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 a *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 a number of other compounds.

Surface water, generally, contains *suspended matter,* which often contains the *disease-producing (or pathogenic) bacterias.* 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 meet a hard rock, when it retreads 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.*

(1)

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 any 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 chromium and appreciable amount of organic matter. *Yellowish-red* colour indicates the presence of iron , while *red-brow* colour indicate the presence of peaty matter.

(b) *Turbidity* is due to the colloidal, extremely fine suspension such as clay, silt, 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 in straight lines. The turbidity depends not only on the quantity of insoluble substances, but also on their 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 of 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 is 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 protiens 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 immature) released from dyes, paints, and vanishes, drugs, insecticides, pesticides, detergent, pulp and textiles, industries, tanneries, etc. . All these pollute water bodies, (ii) *acids* discharged in water by DDT, high explosives, battery, 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 atmosphere 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, 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.
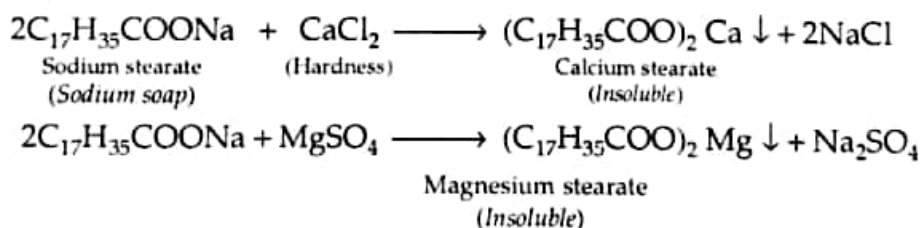
(3) **Biological impurities** are algae, pathogenic bacteria, fungi, viruses, pathogens, parasite worms, etc. The source of these contamination is discharge of domestic and sewage wastes, excreta (from man, animals and birds), etc.

(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 – 35°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 inhabitated 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 :

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2 Ca \downarrow + 2NaCl$$

Sodium stearate   (Hardness)   Calcium stearate
(Sodium soap)   (Insoluble)

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2 Mg \downarrow + Na_2SO_4$$

Magnesium stearate
(Insoluble)

Thus, water which does not produce lather with soap solution readily, but forms a while 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.

Plumbosolvency : Lead is not attacked by pure air-free water (except at the boiling point). It is readily corroded by water containing dissolved air, form $Pb(OH)_2$, 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 salt/ion	Molar mass	Chemical equivalent	Multiplication factor for conveting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	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
$FeSO_4.7H_2O$	278	139	100/278
H^+	1	1	100/2
HCl	36.5	1	100/73

The equivalents of $CaCO_3$

$$= \frac{\left[\begin{array}{c} \text{Mass of hardness} \\ \text{producing substance} \end{array}\right] \times \left[\begin{array}{c} \text{Chemical equivalent} \\ \text{of } CaCO_3 \end{array}\right]}{\text{Chemical equivalent of hardness–producing substance}}$$

$$= \frac{\text{Mass of hardness–producing substance} \times 50}{\text{Chemical equivalent of hardness-producing substance}}$$

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 mg/L = 1 mg of $CaCO_3$ 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 mg/L = 1 mg of $CaCO_3$ eq per 10^6 mg of water.

$$= 1 \text{ part of } CaCO_3 \text{ eq per } 10^6 \text{ parts of water} = 1 \text{ ppm}.$$

(3) Clarke's degree (°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° Clarke = 1 grain of $CaCO_3$ eq hardness per gallon of water.

or 1° Cl = 1 part of $CaCO_3$ eq hardness per 70,000 parts of water.

(4) Degree French (°Fr) *is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.* Thus :

1° Fr = 1 part of $CaCO_3$ hardness eq per 10^5 parts of water.

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

1 meq/L = 1 meq of $CaCO_3$ per L of water

$$= 10^{-3} \times 50 \text{ g of } CaCO_3 \text{ eq per litre}$$

$$= 50 \text{ mg of } CaCO_3 \text{ eq per litre}$$

$$= 50 \text{ mg/L of } CaCO_3 \text{ eq} = \mathbf{50 \text{ ppm}}.$$

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

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 :

Priming can be avoided by : (i) fitting mechanical steam p........ in steaming rate , (iii) maintaining low water levels in boilers, and (iv) efficient softening and filtration of the boiler-feed water.
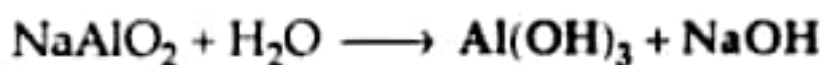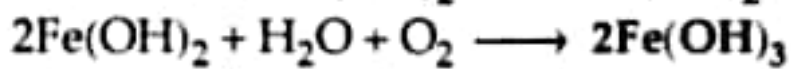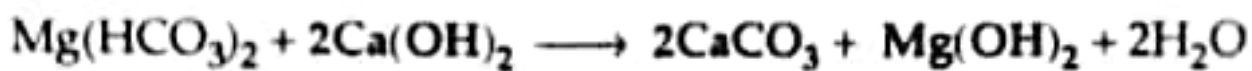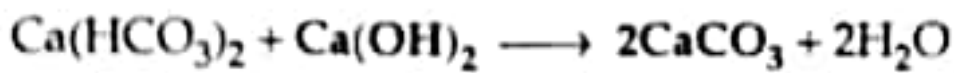
Foaming can be avoided by : (i) adding anti-foaming chemicals like castor oil, or (ii) removing oil from boiler water by adding compounds like sodium aluminate.

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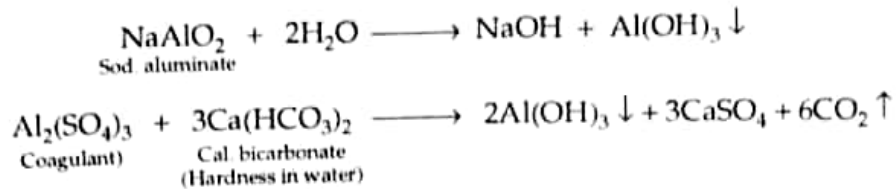
(1) **Lime-soda process** : In this method, the soluble calcium and magnesium salts in water are chemically converted into **insoluble compounds**, by adding calculated amounts of *lime* [$Ca(OH)_2$] and *soda* [Na_2CO_3]. *Calcium carbonate* [$CaCO_3$] and *magnesium hydroxide* [$Mg(OH)_2$], so-precipitated,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

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$
$$2HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + CO_3^{2-}$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$
$$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$$
$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$

$$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2 + Ca^{2+}$$
$$2Fe(OH)_2 + H_2O + O_2 \longrightarrow 2Fe(OH)_3$$
$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$$

$$2Al^{3+} + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3Ca^{2+}$$
$$3Ca^{2+} + 2Na_2CO_3 \longrightarrow 3CaCO_3 + 6Na^+$$

$$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$$

$$2NaOH \text{ is eq to } Ca(OH)_2$$

⑧

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.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3 \downarrow$$
Sod. aluminate

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 6CO_2 \uparrow$$
Coagulant)　Cal. bicarbonate
(Hardness in water)

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.
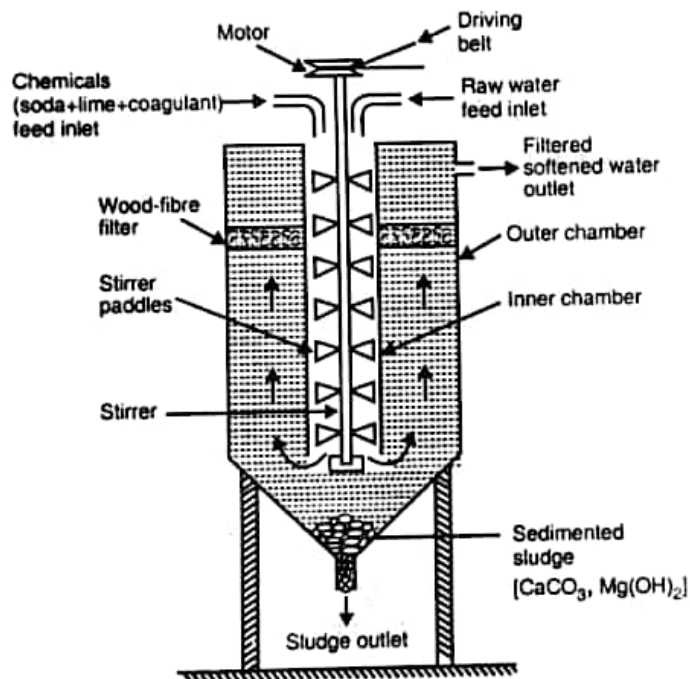

Fig. 3. Continuous cold lime-soda softener.

(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 CO_2 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.
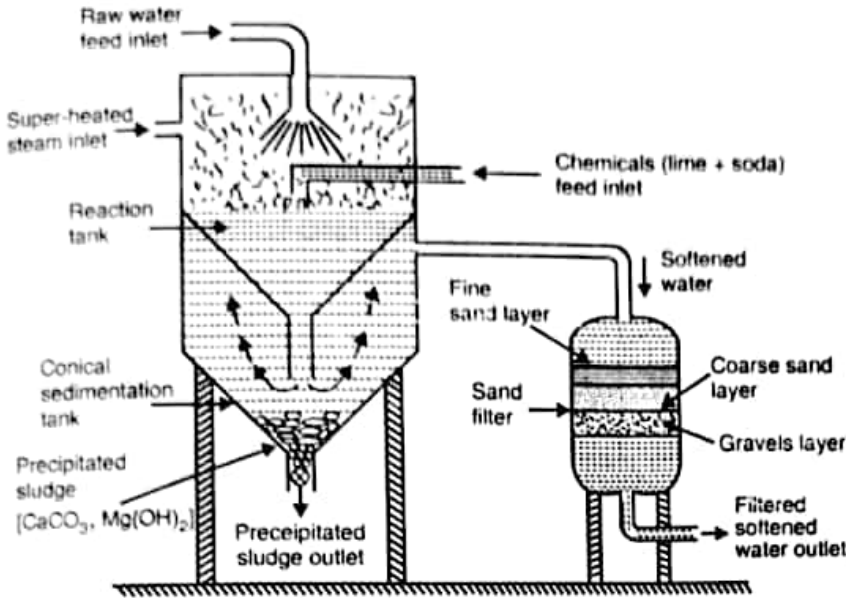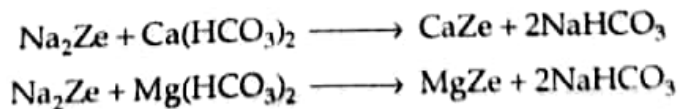

Fig. 4. Continuous hot lime-soda softener

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 bacterias in water is considerably reduced.

