

WATER TREATMENT

"Although water is nature's most wonderful, abundant and useful compound, yet is also the most misused one."

1 INTRODUCTION

Water is nature's most wonderful, abundant and useful compound. Of the many essential elements for the existence of human beings, animals and plants (*viz.* air, water, food, shelter, etc.), water is rated to be of the greatest importance. *Without food, human can survive for a number of days, but water is such an essential that without it one cannot survive.*

Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. *Probably, its most important use as an engineering material is in the 'steam generation'.* Water is also used as *coolant* in power and chemical plants. In addition to it, water is widely used in other fields such as production of steel, rayon, paper, atomic energy, textiles, chemicals, ice, and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, fire-fighting, etc.

SOURCES OF WATER : (A) *Surface waters* : 1. Rain water is probably the *purest form of natural water*, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards through the atmosphere, it dissolves a considerable amount of industrial *gases* (like CO_2 , SO_2 , NO_2 , etc.) and *suspended solid particles*, both of organic and inorganic origin.

2. *River water* : Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. *In general, the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water.* River water thus contains *dissolved minerals* of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains the *organic matter*, derived from the decomposition of plants, and small particles of *sand and rock in suspension*. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

3. *Lake water* has a more *constant chemical composition*. *It, usually, contains much lesser amounts of dissolved minerals than even well water*, but quantity of organic matter present in it is quite high.

4. *Sea water is the most impure form of natural water* : Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphate of sodium ;

bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and number of other compounds.

Surface water, generally, contains *suspended matter*, which often contains the *disease-producing (or pathogenic) bacteria*. Hence, such waters as such are not considered to be safe for human consumption.

(B) *Underground waters*: A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it meets hard rock, when it reappears upwards and it may even come out in the form of 'spring'.

Spring and well water (or underground water), in general, is clearer in appearance, due to the filtering action of the soil, but contains more of the dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of *high organic purity*.

2 CHARACTERISTICS IMPARTED BY IMPURITIES IN WATER

The natural water is, usually, contaminated by different types of impurities. The characteristic and consequent effects of impurities on the quality of water are discussed under the following three heads :

(1) *Physical impurities* : (a) *Colour* in water is caused by *metallic substances* like salts of iron, manganese, humus materials, tannins, peat, algae, weeds, protozoa, industrial effluents (from paper and pulp, textile, tanneries, etc). Actually, colour in water is due to dissolved substances and substances present as fine colloids. The change in colour of water is not harmful, unless it is associated with an chemical of toxic nature. Variations in colour of water from the same source (say a river) with time often serves as indices of quality of water. Usually, *yellowish* tinge indicates the presence of chromium and appreciable amount of organic matter. *Yellowish-red* colour indicates the presence of iron ; while *red-brown* colour indicate the presence of peaty matter.

(b) *Turbidity* is due to the colloidal, extremely fine suspension such as clay, slit, finely divided matters (organic and inorganic), micro-organisms like plankton, etc. Turbidity expresses the optical properties of water containing insoluble substances, which scatter light rather than to transmit it in straight lines. The turbidity depends not only on the quantity of insoluble substances, but also on the size, shape and reflective index. Turbidity in water can be eliminated by sedimentation, followed by coagulation, filtration, etc.

(c) *Taste* is, usually, interlinked directly with *odour*. However, in some waste water, taste is not accompanied by odour. Thus, presence of dissolved mineral in water produces taste, but not odour. For example;

- (i) *Bitter* taste can be due to the presence of iron, aluminium, manganese, sulphate or excess lime.
- (ii) *Soapy* taste can be due to the presence of large amount of sodium bicarbonate.
- (iii) *Brackish* taste is due to the presence of unusual amount of salts.
- (iv) *Palatable* taste is due to the presence of dissolved gases (CO_2) and minerals (like nitrates) in water.

(d) *Odour* in water is undesirable for domestic as well as industrial purposes. Disagreeable odour in water may be caused by the presence of living organisms, decaying vegetation including algae, bacteria, fungi and weeds. The receiving water may be offensive where heavy pollution is caused by sewage/industrial effluents. The most common disagreeable odour in water bodies is due to presence of small quantity of *sulphides*. The causes of odour in polluted rivers are :

- (i) presence of inorganic and organic compounds of N, S and P and the putrefaction of protein and other organic materials present in sewage ;

(ii) industrial effluents containing organic substances such as alcohols, aldehydes, phenols, esters, ketones, etc. flowing into the water bodies.

Besides these : (i) presence of algae in water bodies impart a strong *grassy odour*, due to the liberation of traces of essential oils from their bodies, (ii) growth of *iron and sulphur bacteria* may produce offensive odours, (iii) presence of *colloidal vegetable matter* in surface-water evolves a faint flavour, called '*peaty*' odour, (iv) clay and sand in finely divided state impart a faint earthy odour, (v) improper bituminous coating on cast iron main pipes may give off a *tarry odour* to water, which passes through it, (vi) a *faint odour* is imparted to water passing through new iron or galvanized. This odour is due to the impure hydrogen.

(2) **Chemical impurities in water** includes : (i) *inorganic and organic chemicals* (some which are toxic in nature) released from dyes, paints, and vanishes, drugs, insecticides, pesticides, detergents, pulp and textiles, industries, tanneries, etc. . All these pollute water bodies. (ii) *acids* discharged in water by DDT, high explosives, batteries, industries, etc. The use of this type of contaminated water causes harmful effects on health of human-beings.

(a) *Acidity* is not any specific pollutant and it simply determines the power to neutralise hydroxyl ions and is, usually, expressed in terms of ppm (or mg/L) of calcium carbonate equivalent. Surface waters and ground waters attain acidity from industrial wastes like acid, mine, drainage, pickling liquors, etc. Usually, acidity is caused by the presence of free CO_2 , mineral acids (e.g., H_2SO_4) and weakly dissociated acids. Mineral acids are released, when iron and aluminium salts hydrolyse.

(b) *Gases* : (i) All natural waters contain dissolved atmospheric CO_2 . Its solubility depends upon temperature, pressure and dissolved mineral content of water. Also polluted waters acquire CO_2 from the biological oxidation of organic matter. Its presence in water is of no significance.

(ii) Concentration of dissolved atmospheric O_2 in waters depends on temperature, pressure and salt content in water. Dissolved O_2 in industrial waters is *nuisance*, since it induces corrosion reactions. On the other hand, dissolved O_2 in water is essential to the life of aquatic organisms such as fishes.

(iii) Dissolved NH_3 in water arises from the decomposition (aerobic or anaerobic) of nitrogenous organic matter. Polluted waters and sewages contains nitrogen in the form of nitrogenous organic compounds and urea, which are partially converted into NH_3 .

