follows :



Thus, water which does not produce lather with soap solution readily, but forms a white curd, is called hard water. On the other hand, water which lathers easily on shaking with soap solution, is called soft water. Such a water, consequently, does not contain dissolved calcium and magnesium salts in it.

(1) **Temporary or carbonate hardness** is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel. Thus :



(2) **Permanent or non-carbonate hardness** is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

EQUIVALENTS OF CALCIUM CARBONATE

The concentration of hardness as well as non-hardness constituting ions are, usually, expressed in terms of equivalent amount of CaCO_3 , since this mode permits the multiplication and division of concentration, when required. *The choice of CaCO_3 in particular is due to its molecular weight is 100 (equivalent weight = 50) and moreover, it is the most insoluble salt that can be precipitated in water treatment.* The equivalents of CaCO_3

$$\begin{aligned} & \left[\begin{array}{l} \text{Mass of hardness} \\ \text{producing-substance} \end{array} \right] \times \left[\begin{array}{l} \text{Chemical equivalent} \\ \text{of } \text{CaCO}_3 \end{array} \right] \\ = & \frac{\text{Chemical equivalent of hardness-producing substance}}{\text{Mass of hardness-producing substance} \times 50} \\ = & \frac{\text{Chemical equivalent of hardness-producing substance}}{\text{Chemical equivalent of hardness-producing substance}} \end{aligned}$$

. Calculation of equivalents of calcium carbonate.

<i>Dissolved salt/ion</i>	<i>Molar mass</i>	<i>Chemical equivalent</i>	<i>Multiplication factor for converting into equivalents of CaCO₃</i>
Ca(HCO ₃) ₂	162	81	100/162
Mg(HCO ₃) ₂	146	73	100/146
CaSO ₄	136	68	100/136
CaCl ₂	111	55.5	100/111
MgSO ₄	120	60	100/120
MgCl ₂	95	47.5	100/95
CaCO ₃	100	50	100/100
MgCO ₃	84	42	100/84
CO ₂	44	22	100/44
Ca(NO ₃) ₂	164	82	100/164
Mg(NO ₃) ₂	148	74	100/148
HCO ₃ ⁻	61	61	100/122
OH ⁻	17	17	100/34
CO ₃ ²⁻	60	30	100/60
NaAlO ₂	82	82	100/164
Al ₂ (SO ₄) ₃	342	57	100/114
FeSO ₄ .7H ₂ O	278	139	100/278
H ⁺	1	1	100/2
HCl	36.5	1	100/73

UNITS OF HARDNESS

(1) **Parts per million (ppm)** is the parts of calcium carbonate equivalent hardness per 10^6 parts of water, i.e., 1 ppm = 1 part of CaCO_3 eq hardness in 10^6 parts of water.

(2) **Milligrams per litre (mg/L)** is the number of milligrams of CaCO_3 equivalent hardness present per litre of water. Thus :

$$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness of 1 L of water}$$

But 1 L of water weighs

$$= 1 \text{ kg} = 1,000 \text{ g} = 1,000 \times 1,000 \text{ mg} = 10^6 \text{ mg.}$$

$$\therefore 1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq per } 10^6 \text{ mg of water.}$$

$$= 1 \text{ part of } \text{CaCO}_3 \text{ eq per } 10^6 \text{ parts of water} = 1 \text{ ppm.}$$

(3) **Clarke's degree ($^{\circ}\text{Cl}$)** is number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water. Or it is parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus :

$$1^{\circ} \text{ Clarke} = 1 \text{ grain of } \text{CaCO}_3 \text{ eq hardness per gallon of water.}$$

or

$$1^{\circ} \text{ Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ eq hardness per 70,000 parts of water.}$$

(4) **Degree French ($^{\circ}\text{Fr}$)** is the parts of CaCO_3 equivalent hardness per 10^5 parts of water. Thus :

$$1^{\circ} \text{ Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ hardness eq per } 10^5 \text{ parts of water.}$$