Disadvantage of L-S process : (i) For efficient and economical softening, careful operation and skilled supervision in 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 boilers.

(2) **Zeolite or permutit process** : Chemical structure of sodium zeolite may be represented as: $Na_2O.Al_2O_3. x SiO_2. y,H_2O$ 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 permutits. Zeolites are of *two* types : (i) *Natural zeolites* are *non-porous.* For example, natrolite, $Na_2O.Al_3O_3.4SiO_2.2H_2O$. (ii) *Synthetic zeolites* are porous and possess gel *structure.* They are prepared by heating together china clay, faldspar 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 :

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$
$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$

$$Na_2Ze + CaCl_2 \text{ (or } CaSO_4) \longrightarrow CaZe + 2NaCl \text{ (or } Na_2SO_4)$$

$$Na_2Ze + MgCl_2 \text{ (or } MgSO_4) \longrightarrow MgZe + 2NaCl \text{ (or } Na_2SO_4)$$

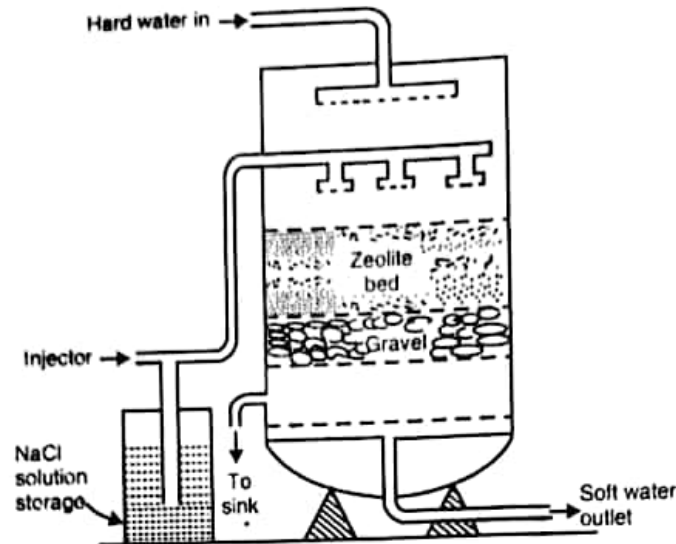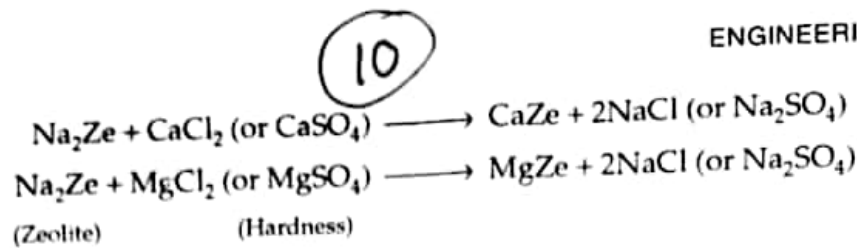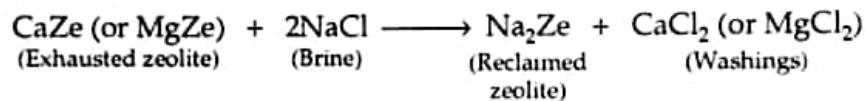(Zeolite)   (Hardness)

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.

$$CaZe \text{ (or } MgZe) + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \text{ (or } MgCl_2)$$

(Exhausted zeolite)   (Brine)   (Reclaimed   (Washings)
                                      zeolite)

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 maganese 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 hydrolysies 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.

Permutit method	Lime-soda method
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, filteration 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.
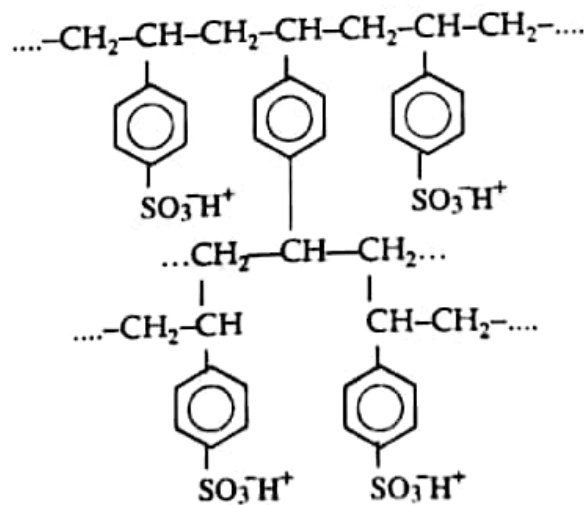

Fig. 6. Acidic or cation exchange resin (sulphonate form).

(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.
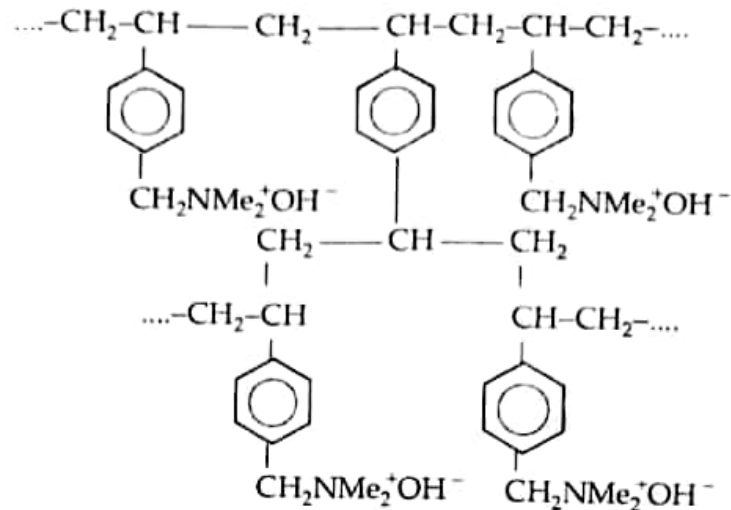

**Fig. 7.** Basic or anion exchange resin (hydroxide form).

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 :

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$

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 :

$$R'OH^- + Cl^- \longrightarrow R'Cl^- + OH^-$$

$$2R'OH^- + SO_4^{2-} \longrightarrow R'_2SO_4^{2-} + 2OH^-$$

$$2R'OH^- + CO_3^{2-} \longrightarrow R'_2CO_3^{2-} + 2OH^-$$

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

$$H^+ + OH^- \longrightarrow H_2O$$
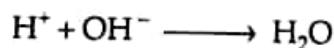
Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as deionized or demineralised water.

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 :
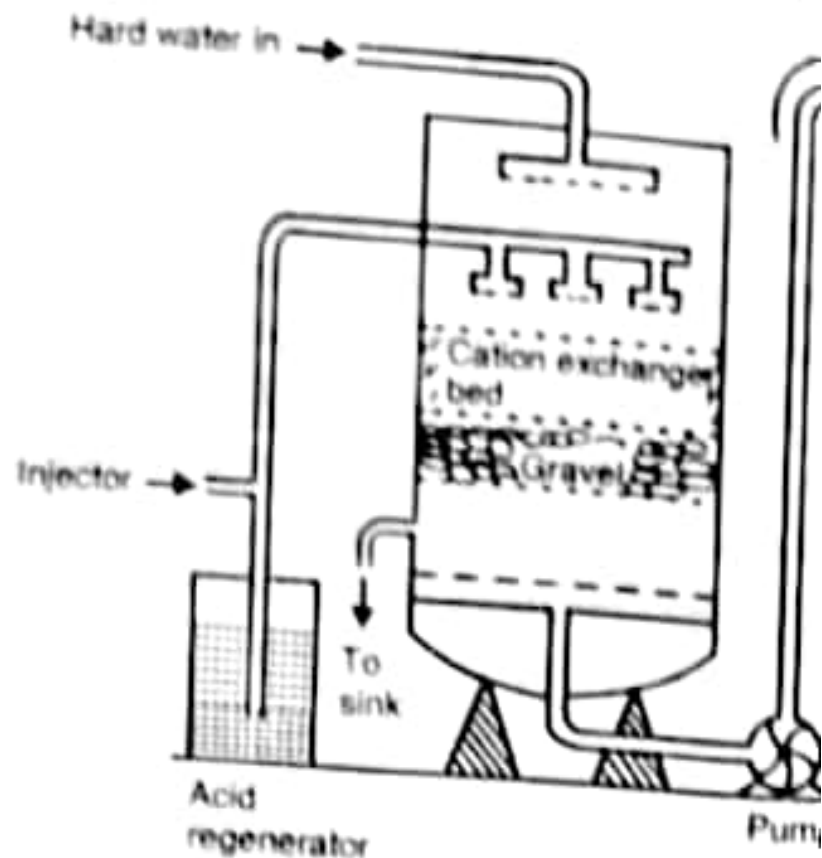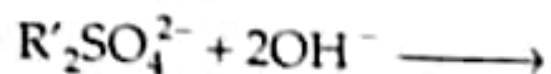
$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+} \text{ (washing)}$$
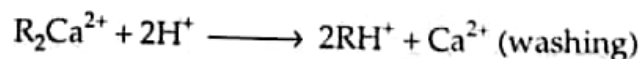
Fig. 8. Deminer:

The column is washed with deionised wa and Cl^- or SO_4^{2-} ions) is passed to sink or drain.