(d) *Mineral matters* have origin from rocks and industrial effluents. These include mineral acids of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , CO_3^{2-} , Mn^{2+} , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , F^- , SiO_2 , etc. However, from industrial point of view, *alkalinity* and *hardness* are important. These are discussed separately at a latter stage.

(3) **Biological impurities** are algae, pathogenic bacteria, fungi, viruses, pathogens, parasitic worms, etc. The source of these contamination is discharge of domestic and sewage wastes, excreta (from man, animals and birds), etc.

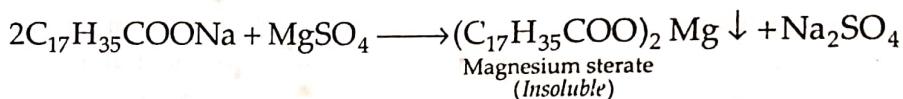
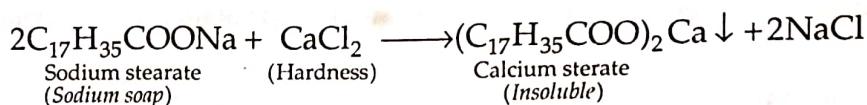
(a) *Micro-organisms* are, usually, abundant in surface waters, but their count is often quite low or even nil in deep-well waters. The commonest type of micro-organisms from the point of treatment are algae, fungi and bacteria, which often form '*slime*', thereby causing fouling as well as corrosion. The slime so-formed clogs the spray nozzles and screens of the circulating pumps in air-conditioning and other industrial plants. The growth of micro-organisms takes place at temperature between 20–30°C. In order to control the micro-organisms, chemical treatment like chlorination is done.

(b) *Water bodies* in water includes : (i) bacteria, organisms inhabitating the bottom sludge, and (ii) organisms and planktons developed at the water surface. These are inhabited by

different group of worms like flat worms, hair worms, tiny round worms, oligochetes, rotifers, etc. Usually, most worms are *parasite* in nature and these water bodies are not only harmful to fishes, but also to human health.

3 HARDNESS OF WATER

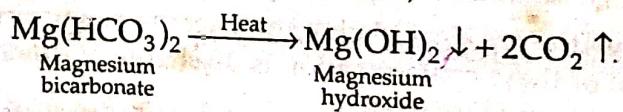
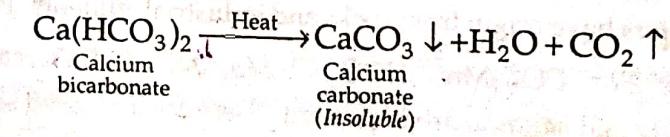
Hardness in water is that characteristic, which "prevents the lathering of soap". This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic 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.

* **Plumbosolvency**: Lead is not attacked by pure air-free water (except at the boiling point). It is readily corroded by water containing dissolved air, forms $Pb(OH)_2$, which is quite soluble in water. The dissolution action of water on lead is called *plumbosolvency*. The reaction is, however, retarded by certain salts like carbonates and sulphates, since they form insoluble coating of $PbCO_3$ or $PbSO_4$ on the surface of the metal, thereby protecting the metal from further action. Consequently, hard water has no solvent action on lead. In other words, plumbosolvency problem is maximum in case of transportation of soft water through lead pipes.

Dissolved salts

Ca(H)

Mg(H)

CaSO₄

CaCl₂

MgSO₄

MgCl₂

CaCO₃

MgCO₃

CO₂

Ca(N)

Mg(N)

HCO₃

OH⁻

CO₃²⁻

NaAlO₂

Al₂(SO₄)₂

FeSO₄

H⁺

HCl

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4 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.

Table 1. Calculation of equivalents of calcium carbonate.

Dissolved salt/ion	Molar mass mass	Chemical equivalent	Multiplication factor for converting into equivalents of CaCO_3
$\text{Ca}(\text{HCO}_3)_2$	162	81	100/162
$\text{Mg}(\text{HCO}_3)_2$	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
$\text{Ca}(\text{NO}_3)_2$	164	82	100/164
$\text{Mg}(\text{NO}_3)_2$	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
$\text{Al}_2(\text{SO}_4)_3$	342	57	100/114
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	139	100/278
H^+	1	1	100/2
HCl	36.5	1	100/73

The equivalents of CaCO_3

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

5 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 water.

Thus :

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

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

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

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

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

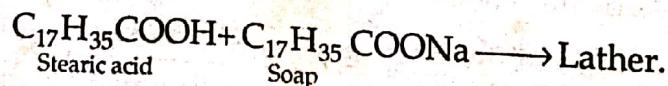
$$= 50 \text{ mg of } \text{CaCO}_3 \text{ eq per litre} = 50 \text{ mg/L of } \text{CaCO}_3 \text{ eq} = 50 \text{ ppm}$$

Relationship between various units of hardness :

1 ppm	= 1 mg/L	= 0.1 {}^\circ \text{ Fr}	= 0.07 {}^\circ \text{ Cl}	= 0.02 meq/L
1 mg/L	= 1 ppm	= 0.1 {}^\circ \text{ Fr}	= 0.07 {}^\circ \text{ Cl}	= 0.02 meq/L
1 {}^\circ \text{ Cl}	= 1.433 {}^\circ \text{ Fr}	= 14.3 ppm	= 14.3 mg/L	= 0.286 meq/L
1 {}^\circ \text{ Fr}	= 10 ppm	= 10 mg/L	= 0.7 {}^\circ \text{ Cl}	= 0.2 meq/L
1 meq/L	= 50 mg/L	= 50 ppm	= 5 {}^\circ \text{ Fr}	= 0.35 {}^\circ \text{ Cl}

6 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, have 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 colouration 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.

7 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.

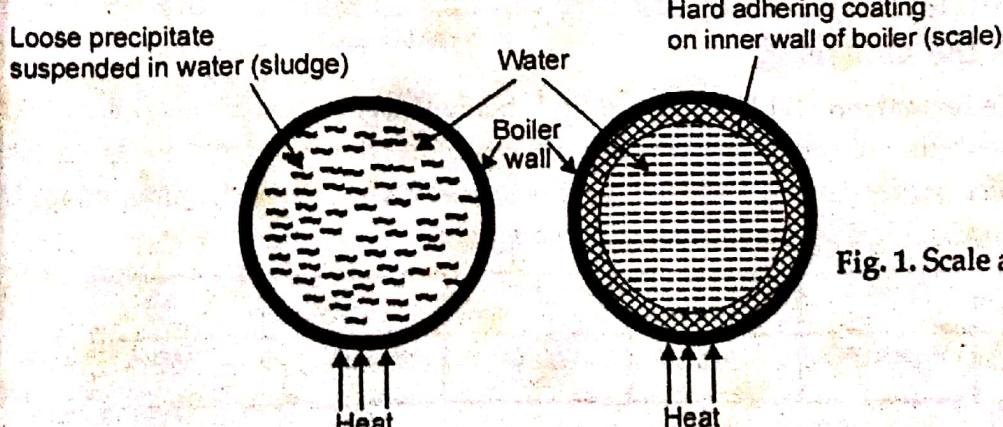


Fig. 1. Scale and sludge formation in boilers.