(5) **Milliequivalent per litre (meq/L)** is the number of milli equivalents of hardness present per litre. Thus :

$$1 \text{ meq/L} = 1 \text{ meq of } \text{CaCO}_3 \text{ per L of water}$$

$$= 10^{-3} \times 50 \text{ g of } \text{CaCO}_3 \text{ eq per litre}$$

$$= 50 \text{ mg of } \text{CaCO}_3 \text{ eq per litre}$$

$$= 50 \text{ mg/L of } \text{CaCO}_3 \text{ eq} = 50 \text{ ppm.}$$

Relationship between various units of hardness :

1 ppm	= 1 mg/L	= 0.1° Fr	= 0.07° Cl	= 0.02 meq/L
1 mg/L	= 1 ppm	= 0.1° Fr	= 0.07° Cl	= 0.02 meq/L
1° Cl	= 1.433° Fr	= 14.3 ppm	= 14.3 mg/L	= 0.286 meq/L
1° Fr	= 10 ppm	= 10 mg/L	= 0.7° Cl	= 0.2 meq/L
1 meq/L	= 50 mg/L	= 50 ppm	= 5° Fr	= 0.35° Cl

DISADVANTAGES OF HARD WATER

(1) *In domestic use* : (i) *Washing* : Hard water, when used for washing purposes, does not lather freely with soap. On the other hand, it produces *sticky precipitates* of calcium and magnesium soaps. The formation of such insoluble, sticky precipitates continues, till all calcium and magnesium salts present in water are precipitated. After that, the soap (e.g., sodium stearate) gives lather with water. Thus :



This causes a wastage of lot of soap being used. Moreover, the sticky precipitate (of calcium and magnesium soaps) adheres on the fabric/cloth giving spots and streaks. Also presence of iron salts may cause staining of cloth.

(ii) **Bathing** : Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is depressed and a lot of it is wasted.

(iii) **Cooking** : Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an unpleasant taste and muddy-looking extract. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

(iv) **Drinking** : Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

(2) **In industrial use** : (i) **Textile industry** : Hard water causes much of the soap (used in washing yarn, fabric, etc.) to go as waste, because hard water cannot produce good quality of lather. Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed latter on, do not produce exact shades of colour. Iron and manganese salts-containing water may cause coloured spots on fabrics, thereby spoiling their beauty.

(ii) **Sugar industry** : Water containing sulphates, nitrates, alkali carbonates, etc., if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(iii) **Dyeing industry** : The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitates, which yield impure shades and give spots on the fabrics being dyed.

(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.

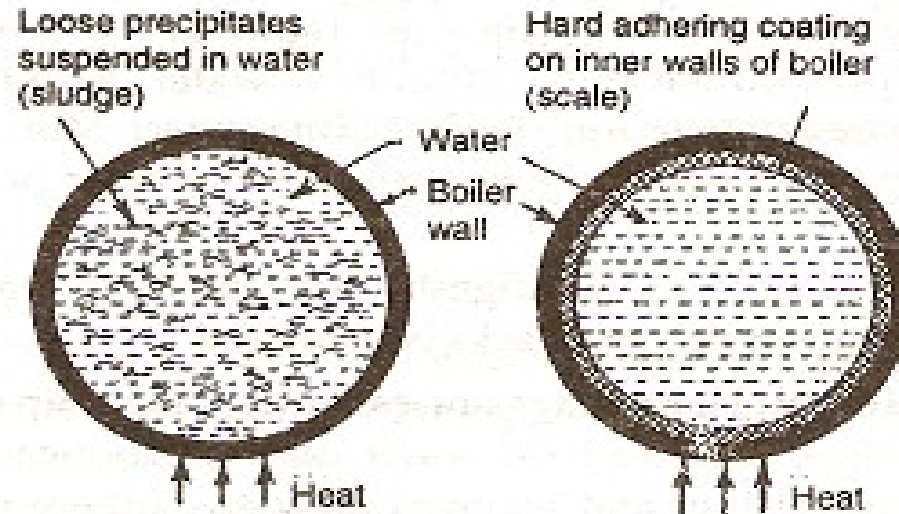
(vii) **Pharmaceutical industry** : Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.,) may produce certain *undesirable products* in them.