The *exhausted anion exchange column* is reg regeneration can be represented as :

$$R'_2SO_4^{2-} + 2OH^- \longrightarrow$$

The column is washed with deionised wat Cl^- ions) is passed to sink or drain.

The regenerated ion exchange resins are t

Advantages : (1) The process can be used to s water of very low hardness (say 2 ppm). So it is very g

Disadvantages : (1) The equipment is costly a contains turbidity, then the output of the process is red it has to be removed first by coagulation and filtration

Mixed-bed deionizer *consists essentially of a si*
exchanger and strongly basic anion exchanger. When

number of times, with the two kinds of exchangers alternatively. Consequently, the net affect 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.

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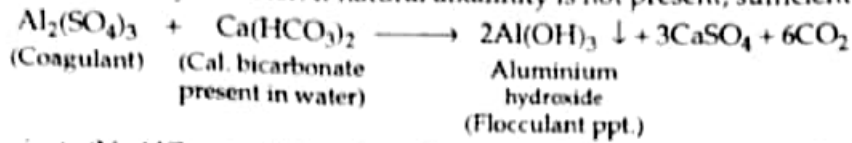
(A) *Removal of suspended impurities* : (1) **Screening** : The raw water is passed through screens, having large number of holes, when floating matters are retained by them.

(2) **Sedimentation** *is a process of allowing water to stand undisturbed in big tanks, about 5 m deep, when most of the suspended particles settle down at the bottom, due to the force of gravity.* The clear supernatant water is then drawn from tank with the help of pumps. The retention period in a sedimentation tank ranges from 2-6 hours.
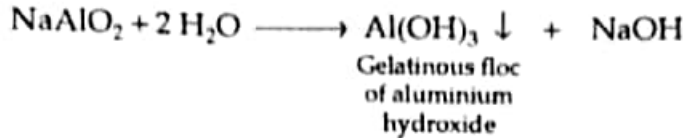
When water contains fine clay particles and colloidal matter, it becomes necessary to apply sedimentation with coagulation for removing such impurities. **Sedimentation with coagulation** *is the process of removing fine suspended and colloidal impurities by the addition of requisite amount of chemicals (called coagulants) to water before sedimentation. Coagulant, when added to water, forms an insoluble gelatinous, flocculant precipitate, which descent through the water, adsorbs and entangles very fine suspended impurities forming bigger flocs, which settle down easily.* Coagulants like alum or ferrous sulphate provide Al^{3+} or Fe^{3+} ions, which neutralise the negative charge on the colloidal clay particles. After losing their charge, the tiny clay particles come nearer to one another and combine to form *bigger particles*, which settle down, due to the force of gravity. Thus, coagulant forces even colloidal particles to settle down. The coagulants (or *flocculants*) are, generally, added in solution form. For proper mixing of coagulants with water, mixers are employed. Properly mixed water is then *sedimented*.

**Chemical coagulants** : The following are the most commonly used coagulants :

(i) *Alum* [$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$] is the most widely used in water treatment plants. Alum reacts in water in the presence of alkalinity of water. If natural alkalinity is not present, sufficient lime is also added.
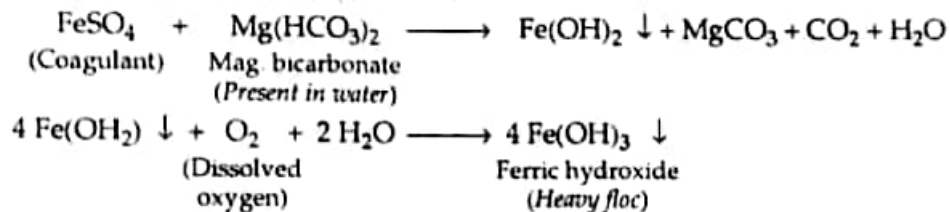
$$Al_2(SO_4)_3 + Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 6CO_2$$

   (Coagulant)   (Cal. bicarbonate   Aluminium
           present in water)   hydroxide
                              (Flocculant ppt.)

(ii) *Sodium aluminate* ($NaAlO_2$) is obtained from bauxite refineries in the form of a thick solution. This can very easily be used for treating water having *no alkalinity* (*i.e.*, pH less than 7). pH range for best results is 5.5 – 8.0.

$$NaAlO_2 + 2 H_2O \longrightarrow Al(OH)_3 \downarrow + NaOH$$

                           Gelatinous floc
                           of aluminium
                           hydroxide

The aluminium hydroxide floc causes sedimentation. The sodium hydroxide thus-produced, precipitates magnesium salts as $Mg(OH)_2$.

$$MgSO_4 + 2 NaOH \longrightarrow Mg(OH)_2 \downarrow + Na_2SO_4$$
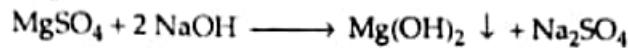
(iii) *Copperas or ferrous sulphate* [$FeSO_4 . 7 H_2O$] is also commonly used for coagulation purposes. It gives good results above pH values of 8.5, (*i.e.*, *slightly alkaline*). Copperas reacts in water in the presence of alkalinity. If alkalinity is not present, sufficient lime is also added.

$$FeSO_4 + Mg(HCO_3)_2 \longrightarrow Fe(OH)_2 \downarrow + MgCO_3 + CO_2 + H_2O$$

  (Coagulant)   Mag. bicarbonate
           (*Present in water*)

$$4 Fe(OH)_2 \downarrow + O_2 + 2 H_2O \longrightarrow 4 Fe(OH)_3 \downarrow$$

       (Dissolved   Ferric hydroxide
       oxygen)   (*Heavy floc*)

$Fe(OH)_3$ is in the form of *heavy floc*, which causes quick sedimentation.

(3) Filtration *is the process of removing colloidal matter and most of the bacterias, micro-organisms, etc., by passing water through a bed of fine sand and other proper-sized granular materials. Filtration is carried out by using sand filter.*
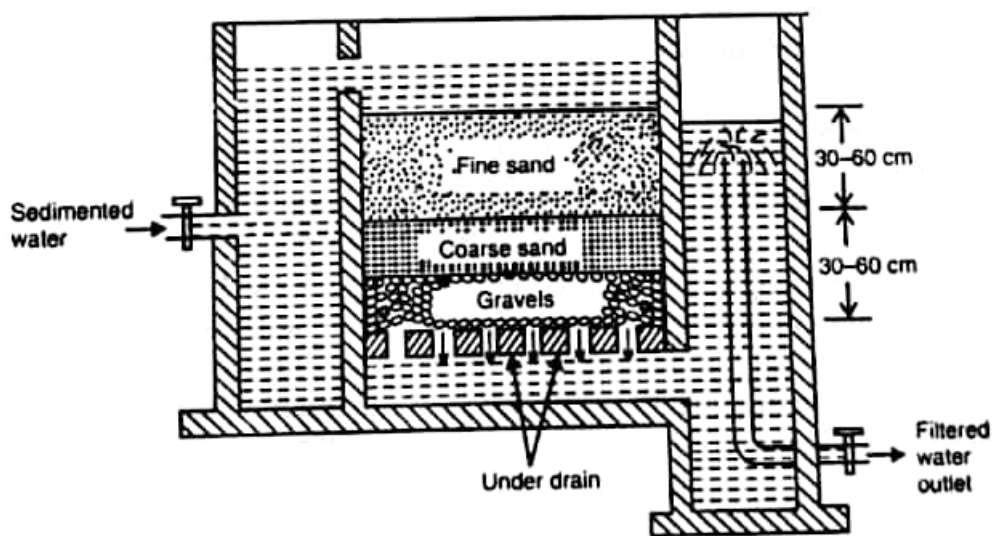

Fig. 10. Sand filter.

Operation of sand filter : A sand filter consists of a thick top layer of *fine sand* placed over *coarse sand layer* and *gravels*. It is provided with an *inlet* for water and an *underdrain channel* at the bottom for exit of filtered
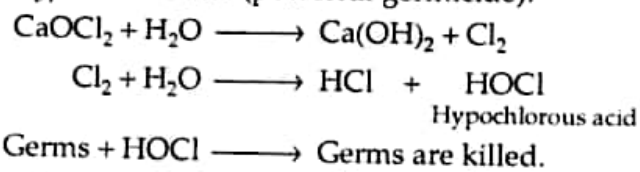
water. Sedimented water entering the sand filter is uniformly distributed over the entire find sand bed. During filtration, the sand pores get clogged, due to retention of impurities in the pores. *When the rate of filtration become slow, the working of filter is stopped and about 2–3 cm of the top fine sand layer is scrapped off and replaced with clean sand and the filter is put back into use again.* The scrapped sand is washed with water, dried and stored for refuse at the time of next scrapping operation.

(B) *Removal of micro-organisms* : Water after passing through sedimentation, coagulation and filtration operations still contains a small percentage of *pathogenic bacteria* (disease-producing). Consequently, water used, particularly for drinking or municipal purposes, must be freed from these disease-producing bacteria, micro-organisms, etc. *The process of destroying/killing the disease-producing bacteria, micro-organisms, etc., from the water and making it safe for use, is called disinfection. The chemicals or substances, which are added to water for killing the bacteria, etc., are known as disinfectants.* The disinfection of water can be carried out by following methods :

(1) By boiling water for 10-15 minutes, all the disease-producing bacterias are killed and water becomes safe for use.

Note : *This process can kill only the existing germs in water at the time of boiling, but does not provide any protection against future possible contamination. Moreover, this method is very costly and can be used only in individual cases, particularly during the break up of epidemics in the town or city, and it is impossible to employ it in municipal water-works.* ‑
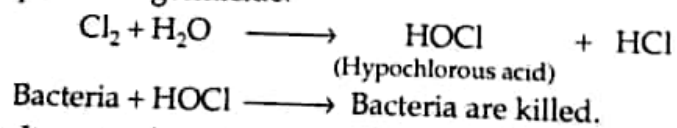
(2) By adding bleaching powder : In small water-works, about 1 kg of bleaching powder per 1,000 kilolitres of water is mixed and water allowed to stand undisturbed for several hours. The chemical action produces *hypochlorous acid* (powerful germicide).