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.

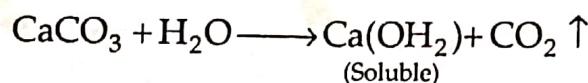
Prevention of sludge formation : (1) By using well softened water. (2) By frequently 'blow-down operation', i.e., drawing off a portion of the concentrated water.

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 :*



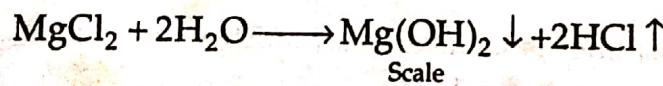
However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, CaCO_3 is soluble.



(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 :

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.

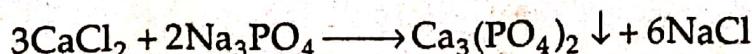
Notes : (i) *Blow down operation* is partial removal of hard water through top at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.

(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.



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*).

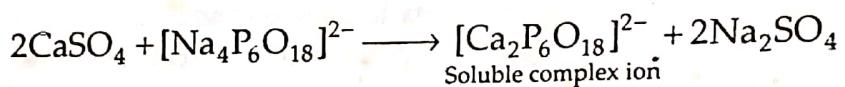
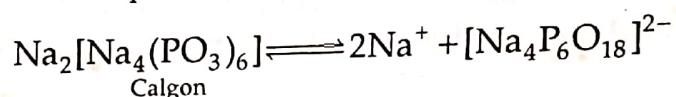
Note : The choice of salt depends upon the *alkalinity* of the boiler-feed water. Calcium cannot be precipitated properly below a pH of 9.5, so select a phosphate that adjusts pH to optimum value (9.5–10.5). Trisodium phosphate is most suitable for treatment, when the alkalinity of boiler water is low,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

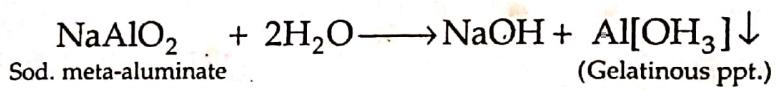


Consequently, deposition of CaSO_4 as scale does not take place and calcium is precipitated as loose sludge of CaCO_3 , which can be removed by blow-down operation.

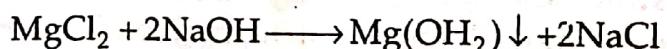
(iv) **Calgon conditioning** involves in adding *calgon* [sodium hexa meta phosphate (NaPO_3)₆] to boiler water. It prevents the scale and sludge formation by forming *soluble complex compound* with CaSO_4 .



(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 $\text{Mg}(\text{OH})_2$ plus $\text{Al}(\text{OH})_3$, 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 prevent 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).

8 CAUSTIC EMBRITTLEMENT

Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. During softening process by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide,



and this makes the boiler water "caustic". The NaOH containing water flows into the minute hair-cracks, always present in the inner side of boiler, by capillary action. Here water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate. This causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler. Caustic cracking can be explained by considering the following concentration cell :

Iron at rivels, bends, joints, etc.	+ Concentrated NaOH solution	Dilute NaOH solution -	Iron at plane surfaces
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The iron surrounded by the dilute NaOH becomes the *cathodic side*; while the iron in contact with rather concentrated NaOH becomes *anodic part*, which is consequently dissolved or corroded.

Caustic embrittlement can be avoided : (i) by using sodium phosphate as softening reagent, instead of sodium carbonate ;

(ii) by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these ;

(iii) by adding sodium sulphate to boiler water : Na_2SO_4 also blocks hair-cracks, thereby preventing infiltration of caustic soda solutions in these. It has been observed that caustic cracking can be prevented, if Na_2SO_4 is added to boiler water so that the ratio :

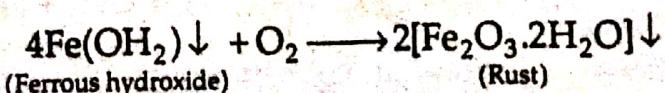
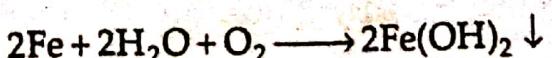
$$\frac{[\text{Na}_2\text{SO}_4 \text{ concentration}]}{[\text{NaOH concentration}]}$$

is kept as 1 : 1, 2 : 1 and 3 : 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

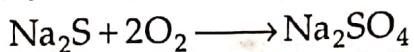
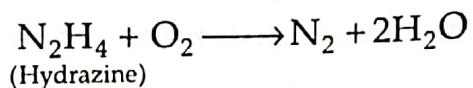
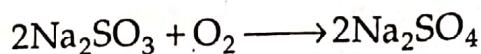
9 BOILER CORROSION

Boiler corrosion is decay of boiler material by a chemical or electro-chemical attack by its environment. Main reasons for boiler corrosion are :

(1) **Dissolved oxygen** : Water usually contains about 8 mL of dissolved oxygen per litre at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material :



Removal of dissolved oxygen : (1) By adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide. Thus :



Note. "Hydrazine" is an ideal internal treatment 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 concentration of dissolved solids / salts. On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate so-formed is liable to decompose giving SO_2 , particularly in high-pressure boilers. The SO_2 enters the steam pipes and appears as sulphurous acid (H_2SO_3) in the steam condensate. So as a rule, a very low concentration of 5 to 10 ppm of Na_2SO_3 in the boiler is maintained ; rather adding it intermittently. Recently developed, Azamina 8001-RD (a polyvalent organic compound) has been employed for degassing water in minimum time.

(2) By mechanical de-aeration, i.e., water spraying in a perforated plate-fitted tower, heated from sides and connected to vacuum pump (see Fig. 2). High temperature, low pressure and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water.

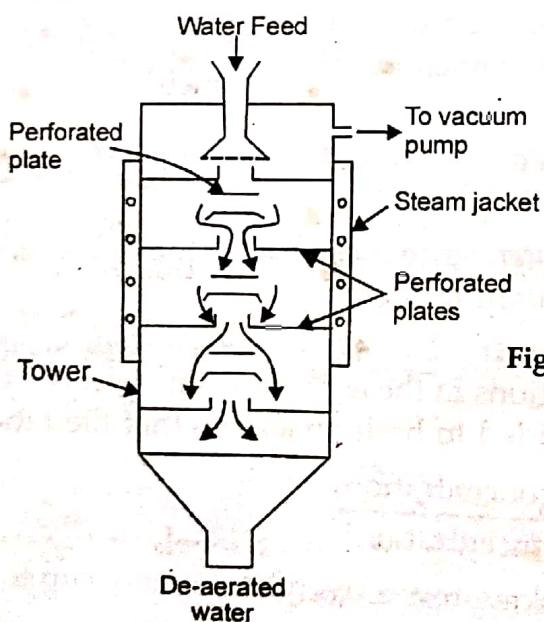
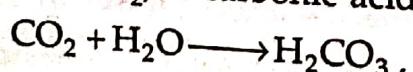


Fig. 2. Mechanical de-aeration of water.