(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 alkalinity – $0.15 - 0.45$ 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.

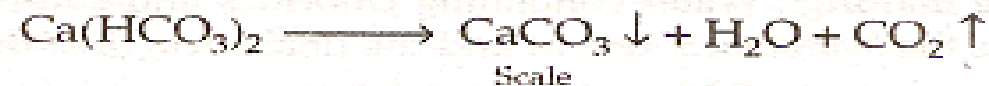
- (i) Scale or sludge formation
- (ii) Corrosion
- (iii) Priming
- (iv) Foaming
- (v) Caustic embrittlement
- (vi) Scale formation due to presence of silica

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 :*



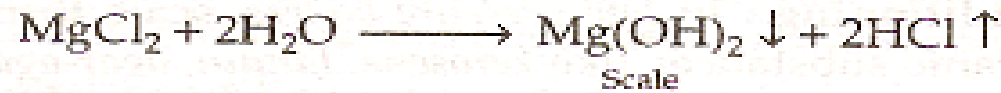
However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, CaCO_3 is soluble.



(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.,*



(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 :

<i>Thickness of scale (mm)</i>	0.325	0.625	1.25	2.5	12
<i>Wastage of fuel</i>	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.,



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)*.

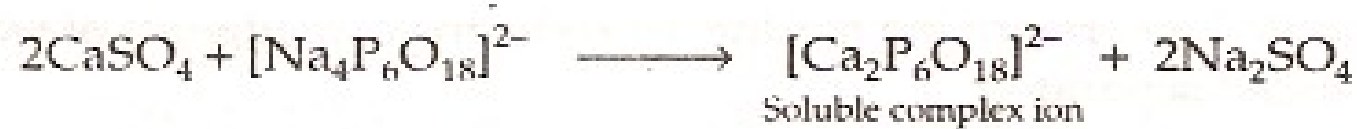
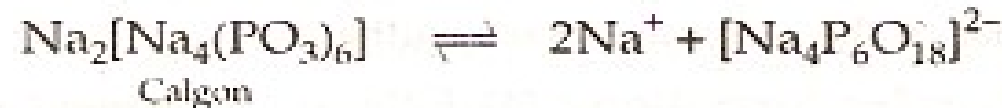
Note : The choice of salt depends upon the *alkalinity* of the boiler-feed water. Calcium cannot be precipitated properly *below a pH of 9.5*, so select a phosphate that adjusts pH to optimum value (9.5–10.5). Trisodium phosphate is most suitable for treatment, when the alkalinity of boiler water is 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*.



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 .



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



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



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 adhere/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.

(viii) **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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before put to use. *The process of removing hardness-producing salts from water, is known as softening of water.* In industry, main three methods employed for softening of water are :

(1) Lime-soda process : In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of *lime* [$\text{Ca}(\text{OH})_2$] and *soda* [Na_2CO_3]. *Calcium carbonate* [CaCO_3] and *magnesium hydroxide* [$\text{Mg}(\text{OH})_2$], so-precipitated, are filtered off.

Note : It may be pointed here that *the chemical reactions taking place during lime-soda treatment are rather slow.* Moreover, the precipitates formed, particularly of CaCO_3 and $\text{Mg}(\text{OH})_2$, are fine and they tend to produce a super-saturated solution. This eventually results in "after deposition", later in the pipes and boiler tubes, producing sludges. These in-turn decrease the effective diameters of pipes, clog tubes and valves, cause their corrosion, etc. Consequently, these drawbacks partly offsets the purpose of water softening. To overcome these drawbacks, the following arrangements are made :

(i) *Thorough mixing* of the chemicals and water is carried out. (ii) *Proper time for completion of reactions, these, is given.* Alternatively, means are adopted for accelerating the reaction (e.g., by using hot lime-soda method). (iii) *Substances that bring down the fine particles of precipitates called accelerators (like activated charcoal) are added.* (iv) *Substances that help in the formation of coarse precipitates are added.* These are called coagulants or flocculents, e.g., alum. (v) *Suitable sedimentation chamber is provided before final filtration.*