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl \ + \ \underset{\text{Hypochlorous acid}}{HOCl}$$

$$Germs + HOCl \longrightarrow Germs\ are\ killed.$$

The disinfecting action of bleaching powder is due to the chlorine made available by it.

Drawbacks : (1) Bleaching powder introduces calcium in water, thereby making it *more hard.* (2) Bleaching powder *deteriorates*, due to its continuous decomposition during storage. So, whenever it is to be added, it has to be analysed for its effective chlorine content. (3) Only calculated quantity of bleaching powder should be used, since an excess of it gives a *bad taste* and *smell* to treated-water.

(3) By chlorination : Chlorine (either gas or in concentrated solution form) produces *hypochlorous acid*, which is a powerful germicide.

$$Cl_2 + H_2O \longrightarrow \underset{\text{(Hypochlorous acid)}}{HOCl} \ + \ HCl$$

$$Bacteria + HOCl \longrightarrow Bacteria\ are\ killed.$$

Mechanism of action : It was earlier believed that the disinfecting action of chlorine was due to the neascent oxygen liberated, which oxidises harmful bacteria, etc. However, Gleen and Stumpf, after long experimentation, reported that the death of micro-organisms, bacteria, etc., results from *chemical reaction of hypochlorous acid* (HOCl) with the enzymes in the cells of the organisms, etc. Since enzyme is essential for the metabolic processes of the micro-oganisms, so *death of micro-organisms results due to inactiviation of enzyme (in the cells of organisms) by hypochlorous acid,*
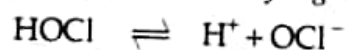
$$HOCl \rightleftharpoons H^+ + OCl^-$$

producing OCl⁻ (hypochlorite ions), which cannot combine with enzymes in the cells of micro-organisms. This explains the fact that chlorine is found to be more effective disinfectant at lower pH values (below 6.5). This is due to the fact that HOCl is about 80 times more destructive to bacterias than OCl⁻ ions.

Liquid chlorine is most effective, when applied to filtered water at such a point where adequate mixing is done. Chlorine is the most widely used disinfectant throughout the world. Apparatus used for this purpose is known as *chlorinator* (see Fig. 11), which is a high tower, having a number of baffle plates. Water and proper quantity of concentrated chlorine solution are introduced at its top. During their passage through the tower, they get thoroughly mixed. The treated-water is taken out from the bottom. For filtered-water, about 0.3 to 0.5 ppm of chlorine is sufficient.

Raw water inlet

Concentrated chlorine solution

Baffle plates

High tower

Sterilized water outlet
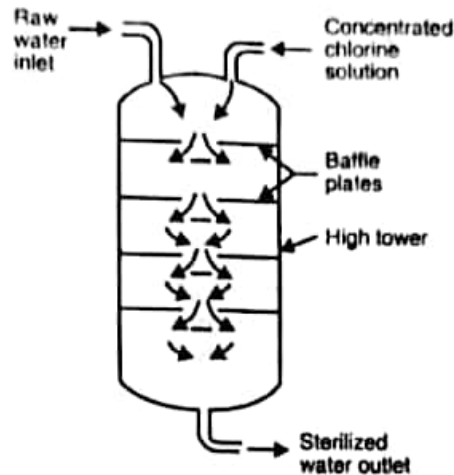
Fig. 11. Chlorinator

Factors affecting efficiency of chlorine : (i) *Time of contact :* It has been experimentally shown that number of micro-organisms destroyed by chlorine per unit time is proportional to the number of micro-organisms remaining alive. Consequently, the death rate is maximum to start with and it goes on decreasing with time. (ii) *Temperature of water :* The rate of reaction with enzymes increases with temperature. Consequently, death rate of micro-organisms by chlorine increases with rise in water temperature. (iii) *pH value of water :* It has been found that at lower pH values (between 5–6.5), a small contact period is required to kill same percentage of organisms.

Advantages of chlorine : (i) It is effective and *economical.* (ii) It requires *very little space* for storage. (iii) It is *stable* and does not deteriorate on keeping. (iv) It can be used at *low as well as high temperatures.* (v) It introduces *no salt* impurities in the treated-water. (vi) It is *most ideal* disinfectant.

Disadvantages : (1) Excess of chlorine, if added, produces a characteristic *unpleasant taste and odour.* Moreover, its excess produces an *irritation* on muscus membrane. The quantity of free chlorine in treated-water should *not* exceed 0.1 to 0.2 ppm. (2) It is more effective below 6.5 pH and less effective at higher pH values.

Break-point chlorination (or *free-residual chlorination*) *involves in addition of sufficient amount of chlorine to oxidise :* (a) *organic matter,* (b) *reducing substances,* and (c) *free ammonia is raw water, leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing (patho-genic) bacterias.*

When the dosage of applied chlorine to water rich in organic compound or ammonia is gradually increased, the results obtained can be depicted graphically in Fig. 12, in which appearance of following *four* stages occurs :

The addition of chlorine at the dip or break, is called "break-point" chlorination. This indicates the point at which free residual chlorine begins to appear. Usually, all tastes, odours (chlorinous and others) disappear at break-point, resulting in appearance of water, free from bad tastes and odours. Moreover, because of the highly persistent and powerful disinfection possessed by available free chlorine, any type of pathogenic organisms present in water are destroyed, thereby making disinfection highly efficient.

Applied chlorine dose ⟶

Advantages of break-point chlorination : (1) It *oxidises completely* organic compounds, ammonia and other reducing compounds. (2) It *removes colour* in water, due to the presence of organic matters. (3) It destroys completely (100%) all the *disease-producing bacteria.* (4) It removes both *odour and taste* from the water. (5) It prevents the *growth of any weeds* in water.

De-chlorination : Over-chlorination after the 'break-point' produces unpleasant taste and odour in water. These objectionable qualities may be removed by filtering the over-chlorinated water through a bed of molecular carbon. Alternatively, a small percentage of *activated carbon* may be added directly to the water and after allowing a short reaction period, it is then removed by filtration. Objectionable qualities resulting from over-chlorination may also be remedied by the addition of a small percentage of *sulphur dioxide* or *sodium sulphite* or sodium thiosulphate, etc.,

$$SO_2 + Cl_2 + 2 H_2O \longrightarrow H_2SO_4 + 2 HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2 HCl$$
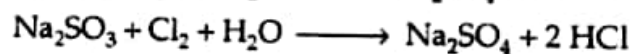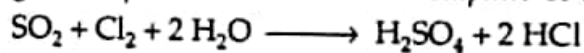
(4) By using chloramine (ClNH$_2$) : When chlorine and ammonia are mixed in the ratio 2 :
1 by volume

The *nascent oxygen* is very powerful oxidising agent and kills all the bacterias as well as oxidises the organic matter present in water

For carrying out the disinfection by ozone, ozone is released/injected into the water and the two are allowed to come in contact in a *sterilizing tank* (see Fig. 13). The disinfected water is removed from the top. The contact period is about 10–15 minutes and the usual dose strength is 2–3 ppm.
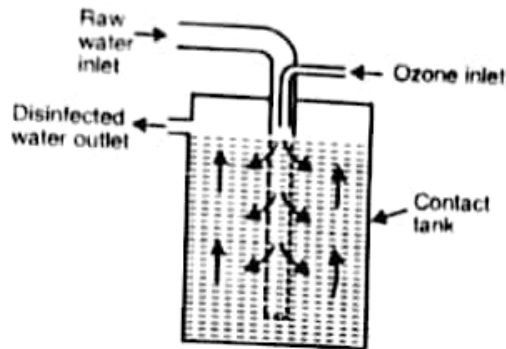

Fig. 13. Ozone sterilizer

Disadvantage : This method is *quite expensive* and hence, not employed for disinfection of municipal water supply.

Advantages . Disinfection by ozone is costlier than chlorine, but it simultaneously removes colour, odour and taste without giving any residue. Its excess is not harmful, since it is unstable and decomposes into oxygen.

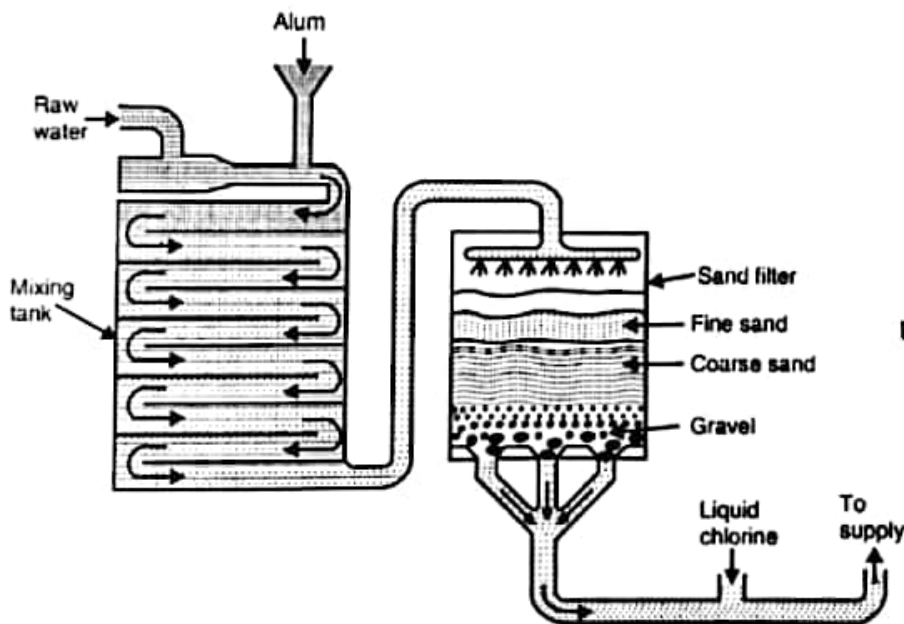Thus, municipal water treatment in short may be illustrated by *flow diagram* shown in Fig. 14.

Fig. 14. Flow diagram of drinking water treatment plant.