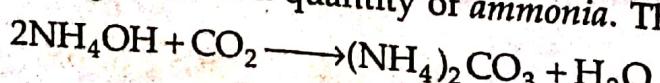
(2) Dissolved carbon dioxide (CO_2) is carbonic acid,



which has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonate, e.g.,

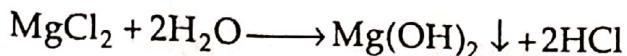


Removal of CO_2 : (1) By adding calculated quantity of ammonia. Thus :

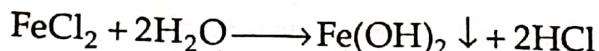
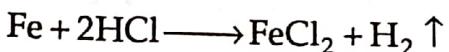


(2) By mechanical-aeration process alongwith oxygen.

(3) Acids from dissolved salts : Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,



The liberated acid reacts with iron (of the boiler) in *chain-like reactions* producing HCl again and again. Thus :



Consequently, presence of even a small amount of MgCl_2 will cause corrosion of iron to a large extent.

10 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.

11 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 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 $[Ca(OH)_2]$ and soda $[Na_2CO_3]$. Calcium carbonate $[CaCO_3]$ and magnesium hydroxide $[Mg(OH)_2]$, so-precipitated, are filtered off.

Notes : (1) 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 $Mg(OH)_2$, 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 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.

(2) If $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are considered as ions $(Ca^{2+} + 2HCO_3^-)$ and $(Mg^{2+} + 2HCO_3^-)$ respectively, then calculation results will be same.

(3) Equivalent weight of $NaAlO_2$ is equal to its molar mass.

(4) If treated water contains OH^- and CO_3^{2-} ions, then these are formed from excess eq each of $Ca(OH)_2$ plus Na_2CO_3 and Na_2CO_3 respectively. So these excess amounts should be added to the calculations.

(5) When the impurities are given as $CaCO_3$ and/or $MgCO_3$, these should be considered due to bicarbonates of calcium and/or magnesium respectively.

(6) Substances like $NaCl$, KCl , Na_2SO_4 , SiO_2 , Fe_2O_3 etc. do not impart any hardness and, therefore, these do not consume any lime or soda. These should not be taken into consideration for calculating the lime and soda requirements.

Now 100 parts by mass of $CaCO_3$ are equivalent to :

(i) 74 parts of $Ca(OH)_2$, and

(ii) 106 parts of Na_2CO_3 .

\therefore Lime requirement for softening

$$= \frac{74}{100} \left[\begin{array}{l} \text{Temp. } Ca^{2+} + 2 \times \text{Temp. } Mg^{2+} + \text{Perm. } (Mg^{2+} + Fe^{2+} + Al^{3+}) \\ + CO_2 + H^+ (\text{HCl or } H_2SO_4) + HCO_3^- - NaAlO_2 \\ \text{all in terms of } CaCO_3 \text{ eq} \end{array} \right]$$

\therefore Soda requirement for softening

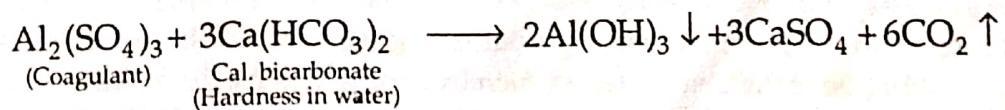
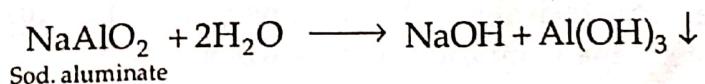
$$= \frac{106}{100} \left[\begin{array}{l} \text{Perm. } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+}) + H^+ (\text{HCl or } H_2SO_4) - HCO_3^- \\ \text{all in terms of } CaCO_3 \text{ eq} \end{array} \right]$$

WATER TREATMENT

Table 2. Calculation of lime-soda requirement.

Constituent	Reaction	Need
Ca ²⁺ (Perm. Ca)	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	S
Mg ²⁺ (Perm. Mg)	$\text{Mg}^{2+} + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 + \text{Ca}^{2+}$	
HCO ₃ ⁻ (e.g., NaHCO ₃)	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$ $2\text{HCO}_3^- + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_3^{2-}$	L + S L - S
Ca(HCO ₃) ₂ (Temp. Ca)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	L
Mg(HCO ₃) ₂ (Temp. Mg)	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 + \text{Mg(OH)}_2 + 2\text{H}_2\text{O}$	2L
CO ₂	$\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
H ⁺ (free acid, HCl, H ₂ SO ₄ , etc.)	$2\text{H}^+ + \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
Coagulants :		
FeSO ₄	$\text{Fe}^{2+} + \text{Ca(OH)}_2 \rightarrow \text{Fe(OH)}_2 + \text{Ca}^{2+}$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe(OH)}_3$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
Al ₂ (SO ₄) ₃	$2\text{Al}^{3+} + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{Ca}^{2+}$ $3\text{Ca}^{3+} + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 6\text{Na}^+$	L + S
NaAlO ₂	$\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NaOH}$ 2NaOH is eq. to Ca(OH) ₂	- L

(i) Cold lime-soda process : In this method, calculated quantity of chemical (lime and soda) are mixed with water at room temperature. At room temperature, the precipitates formed are *finely divided*, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of *coagulants* (like alum, aluminium sulphate, sodium aluminate, etc.), which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminate as coagulant also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.



Method : Raw water and calculated quantities of chemicals (lime + soda + coagulant) are fed from the top into the inner vertical circular chamber, fitted with a vertical rotating shaft carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer co-axial chamber, it rises upwards. The heavy sludge (or precipitated floc) settles down in the outer chamber by the time the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibres) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top (see Fig. 3) Sludge settling at the bottom of the outer chamber is drawn off occasionally.

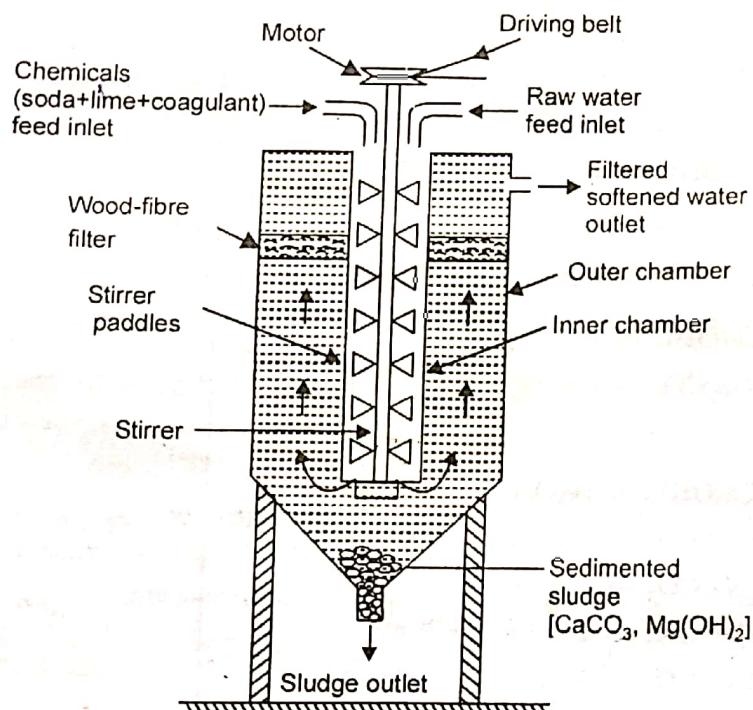


Fig. 3. Continuous cold lime-soda softener.

(ii) **Hot lime-soda process** involves in treating water with softening chemicals at a temperature of 80 to 150°C. Since hot process is operated at a temperature close to the boiling point of the solution, so : (a) the reaction proceeds faster ; (b) the softening capacity of hot process is increased to many fold ; (c) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed ; (d) much of the dissolved gases (such as CO₂ and air) driven out of the water ; (e) viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters, and (f) hot lime-soda process produces water of comparatively lower residual hardness of 15 to 30 ppm.

Hot lime-soda plant consists essentially (see Fig. 4) of three parts: (a) a 'reaction tank' in which raw water, chemicals and steam are thoroughly mixed ; (b) a "conical sedimentation vessel" in which sludge settles down, and (c) a "sand filter" which ensures complete removal of sludge from the softened water.

Advantages of L.S. process: (i) It is very economical. (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed. (iii) The process increases the pH value of the treated-water, thereby corrosion of the distribution pipes is reduced. (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced. (v) To certain

extent, iron and manganese are also removed from the water. (vi) Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced.

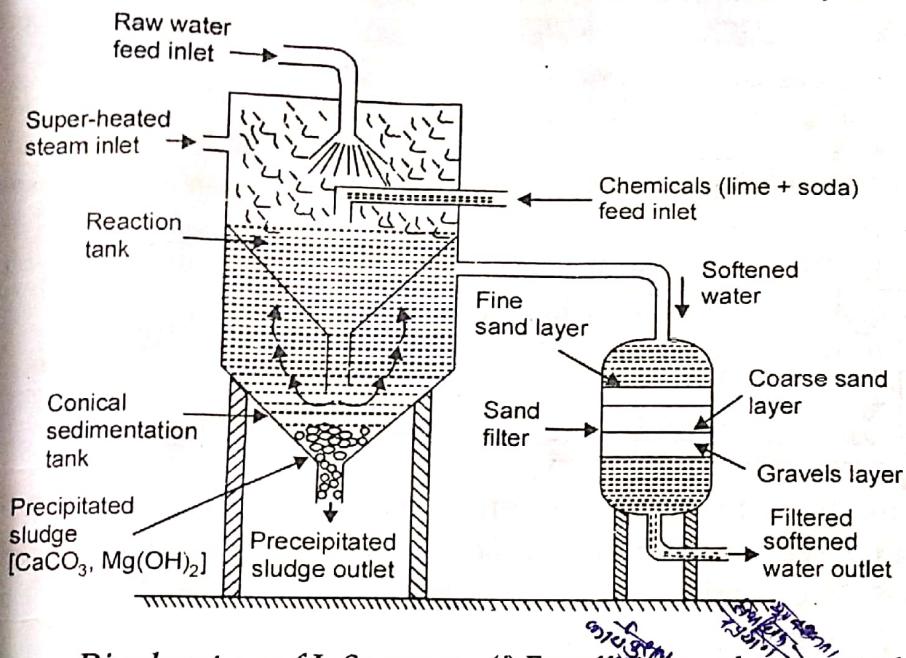


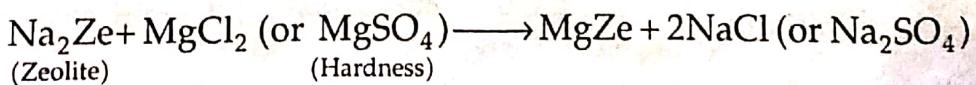
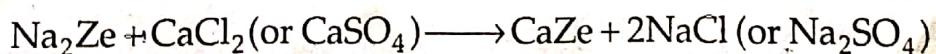
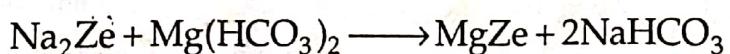
Fig. 4. Continuous hot lime-soda softener.

Disadvantage of L-S process : (i) For efficient and economical softening, careful operation and skilled supervision is required. (ii) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city. (iii) This can remove hardness only upto 15 ppm, which is not good for high-pressure boilers.

(2) **Zeolite or permutit process :** Chemical structure of sodium zeolite may be represented as : $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where $x = 2 - 10$ and $y = 2 - 6$. Zeolite is hydrated sodium alumino silicate, capable of *exchanging reversibly* its sodium ions for hardness-producing ions in water. Zeolites are also known as *permuts*. Zeolites are of two types :

- (i) **Natural zeolites** are *non-porous*. For example, natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.
- (ii) **Synthetic zeolites** are porous and possess *gel structure*. They are prepared by heating together china clay, feldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.

Process : For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder (see Fig. 5). The hardness-causing ions (Ca^{2+} , Mg^{2+} , etc.) are retained by the zeolite as CaZe and MgZe ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are :



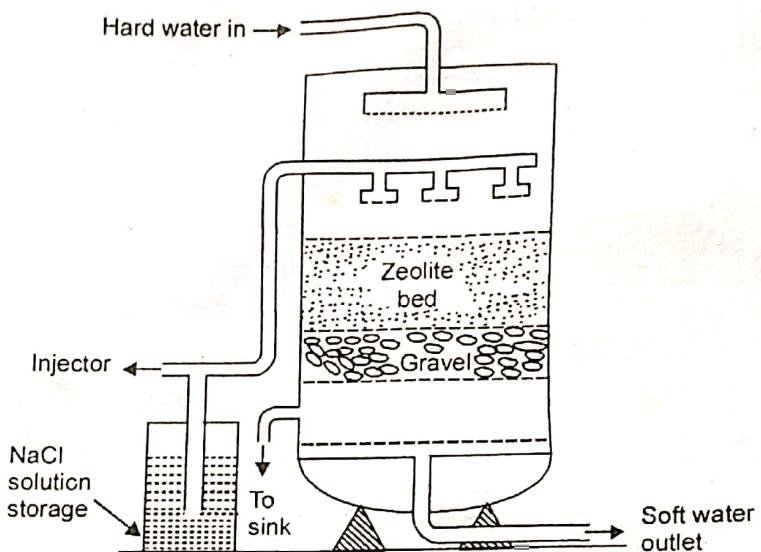
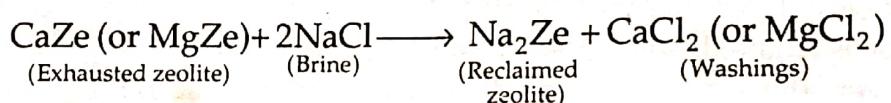


Fig. 5. Zeolite softener.