13 DESALINATION OF BRACKISH WATER

The process of removing common salt (sodium chloride) from the water, is known as **desalination.** The water containing dissolved salts with a peculiar salty (or brackish) taste, is called brackish water. Sea water, containing on an average about 3.5% salts, comes under this category. Brackish water is *totally unfit* for drinking purpose. Commonly used methods for the desalination of brackish water are .

(1) **Electrodialysis** *is a method in which the ions (of the salts present) are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair (natural or synthetic)* Fig. 15. illustrates the method of desalination by electrodialysis. When direct electric current is passed through saline water, the sodium ions (Na^+) start moving towards negative pole (cathode) ;
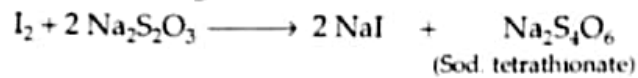
(20)

14 CHEMICAL ANALYSIS OF WATER

(1) Estimation of free chlorine : Free chlorine in water, if present beyond a certain limit, makes the municipal water unfit for drinking purposes, because chlorine gas is *injurious to human metabolism*. The estimation of free chlorine in water is based on the *oxidation of potassium iodide by free chlorine*. Thus, when the water sample is treated with an excess of potassium iodide solution, the free chlorine, present in water, oxidizes potassium iodide and liberates an equivalent amount of *iodine*, which dissolves in excess potassium iodide forming a *deep-violet coloured complex*.

$$Cl_2 + 2\,KI \longrightarrow 2\,KCl + I_2$$

$$KI + I_2 \longrightarrow KI_3$$
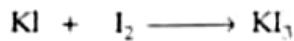
(Violet coloured complex)

The amount of *liberated 'iodine'* can be estimated by titrating the resulting solution against standard sodium thiosulphate solution using starch as final indicator.

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow 2\,NaI + Na_2S_4O_6$$

(Sod. tetrathionate)

$$I_2 + Starch \longrightarrow Deep\text{-}blue\ complex.$$

Procedure : Take about 10 mL of 10% KI solution in a stoppered 250 mL conical flask. Add to it 50 mL of water sample, holding the point of the pipette just above the iodide solution. Put on the stopper and shake the flask vigorously. Remove the stopper and wash the adhering solution into flask, with about 5–10 mL of distilled water. Then, titrate the solution against N/50 sodium thiosulphate solution, using starch as final indicator. The end-point is the change of colour from *deep-blue to just colourless.*

Calculations : Let 50 mL of water sample
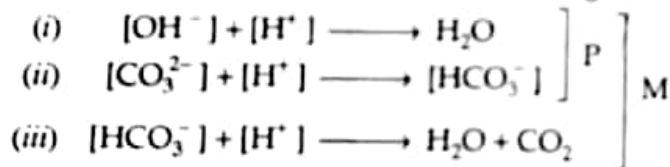
$$\equiv V \text{ mL N/50 } Na_2S_2O_3 \text{ soln.}$$

∴ $50 \times$ Normality of free chlorine $= V \times (N/50)$

∴   Normality of free chlorine $= V/2{,}500$

and   strength of free chlorine $= \dfrac{V \times 35.5}{2{,}500} \text{ g/L} = \dfrac{V \times 35.5 \times 10^6}{2{,}500 \times 1{,}000} \text{ ppm}$

$$= 14.2\ V \text{ ppm.}$$

(2) Alkalinity : The alkalinity of water is attributed to the presence of the : (i) *caustic alkalinity* (due to OH^- and CO_3^{2-} ions), and (ii) *temporary hardness* (due to HCO_3^- ions). These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators. The determination is based on the following reactions :

(i) $[OH^-] + [H^+] \longrightarrow H_2O$

(ii) $[CO_3^{2-}] + [H^+] \longrightarrow [HCO_3^-]$ $\left. \phantom{\begin{matrix}P\\M\end{matrix}} \right\} P$

(iii) $[HCO_3^-] + [H^+] \longrightarrow H_2O + CO_2$ $\left. \phantom{\begin{matrix}P\\M\\M\end{matrix}} \right\} M$

The titration of the water sample against a standard acid upto *phenolphthalein end-point* marks the completion of reactions (i) and (ii) only. This amount of acid used thus corresponds to *hydroxide plus one-half of the normal carbonate present.* On the other hand, titration of the water sample against a standard acid to *methyl orange end-point* marks the completion of reactions (i), (ii) and (iii). Hence, the amount of acid used *after the phenolphthalein end-point* corresponds to one-half of normal carbonate plus all the bicarbonates ; while the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions).

The possible combinations of ions causing alkalinity in water are : (i) OH^- only or (ii) CO_3^{2-} only or (iii) HCO_3^- only or (iv) OH^- and CO_3^{2-} together or (v) CO_3^{2-} and HCO_3^- together. The possibility of OH^- and HCO_3^- ions together is ruled out, because they combine instantaneously to form CO_3^{2-} ions.

$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$$

e.g.,

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O$$
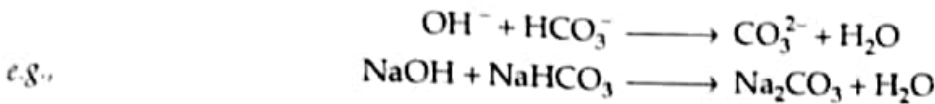
Thus, OH^- and HCO_3^- ions *cannot exist together in water*. On the basis of same reasoning, all the three (OH^-, CO_3^{2-} and HCO_3^-) *cannot exist together*.

Procedure : Pipette out 100 mL of the water sample in a clean titration flask. Add to it 2 to 3 drops of a phenolphthalein indicator. Run in N/50 H_2SO_4 (from a burette), till the *pink colour is just discharged*. Then to the same solution, add 2 or 3 drops of methyl orange. Continue the titration, till the *pink colour reappears*.

Calculations : Let volume of acid used to phenolphthalein end-point = V_1 mL and extra volume of acid used to methyl orange end-point = V_2 mL.

∴ Phenolphthalein alkalinity (in terms of $CaCO_3$ equivalents),

$$P = \frac{V_1 \times 50 \times 1,000,000}{50 \times 100 \times 1000} = 10V_1 \text{ ppm.}$$

and methyl orange alkalinty (in terms of $CaCO_3$ equivalents),

$$M = \frac{(V_1 + V_2) \times 50 \times 1,000,000}{50 \times 100 \times 1000} = 10(V_1 + V_2) \text{ ppm.}$$

(1) *When $P = 0$,* both OH^- and CO_3^{2-} are *absent* and alkalinity in that case is due to HCO_3^- only.

(2) *When $P = \frac{1}{2}M$,* only CO_3^{2-} is present, since half of carbonate neuralization reaction (i.e., $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$) takes place with phenolphthalein indicator; while complete carbonate neutralization reaction (i.e., $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$; $HCO_3^- + H^+ \longrightarrow H_2O + CO_2$) occurs when methyl orange indicator is used. Thus, alkalinity due to $CO_3^{2-} = 2P$.

(3) *When $P = M$, only OH^- is present,* because neither CO_3^{2-} nor HCO_3^- ions are present. Thus, alkalinity due to $OH^- = P = M$.

(4) *When $P > \frac{1}{2}M$.* In this case, besides CO_3^{2-}, OH^- ions are also present. Now half of CO_3^{2-} (i.e., $HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$) equal to $(M-P)$.

So, alkalinity due to complete $CO_3^{2-} = 2(M-P)$

∴ 　　 Alkalinity due to $OH^- = M - 2(M-P) = (2P - M)$.

(5) *When $P < \frac{1}{2}M$.* In this case, besides CO_3^{2-}, HCO_3^- ions are also present.
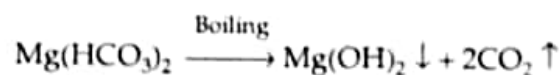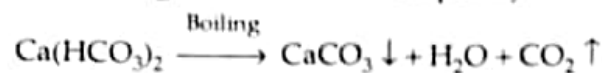
Now alkalinity due to $CO_3^{2-} = 2P$

∴ 　　 Alkalinity due to $HCO_3^- = (M - 2P)$.

Alakinity	OH (ppm)	CO_3^{2} (ppm)	HCO_3 (ppm)
$P = 0$	0	0	M
$P = \frac{1}{2}M$	0	2 P	0
$P < \frac{1}{2}M$	0	2 P	$(M - 2P)$
$P > \frac{1}{2}M$	$(2P - M)$	$2(M - P)$	0
$P = M$	$P = M$	0	0

Note If alkalinity is to be expressed in terms of individual components, then their chemical equivalents should be used instead of 50 (for $CaCO_3$).

(3) **Hardness** : The estimation of water hardness as applied to boiler water and other water is of great interest for the chemical industry in general. Determination of hardness of water can be done by using any of the following methods :

(i) *O. Hehner's method* : (a) *Temporary hardness is determined* by finding the alkalinity of water before boiling and that left after boiling. This is because temporary hardness is removed on boiling.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boiling}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boiling}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

Procedure : Pipette out 50 mL of water sample in a conical flask. Add 2-3 drops of methyl orange indicator. Titrate against N/50 HCl. Note the volume of acid used (say V_1 mL). Now take 100 mL of water sample in a pyrex beaker and evaporate it to dryness. Add about 50 mL of distilled water, warm, stir to dissolve the soluble portions left. Filter the solution and wash the residue with distilled water. Make up the volume to 100 mL in a measuring flask, by adding distilled water Take 50 mL of this filtrate in a conical flask and titrate against N/50 HCl using methyl orange as indicator. Let the volume of acid used be V_2 mL.