Regeneration: After some time, the zeolite is completely converted into calcium and magnesium zeolites and it ceases to soften water, i.e., it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated (10%) brine (NaCl) solution.



The washings (containing CaCl_2 and MgCl_2) are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.

Limitations of zeolite process: (1) If the supply of water is turbid, the suspended matter must be removed (by coagulation, filtration, etc.), before the water is admitted to the zeolite bed; otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.

(2) If water contains large quantities of coloured ions such as Mn^{2+} and Fe^{2+} , they must be removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.

(3) Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralised with soda, before admitting the water to the zeolite softening plant.

Advantages of zeolite process: (1) It removes the hardness almost completely and water of about 10 ppm hardness is produced. (2) The equipment used is compact, occupying a small space. (3) No impurities are precipitated, so there is no danger of sludge formation in the treated-water at a later stage. (4) The process automatically adjusts itself for variation in hardness of incoming water. (5) It is quite clean. (6) It requires less time for softening. (7) It requires less skill for maintenance as well as operation.

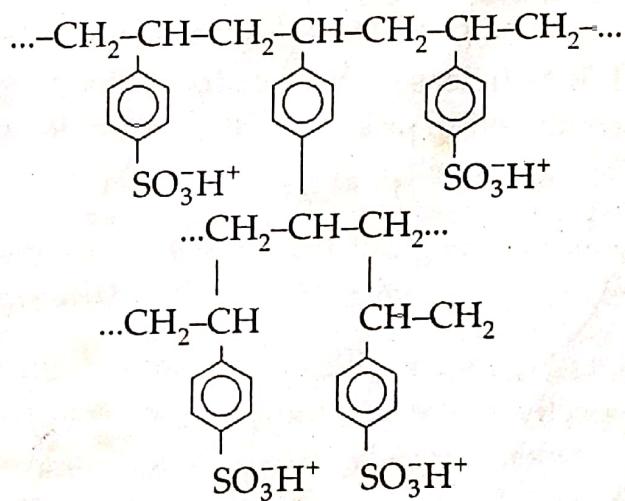
Disadvantages of zeolite process: (1) The treated-water contains more sodium salts than in lime-soda process. (2) The method only replaces Ca^{2+} and Mg^{2+} ions by Na^+ ions, but leaves all the acidic ions (like HCO_3^- and CO_3^{2-}) as such in the softened water. When such softened water (containing NaHCO_3 , Na_2CO_3 , etc.) is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2 , which causes corrosion; and sodium carbonate hydrolyses to sodium hydroxide, which causes caustic embrittlement. (3) High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed, thereby creating problem for its working.

Table 3. Comparison of permutit process with lime-soda process.

<i>Permutit method</i>	<i>Lime-soda method</i>
1. Water of 10-15 ppm residual hardness is obtained.	Water of, generally, 15-50 ppm hardness is obtained.
2. Treated-water contains larger amount of sodium salts than in original raw water.	Treated-water contains lesser amount of sodium salts.
3. Cost of plant and material is higher.	Capital cost is lower.
4. Operation expenses are lower.	Operation expenses are higher.
5. It cannot be used for treating acidic water, because the permutit material undergoes disintegration.	There are no such limitations.
6. The plant occupies less space.	Plant occupies more space.
7. The raw water to be softened must be free from suspended matter ; otherwise the pores of permutit material are blocked and the bed loses its exchange capacity.	There are no such limitations.
8. It can operate under pressure and can be made fully automatic.	It cannot operate under pressure.
9. It involves no problem of settling, co-agulation, filtration and removal of the sludges and precipitates.	It involves difficulty in settling, co-agulation, filtration and removal of precipitates.
10. Control test comprises only in checking the hardness of treated-water.	In order to meet the changing hardness of incoming water, frequent control and adjustment of reagents is needed.
11. Treated-water contains more dissolved solids.	Treated-water contains lesser dissolved solids.

(3) **Ion exchange or de-ionization or de-mineralization process : Ion-exchange resins** are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the "functional groups" attached to the chains are responsible for the ion-exchanging properties. Resins containing acidic functional groups ($-COOH$, $-SO_3H$, etc.) are capable of exchanging their H^+ ions with other cations, which comes in their contact; whereas those containing basic functional groups ($-NH_2 = NH$ as hydrochloride) are capable of exchanging their anions with other anions, which comes in their contact. The ion-exchange resins may be classified as :

(i) **Cation exchange resins (RH^+)** are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water.

**Fig. 6.** Acidic or cation exchange resin (sulphonate form).

(ii) **Anion exchange resins** ($R'OH^-$) are styrene-divinyl benzene or amine-formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH^- anions with anions in water.

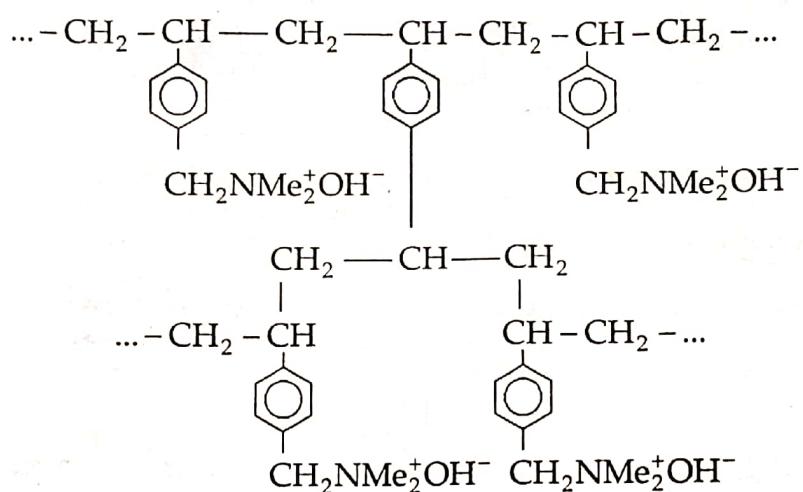
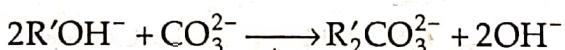
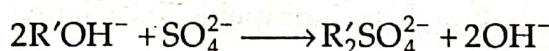


Fig. 7. Basic or anion exchange resin (hydroxide form)

Process : The hard water is passed first through cation exchange column, which removes all the cations (like Ca^{2+} , Mg^{2+} , etc.) from it, and equivalent amount of H^+ ions are released from this column to water. Thus :



After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- , etc. present in the water and equivalent amount of OH^- ions are released from this column to water. Thus :



H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.



Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as *deionized* or *demineralised water*.

Regeneration : When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be *exhausted*.

The *exhausted cation exchange column* is regenerated by passing a solution of dil. HCl or dil. H_2SO_4 . The regeneration can be represented as :

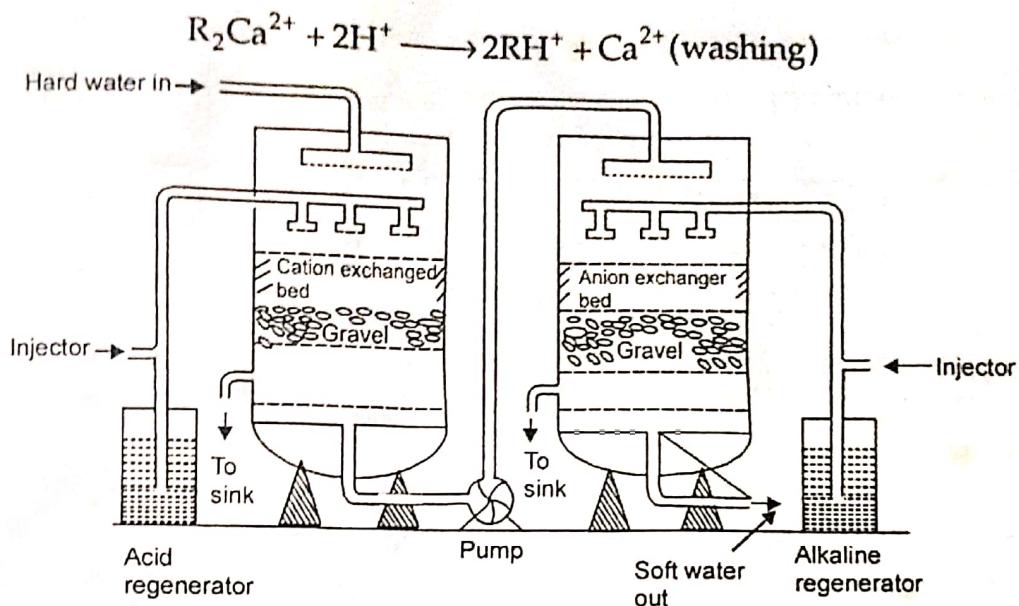
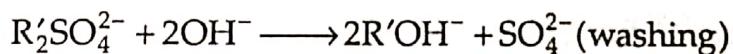


Fig. 8. Demineralization of water.

The column is washed with deionised water and washing (which contains Ca^{2+} , Mg^{2+} , etc. and Cl^- or SO_4^{2-} ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. $NaOH$. The regeneration can be represented as :



The column is washed with deionised water and washing (which contains Na^+ and SO_4^{2-} or Cl^- ions) is passed to sink or drain.

The regenerated ion exchange resins are then used again.

Advantages : (1) The process can be used to soften highly acidic or alkaline waters. (2) It produces water of very low hardness (say 2 ppm). So it is very good for treating water for use in high-pressure boilers.

Disadvantages : (1) The equipment is costly and more expensive chemicals are needed. (2) If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

(4) **Mixed-bed deionizer** consists essentially of a single cylinder containing an intimate mixture of hydrogen exchanger and strongly basic anion exchanger. When water is passed through this bed, it comes in contact, a number of times, with the two kinds of exchangers alternatively. Consequently, the net effect of mixed-bed exchanger is equivalent to passing water through a series of several cation and anion exchangers. The outgoing water from the mixed-bed contains even less than 1 ppm of dissolved salts.

Regeneration : When the resins are exhausted, the mixed-bed is backwashed (by forcing water in the upward direction), when the lighter anion exchanger gets displaced to form an upper layer above the heavier cation exchanger (see Fig. 9.). Thereafter, the anion exchanger is regenerated by passing caustic soda solution from the top and then rinsed. The lower cation exchanger bed is then regenerated by H_2SO_4 solution treatment and then rinsed. The two beds are then mixed again by forcing compressed air. The bed is ready for use again.

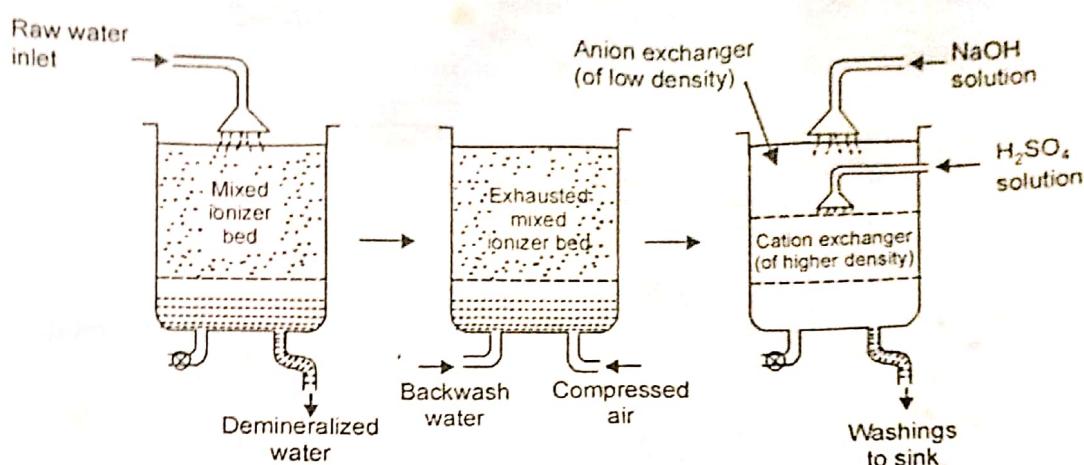


Fig. 9. Regeneration of mixed-bed ion exchanger.

Note : It may be made clear that the mixed-bed exchangers cost more and comparatively more expensive to regenerate, but they are comparatively more convenient to use and afford much more efficient removal of dissolved salts and silica.

12 DRINKING WATER OR MUNICIPAL WATER

Municipalities have to supply *potable water*, i.e., water which is safe to drink. Drinking or potable water, fit for human consumption, should satisfy the following essential requirements :

- (1) It should be sparkling clear and odourless.
- (2) It should be pleasant in taste.
- (3) It should be perfectly cool.
- (4) Its turbidity should not exceed 10 ppm.
- (5) It should be free from objectionable dissolved gases like hydrogen sulphide.
- (6) It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
- (7) Its alkalinity should not be high. Its pH should be about 8.0.
- (8) It should be reasonably soft.
- (9) Its total dissolved solids should be less than 500 ppm.
- (10) It should be free from disease-producing micro-organisms.