∴   Volume of N/50 HCl used by temporary hardness present in 50 mL of water
$$= (V_1 - V_2) \text{ mL}$$

∴   Alkalinity due to temporary hardness in 50 mL of water sample
$$\equiv (V_1 - V_2) \text{ mL of N/50 HCl}$$

∴   Alkanlinity due to *temporary hardness* in terms of $CaCO_3$ eq
$$= \frac{(V_1 - V_2) \times 1 \times 50}{50 \times 50} \text{ g/L}$$

$$= (V_1 - V_2)/50 \text{ g of } CaCO_3 \text{ eq } L^{-1}$$

$$= \frac{(V_1 - V_2) 10^6}{50 \times 10^3} \text{ ppm} = \boxed{20 (V_1 - V_2) \text{ ppm}}$$

(b) *Determination of permanent hardness* is based on the fact that it can be removed by boiling with a known excess of standard sodium carbonate. The chloride and sulphates of calcium and

(23)

magnesium form insoluble carbonates. The residual sodium carbonate is then determined by titrating against a standard acid. The reduction in the amount of soda added is equivalent to permanent hardness.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2\,NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 \downarrow + Na_2SO_4$$
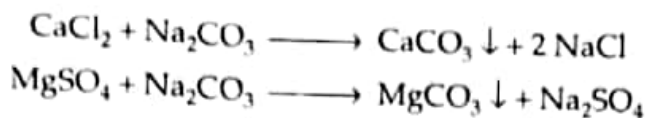
Procedure : Take 50 mL of given water sample in a beaker. Add it to 50 mL of N/50 Na_2CO_3 solution. *Boil* for 15 minutes. Cool the solution. Filter the precipitate, collecting the filtrate in a conical flask. Wash the precipitate on filter paper with distilled water, collecting all the washings in the conical flask. Then, titrate the unused Na_2CO_3 present in the flask against N/50 HCl using methyl orange as indicator. Let the litre value be V mL.

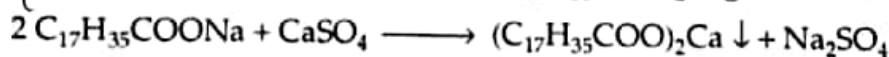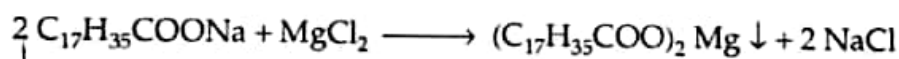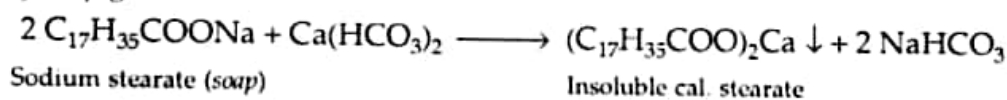∴ Volume of N/50 Na_2CO_3 used for removing permanent hardness in
  50 mL water sample $\qquad = (50 - V)$ mL

∴ Strength of permanent hardness in terms of $CaCO_3$ eq

$$= \frac{(50 - V) \times 50}{50 \times 50} \text{ g of } CaCO_3 \text{ eq} = \frac{(50 - V)}{50} \text{ g of } CaCO_3 \text{ eq}$$

∴ Permanent hardness $= \dfrac{(50 - V) \times 10^6}{50 \times 10^3}$ ppm $= \boxed{20\,(50 - V) \text{ ppm}}$

(ii) *Soap titration method* is based on the fact that *when soluble soap (sodium or potassium salt of higher fatty acid) is added to hard water, it does not give lather, until a sufficient quantity has been added to precipitate all the hardness-producing metal ions. When all hardness-causing ions have been precipitated, further addition of soap gives lather.*

$$2\,C_{17}H_{35}COONa + Ca(HCO_3)_2 \longrightarrow (C_{17}H_{35}COO)_2Ca \downarrow + 2\,NaHCO_3$$
Sodium stearate (*soap*) $\qquad\qquad\qquad\qquad$ Insoluble cal. stearate

$$2\,C_{17}H_{35}COONa + MgCl_2 \longrightarrow (C_{17}H_{35}COO)_2\,Mg \downarrow + 2\,NaCl$$

$$2\,C_{17}H_{35}COONa + CaSO_4 \longrightarrow (C_{17}H_{35}COO)_2Ca \downarrow + Na_2SO_4$$

Procedure : 1. *Preparation of standard hard water :* Dissolve 1.0 g of pure, dry $CaCO_3$ is minimum quantity of dilute HCl. Boil to dryness to expel excess of acid and CO_2. Dissolve the residue in distilled water to make 1 L solution. The hardness of this solution is 1 g/L or 1,000 ppm or 1 mg/mL.

2. *Preparation of soap solution :* Dissolve 100 g of pure dry castile soap in 800 mL of alcohol plus 200 mL of distilled water.

3. *Standardization of soap solution :* Rinse and fill the burette with soap solution. Take 50 mL of standard hard water in a narrow mouth 250 mL glass-stoppered bottle. Add to it soap solution drop by drop, shake the bottle and allow it to stand for some time. See, if a lather is formed or not. Note the time for which lather (if any) persists. Continue titration, till lather formed after vigorous shaking, lasts for *two minutes*. Let the volume of soap solution used be V_1 mL.

4. *Lather factor* of distilled water :* Titrate 50 mL of distilled water against soap solution, till lather persists for two minutes. Let the volume used be V mL. *This volume is to be subtracted from all titre values.*

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* *Lather factor is the amount of standard soap solution required to produce lather which lasts for two minutes, when added to distilled water (of **zero** hardness).*

5. *Total hardness* Repeat above titration, taking 50 mL of water sample. Let the titre value of soap solution be V_2 mL.

6. *Permanent hardness* : Take 250 mL of the water sample in a large beaker. Boil it, till volume is reduced to about 50 mL [when all bicarbonates are decomposed to insoluble $CaCO_3 + Mg(OH)_2$]. Filter, wash the residue with distilled water, collecting filtrate and washings in 250 mL measuring flask. Finally, make up the volume of the filtrate to 250 mL by adding distilled water. Then, titrate 50 mL of the filtrate against soap solution. Let the titre value of solution be V_3 mL.

Calculations : 50 mL of standard hard water

$$\equiv (V_1 - V) \text{ mL of soap soln.}$$

or $\quad\quad\quad 50 \times 1$ mg of $CaCO_3 \quad\quad \equiv (V_1 - V)$ mL of soap soln.

$\therefore \quad\quad\quad$ 1 mL of soap soln. $\quad\quad = \dfrac{50}{(V_1 - V)}$ mg of $CaCO_3$ eq

Also $\quad$ 50 mL of hard water $\quad \equiv (V_2 - V)$ mL of soap soln.

$$= \dfrac{(V_2 - V)}{(V_1 - V)} \text{ mg of } CaCO_3 \text{ eq}$$

$\therefore \quad$ 1 L (1,000 mL) of hard water $\quad = \dfrac{(V_2 - V) \times 1,000}{(V_1 - V)}$ mg of $CaCO_3$ eq

$\therefore \quad$ *Total* hardness of water $\quad\quad = \dfrac{(V_2 - V) \times 1,000}{(V_1 - V)}$ mg/L

$$= \boxed{\dfrac{1,000\,(V_2 - V)}{(V_1 - V)} \text{ ppm}}$$

Also $\quad$ 50 mL of boiled water $\quad\quad = (V_3 - V)$ mL of soap soln.

$$= \dfrac{(V_3 - V) \times 50}{(V_1 - V)} \text{ mg of } CaCO_3 \text{ eq}$$

$\therefore \quad$ 1 L (1,000 mL) of boiled water $\quad = \dfrac{(V_3 - V) \times 1,000}{(V_1 - V)}$ mg of $CaCO_3$ eq

$\therefore \quad$ *Permanent* hardness $\quad\quad = \dfrac{(V_3 - V) \times 1,000}{(V_1 - V)}$ (mg/L) $CaCO_3$ eq

$$= \boxed{\dfrac{1,000\,(V_3 - V)}{(V_1 - V)} - \text{ ppm}} \quad\quad\quad\quad ...(i)$$

Hence, temporary hardness $\quad$ = [Total – Permanent] hardness

$$= \dfrac{1,000}{(V_1 - V)} [(V_2 - V) - (V_3 - V)] \text{ ppm.}$$

or $\quad$ *temporary* hardness $\quad\quad = \boxed{\dfrac{[1,000\,(V_2 - V_3)]}{(V_1 - V)} \text{ ppm}} \quad\quad\quad ...(ii)$

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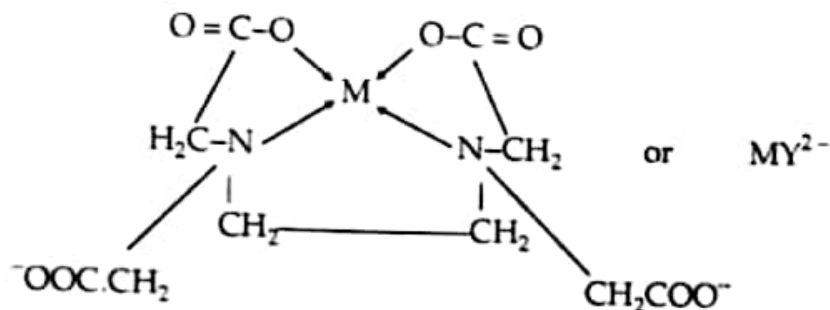(iii) *EDTA method* : This is a *complexometric method*. Ethylene diamine tetraacetic acid (EDTA),

$$\begin{array}{c} HO.OC.CH_2 \\ HO.OC.CH_2 \end{array} \!\!\! > N-CH_2-CH_2-N < \!\!\! \begin{array}{c} CH_2.CO.OH \\ CH_2.CO.OH \end{array}$$
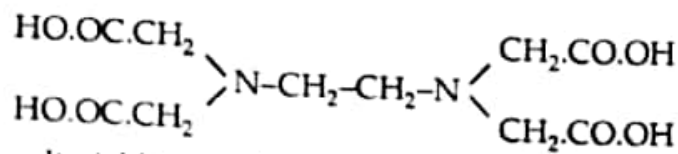
in the form of its sodium salt yields the *anion* :

$$\begin{array}{c} {}^-O.OC.CH_2 \\ {}^-O.OC.CH_2 \end{array} \!\!\! > N.CH_2.CH_2.N < \!\!\! \begin{array}{c} CH_2.CO.O^- \\ CH_2.CO.O^- \end{array}$$
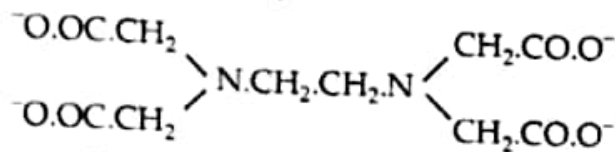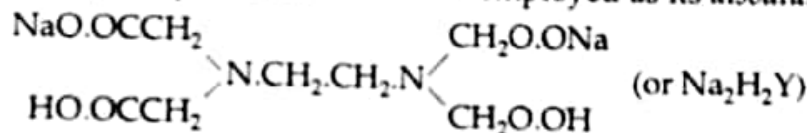
which *forms complex ions* with Ca^{2+} and Mg^{2+}.