Purification of water for domestic use : Natural water from rivers, canals, etc., does not confirm to all the required specifications of drinking water. For removing various types of impurities, the following treatment processes are employed :

Note. Municipal water treatment does not aim at removing the dissolved salts present. Consequently, municipalities do not, generally, supply softened water.

(A) Removal of suspended impurities :

- (1) **Screening :** The raw water is passed through screens, having large number of holes, when floating matters are retained by them.

WATER TREATMENT

28. What is break-point chlorination ?

Ans. It involves in addition of sufficient amount of chlorine to water in order to oxidise organic matter, reducing substances and free ammonia ; leaving behind mainly free chlorine for disinfecting disease-producing bacterias.

29. What is standard hard water ?

Ans. Usually, it a solution containing 1 g of CaCO_3 equivalent hardness in 1 litre, i.e., 1,000 ppm (or 1,000 mg/L) hardness water.

30. What is zeolite ?

Ans. It is hydrated sodium alumino-silicate of formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where $x = 2 - 10$ and $y = 2 - 6$. It is capable of *exchanging reversibly* its Na^+ ions for hardness-producing ions in water.

31. What happens to the hardness of water, when lime is added to it ?

Ans. (i) Temporary calcium hardness is removed, (ii) temporary magnesium hardness is removed, (iii) permanent magnesium hardness is converted into equivalent permanent calcium hardness.

32. What are the advantages of break-point chlorination ?

Ans. It : (i) oxidises completely organic matter, NH_3 , and reducing agents, (ii) removes colours in water, (iii) destroys completely all the disease-producing bacterias, (iv) removes odour from water, (v) prevents, if any, growth of weeds in water.

33. Why is $\text{NH}_3-\text{NH}_4\text{Cl}$ buffer solution added during determination of hardness of water by EDTA titration ?

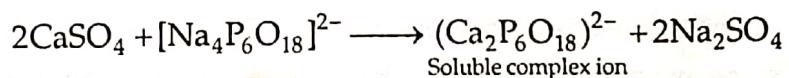
Ans. EDTA titration is carried out by using Eriochrome black-T indicator, which gives end-point (wine red to blue) *only when pH of water sample is maintained around 10*. Hence, basic buffer solution consisting of $\text{NH}_3 + \text{NH}_4\text{Cl}$ mixture of proper concentration is used during EDTA titration.

34. What is the indicator used in EDTA method ? What is the end-point ? (Bharathiar, Nov. 97)

Ans. Indicator : Eriochrome black-T (EBT) ; End-point : Wine red to distinct blue.

35. Calgon treatment prevents scale formation in boilers. Give reasons. (Mangalore, Aug. 97)

Ans. Addition of calgon $[(\text{NaPO}_3)_6]$ to boiler-water prevents the scale formation by forming *soluble complex compound* with scale forming salt, CaSO_4 .



36. Chloramine is preferable to bleaching powder or chlorine for sterilization of drinking water.

Give reason. (Mangalore, Aug. 97)

Ans. Chloramine is preferred over bleaching powder or chlorine, because it : (i) causes no irritating odour, even if used in excess, and (ii) imparts good taste to treated water.

37. In the deionization process, water is usually first passed through the cation exchanger and then through the anion exchanger. Give reason. (Bangalore, Aug. 97)

Ans. Cation-exchangers are *easily attacked by alkalis* ; whereas all types of ion-exchangers are *not attacked by acids*. When water is first passed through a cation exchanger, salts present in water are converted into corresponding acids, which on passing through an anion exchanger do not harm it and finally get converted into pure water. If reverse sequence is used, then alkalis, produced on passing water through anion exchanger, harms the cation-exchanger in subsequent step. Consequently, such a sequence is usually avoided.

Ans. Parts per million (ppm) or milligram per litre (mg/L).

15. Differentiate between scale and sludge.

Ans. Sludge is a soft, loose, slimy deposit formed inside the boiler ; while *scale* is a hard, sticky, adherent deposit formed on the inner surface of the boiler.

16. What is *lather factor* ?

Ans. The amount of standard soap solution required to produce lather, which lasts for two minutes, when added to distilled water.

17. Why do we add buffer solution during titration of hard water against EDTA solution ?

Ans. The indicator used in this titration (EBT) shows colour change at a pH value of about 10. So alkaline buffer ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ mixture) is used.

18. Why is water softened by zeolite process unfit for use in boilers ?

Ans. Water softened by zeolite process causes *caustic embrittlement*, since it contains large quantities of sodium salts (e.g., NaCl and Na_2SO_4).

19. Define ppm.

(Bharathidasan, April 94)

Ans. It is the parts of calcium carbonate equivalent hardness per 10^6 parts of water.

20. What is *degree of hardness* of water ?

(Poona, May 94)

Ans. It is the parts of calcium carbonate equivalent hardness per a particular number of parts of water, depending upon the unit employed.

21. Distinguish between hard water and soft water.

(Marathwada, May 93)

Ans. Hard water is one which *does not* produce lather with soap solution readily, but forms a white curd ; while soft water gives lather easily on shaking it with soap solution. Alternatively, hard water contains dissolved calcium and magnesium salts ; while soft water does not contain dissolved calcium and magnesium salts in it.

22. Why do we express hardness of water in terms of calcium carbonate equivalent ?

Ans. This mode permits easy addition and subtraction of concentrations of hardness-causing constituents, since its molecular mass is 100. Moreover, it has been adopted as standard for expressing hardness.

23. What are the salts responsible for the temporary and permanent hardness of water ?

Ans. Temporary hardness : $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.

Permanent hardness : CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$, etc.

24. Why is hot lime-soda process *better* than the cold process ?

(Rani Durgavati, May 94)

Ans. Hot lime-soda process : (i) is very economical, (ii) requires no coagulant, (iii) is very faster, (iv) precipitated sludge settles down rapidly, (v) produces water of comparatively lower residual hardness.

25. Why is demineralization process preferred over zeolite process for softening of water for use in boilers ?

Ans. Demineralized water is free from all ions ; whereas zeolite-softened water contains sodium salts (e.g., NaCl and Na_2SO_4), which causes *caustic embrittlement* in boilers.

26. The presence of CO_2 in boiler feed-water should be avoided. Why ? (Mangalore, Sept., 94)

Ans. CO_2 forms carbonic acid (H_2CO_3), which slowly attacks the boiler materials, thereby making the latter weaker and weaker progressively.

27. What is meant by *softening* of water ?

Ans. The process of removing hardness-producing salts from water, is called *softening*.