Thus :

where M = Ca or Mg. It may be pointed the EDTA is employed as its *disodium salt*,

$$\begin{array}{c} NaO.OCCH_2 \\ HO.OCCH_2 \end{array} \!\!\! > N.CH_2.CH_2.N < \!\!\! \begin{array}{c} CH_2O.ONa \\ CH_2O.OH \end{array} \quad (or\ Na_2H_2Y)$$
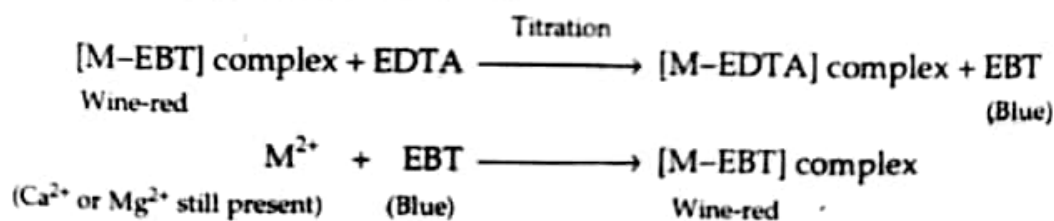
(Mol. wt. = 372.24 ,   Eq. wt. = 186.14), *i.e.*, M soln. = 2 N soln.)

In order to determine the *equivalence point* (*i.e.*, just completion of metal-EDTA complex formation), indicator **eriochrome black-T** or **EBT** (an alcoholic solution of blue dye) is employed, which form *unstable wine-red complex* with Cu^{2+} and Mg^{2+} ions. However, this indicator is effective at a *pH of about 10*. When EBT is added to hard water buffered to a pH of about 10 (by employing NH_4OH–NH_4Cl buffer), a *wine-red* unstable complex is formed. Thus :

$$\underset{\text{(Ca}^{2+}\text{ or Mg}^{2+}\text{ of hard water)}}{M^{2+}} + EBT \xrightarrow{pH = 10} \underset{\text{Wine-red}}{[M-EBT]\ complex}$$
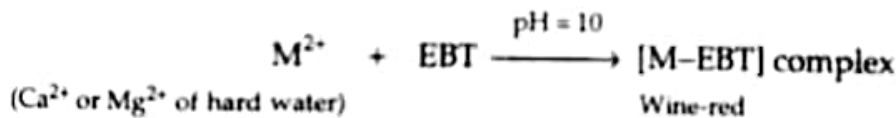
So initially a wine-red coloured is obtained. During the course of titration against EDTA solution, EDTA combines with M^{2+} (or Ca^{2+} or Mg^{2+}) ions from *stable complex*, M-EDTA and releasing free EBT, which instantaneously combines with M^{2+} ions still present in the solution, thereby wine-red colour is retained. Thus :

$$\underset{\text{Wine-red}}{[M-EBT]\ complex} + EDTA \xrightarrow{Titration} [M-EDTA]\ complex + \underset{\text{(Blue)}}{EBT}$$

$$\underset{\text{(Ca}^{2+}\text{ or Mg}^{2+}\text{ still present)}}{M^{2+}} + \underset{\text{(Blue)}}{EBT} \longrightarrow \underset{\text{Wine-red}}{[M-EBT]\ complex}$$

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However, when nearly all M^{2+} (Ca^{2+} or Mg^{2+}) ions have formed [M-EDTA] complex, then next drop of EDTA added displaces the EBT indicator form [M-EBT] complex and the wine-red colour changes to *blue colour* (due to EBT). Thus, at equivalence point,

[M–EBT] complex + EDTA $\longrightarrow$ [M–EDTA] complex + EBT (blue)
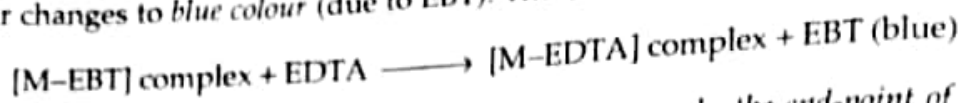
Thus, *change of wine-red colour to distinct blue marks the end-point of titration.* Various steps involved in this method are :

1. *Preparation of standard hard water* : Dissolve 1.0 of pure, dry $CaCO_3$ in minimum quantity of dilute HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 L solution. Each mL of this solution thus contains 1 mg of $CaCO_3$ eq hardness.

2. *Preparation of EDTA solution* : Dissolve 4 g of pure EDTA crystals + 0.1 g $MgCl_2$ in 1 L of distilled water.

3. *Preparation of indicator* : Dissolve 0.5 g of Eriochrome black-T in 100 mL of alcohol.

4. *Preparation of buffer solution* : Add 67.5 g of NH_4Cl to 570 mL of concentrated ammonia solution and then dilute with distilled water to 1 L.

5. *Standardization of EDTA solution* : Rinse and fill the burette with EDTA solution. Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops indicator. Titrate with EDTA solution, till wine-red colour changes to clear blue. Let volume used by V_1 mL.

6. *Titration of unknown hard water* : Titrate 50 mL of water sample just in step (5). Let volume used be V_2 mL.

7. *Titration of permanent hardness* : Take 250 mL of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 mL [when all the bicarbonates are decomposed to insoluble $CaCO_3 + Mg(OH)_2$]. Filter, wash the precipitate with distilled water, collecting filtrate and wash-ings in a 250 mL measuring flask. Finally make up the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in step (5). Let volume used by V_3 mL.

Calculations : 50 mL of standard hard water

 = V_1 mL of EDTA

$\therefore\quad$ 50 × 1 mg of $CaCO_3\quad$ = V_1 mL of EDTA

$\therefore\quad$ 1 mL of EDTA = $50/V_1$ mg of $CaCO_3$ eq

Now 50 mL of given hard water $\quad$ = V_2 mL of EDTA

 = $\dfrac{V_2 \times 50}{V_1}$ mg of $CaCO_3$ eq

$\therefore\quad$ 1 L (1,000 mL) of given hard water

 = 1,000 V_2/V_1 mg of $CaCO_3$ eq

$\therefore\quad$ *Total* hardness of water = 1,000 V_2/V_1 mg/L

 = $\boxed{1,000\ V_2/V_1\ \text{ppm}}$

 ...(i)

Now 50 mL of boiled water $= V_3$ mL of EDTA

$$= \frac{V_3 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq}$$

$\therefore$ 1,000 mL (= 1 L) of boiled water $= 1,000\, V_3/V_1$ mg of $CaCO_3$ eq

$\therefore$ *Permanent* hardness $= 1,000\, V_3/V_1$ ppm   ...(ii)

and   *temporary* hardness $=$ [Total – Permanent] hardness

$$= 1,000 \left[\frac{V_2}{V_1} - \frac{V_3}{V_1} \right] \text{ppm}.$$

$$= \boxed{\frac{1,000\,(V_2 - V_3)}{V_1} \text{ ppm}}$$ ...(iii)

Advantages of EDTA method : This method is definitely preferable to the other methods, because of the : (i) greater accuracy ; (ii) convenience, and, (iii) more rapid procedure.

(4) Dissolved oxygen determination is based on the *oxidation of potassium iodide by dissolved oxygen.* The liberated iodine is titrated against a standard sodium thiosulphate solution using starch as final indicator. However, dissolved molecular oxygen in water is *not* capable of reacting with KI, so an *oxygen-carrier* (such as manganese hydroxide) is used to bring about the reaction between KI and oxygen. Manganese hydroxide is produce by the action of potassium hydroxide and manganous sulphate.

$$2\,KOH + MnSO_4 \longrightarrow Mn(OH)_2 + K_2SO_4$$

$$2\,Mn(OH)_2 + O_2 \longrightarrow 2\,MnO(OH)_2$$

(Oxygen⁻ carrier)   Basic manganic oxide

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2\,H_2O + [O]$$

[Nascent oxygen]

$$2\,KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + H_2O + I_2$$

$$2\,Na_2S_2O_3 + I_2 \longrightarrow 2\,NaI + Na_2S_4O_6$$

$$\text{Starch} + I_2 \longrightarrow \text{Starch-iodine (blue)}.$$
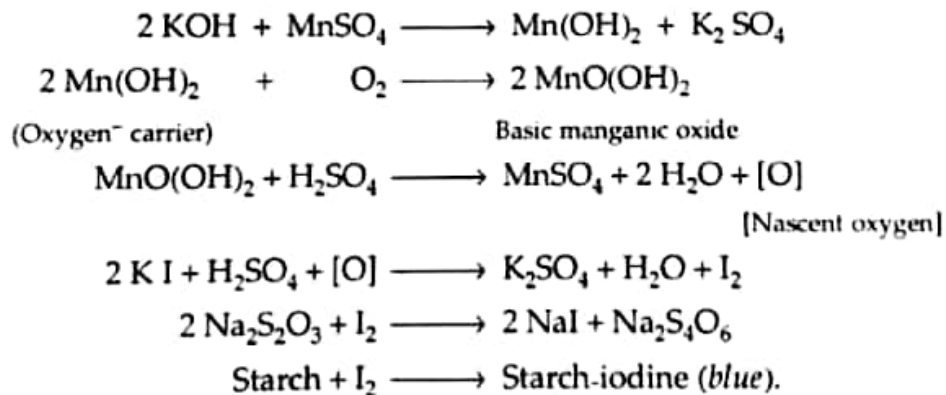
Sometimes, water (like rain water) contains substances like nitrites, sulphites, etc. and determination of dissolved oxygen in their presence will give *wrong* results, since these ions also liberate iodine from KI. Therefore, *sodium azide* (NaN$_3$) is used in alkaline iodide solution to take care that any nitrite, if present in water, *does not liberate iodine* from K I. Sodium azide reacts with nitrite to decompose it as follows :

$$2\,NaN_3 + H_2SO_4 \longrightarrow 2\,HN_3 + Na_2SO_4$$

$$HNO_2 + HN_3 \longrightarrow N_2O \uparrow + N_2 \uparrow + H_2O$$
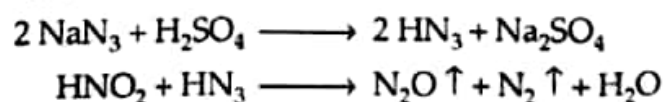
Procedure : Collect 250 mL of water in a bottle *avoiding as for as possible contact with air.* Immediately add 2 mL of manganous sulphate solution (prepared by dissolving 400 g MnSO$_4$ per L) by means of pipette, dipping the end well-below the water surface. Add 2.0 mL of alkaline iodide solution (prepared by dissolving 150 g K I + 500 g NaOH and 20 g sodium azide, NaN$_3$ per L) in the similar manner. Stopper the bottle and shake it thoroughly. Allow the precipitate to settle

∴ Temporary hardness, due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$

$$= (5 + 10) \text{ mg/L} = 15 \text{ mg/L} \quad \text{or} \quad \textbf{15 ppm}.$$

Permanent hardness, due to $MgCl_2$ and $CaSO_4$

$$= (10 + 10) \text{ mg/L} = 20 \text{ mg/L} \quad \text{or} \quad \textbf{20 ppm}.$$

Example 4. *Calculate the temporary and total hardness of a sample of water containing* $Mg(HCO_3)_2 = 73$ *mg/L ;* $Ca(HCO_3)_2 = 162$ *mg/L,* $MgCl_2 = 95$ *mg/L,* $CaSO_4 = 136$ *mg/L.* (Anna, May 04)

Solution. *Calculation of* $CaCO_3$ *equivalents :*

Constituent	Multiplication factor	CaCO₃ equivalent
$Mg(HCO_3)_2 = 73$ mg/L	100/146	$73 \times 100/146 = 50$ mg/L
$Ca(HCO_3)_2 = 162$ mg/L	100/162	$162 \times 100/162 = 100$ mg/L
$MgCl_2 \quad = 95$ mg/L	100/95	$95 \times 100/95 = 100$ mg/L
$CaSO_4 \quad = 136$ mg/L	100/136	$136 \times 100/136 = 100$ mg/L

Constituent	Multiplication factor	CaCO₃ equivalent
$Ca(HCO_3)_2$ = 8.1 mg/L	100/162	$8.1 \times 100/162$ = 5.0 mg/L
$Mg(HCO_3)_2$ = 7.5 mg/L	100/146	$7.5 \times 100/146$ = 5.14 mg/L
$CaSO_4$ = 13.6 mg/L	100/136	$13.6 \times 100/136$ = 5.0 mg/L
$MgSO_4$ = 12.0 mg/L	100/120	$12.0 \times 100/120$ = 10.0 mg/L
$MgCl_2$ = 2.0 mg/L	100/95	$2.0 \times 100/95$ = 2.11 mg/L

Lime requirement for 50,000 L water

$$= 74/100 \ [Ca(HCO_3)_2 + 2 \ Mg(HCO_3)_2 + MgSO_4 + MgCl_2 \ as \ CaCO_3 \ eq] \times Vol. \ of \ water$$

$$= 74/100 \ [5.0 + 2 \times 5.14 + 10.0 + 2.11] \ mg/L \times 50,000 \ L$$

$$= 74/100 \ [27.39 \ mg/L] \times 50,000 \ L = 10,13,430 \ mg$$

$$= 10,13,430 \ mg \times 10^{-6} \ kg/mg = \textbf{1.0134 kg.}$$

Soda requirement for 50,000 L water

$$= 106/100 \ [CaSO_4 + MgSO_4 + MgCl_2 \ as \ CaCO_3 \ eq] \times Vol. \ of \ water$$

$$= 106/100 \ [5.0 + 10.0 + 2.11] \ mg/L \times 50,000 \ L$$

$$= 106/100 \ [17.11 \ mg/L] \times 50,000 \ L = 9,06,830 \ mg$$

$$= 9,06,830 \ mg \times 10^{-6} \ kg/mg = \textbf{0.9068 kg.}$$

Example 7. *A water sample contains the following impurities :* $Ca^{2+} = 20 \ ppm$, $Mg^{2+} = 18 \ ppm$, $HCO_3^- = 183 \ ppm \ and \ SO_4^{2-} = 24 \ ppm$. *Calculate the amount of lime and soda needed for softening.* (Ku, June 04)

Solution. *Conversion into* $CaCO_3$ *equivalents :*

Lime requirement = 74/100 [HCl + Al$_2$(SO$_4$)$_3$ + MgCl$_2$ as CaCO$_3$ eq.] × Vol. of water × (100/% purity)

= 74/100 [10 + 30 + 10] mg/L × 10^5 L × (100/90) = 4.111 × 10^6 mg = 4.111 kg

∴　Lime required (using 10% excess) = 4.111 kg × (110/100) = **4.522 kg.**

Soda requirement = 106/100 [HCl + Al$_2$(SO$_4$)$_3$ + MgCl$_2$ as CaCO$_3$)] × Vol. of water × (100/% purity)

= 106/100 [10 + 30 + 10] mg/L × 10^5 L × (100/98) = 5.488 × 10^6 mg = 5.408 kg.

∴　Soda required (using 10% excess) = 5.408 × (110/100) = **5.949 kg.**

Example 9. *A water sample on analysis gave the following data :*

Ca^{2+} = 30 mg/L ; M$_g^{2+}$ = 24 mg/L ; CO$_2$ = 24 mg/L ; HCl = 50 mg/L ; K$^+$ = 10 mg/L.

Calculate the quantities of lime (90% pure) and soda (94% pure) required to soften one million litres of water sample.　　　　　　　　　　　　　　　　　　　　　　　　　　　　(Amravati, Dec. 2K)

Solution. Conversion in CaCO$_3$ equivalents :

Constituent	Multiplication factor	CaCO$_3$ equivalent
Ca^{2+} = 30 mg/L	100/40	30 × 100/40 = 75.0 mg/L
Mg^{2+} = 24 mg/L	100/24	24 × 100/24 = 100.0 mg/L
CO$_2$ = 24 mg/L	100/44	24 × 100/44 = 54.5 mg/L
HCl = 50 mg/L	100/73	50 × 100/73 = 68.5 mg/L.

Solution. Conversion into $CaCO_3$ equivalents :   (31)

Constituents	Multipliation factor	$CaCO_3$ equivalent
$Ca^{2+} = 30$ mg/L	100/40	$30 \times 100/40 = 75$ mg/L
$Mg^{2+} = 18$ mg/L	100/24	$18 \times 100/24 = 75$ mg/L
$CO_2 = 11$ mg/L	100/44	$11 \times 100/44 = 25$ mg/L
$HCO_3^- = 122$ mg/L	100/122	$122 \times 100/122 = 100$ mg/L

(i) Total hardness = $(75 + 75)$ mg/L = 150 mg/L or **150 ppm**.

Alkalinity present= $(HCO_3^- - CO_2) = (100 - 25)$ mg/L = **75 mg/L or 75 ppm**.

(ii) Lime requirement = 74/100 $[Mg^{2+} + CO_2 + HCO_3^-$ as $CaCO_3$ eq.]

= 74/100 $[75 + 25 + 100]$ mg/L = **148 mg/L**

Soda requirement = 106/100 $[Ca^{2+} + Mg^{2+} - HCO_3^-$ as $CaCO_3$ eq]

= 106/100 $[75 + 75 - 100]$ mg/L = **53 mg/L**.

Example 11. *100 mL of water sample has a hardness equivalent to 12.5 mL of 0.08 N MgSO4. What is its hardness in ppm ?*   (Madras, Oct. 97)

Solution. 100 mL of water sample = 12.5 mL of 0.08 N $MgSO_4$

= 12.5×0.08 mL of 1 N $MgSO_4$

= 1 mL of 1 N $MgSO_4$ = 1 mL of 1 N $CaCO_3$ eq

= 0.001 L of 1 N $CaCO_3$ eq

∴ = 0.001×50 g $CaCO_3$ eq = 0.05 g $CaCO_3$ eq (or 50 mg $CaCO_3$)

∴ 1,000 mL (or/L) of water sample = $\dfrac{50 \text{ mg } CaCO_3 \text{ eq} \times 1{,}000 \text{ mL}}{100 \text{ mL}}$ = 500 mg $CaCO_3$ eq

Hence, the hardness of water sample is 500 mg CaCO3 eq per litre or 500 ppm.

Example 12. *Calculate the quantities of lime and soda needed for softening 2,000 litres of hard water which analysed as follows :*

Analysis of raw water : $Ca^{2+} = 160$ ppm, $Mg^{2+} = 72$ ppm ; $HCO_3^- = 732$ ppm, dissolved $CO_2 = 44$ ppm, HCl = 7.3 ppm.

Analysis of treated water : $CO_3^{2-} = 30$ ppm ; $OH^- = 17$ ppm   (Raj., May 2K)

Solution. *Conversion in $CaCO_3$ equivalents :*

...water, using $NaAlO_2$ as a coagulant at the rate of ... ...g ...hrough a zeolite softener, how much NaCl will be required for its regeneration ?

Solution. (i) *Conversion into* $CaCO_3$ *equivalents* :

Constituents	Multiplication factor
Raw water :	
$Ca^{2+} = 300$ ppm	100/40
$Mg^{2+} = 150$ ppm	100/24
$HCO_3^- = 244$ ppm	100/122
$CO_2 = 60$ ppm	100/44
$NaAlO_2 = 41$ mg/L	100/164
Treated water :	
$OH^- = 65$ ppm	100/34
$CO_3^{2-} = 40$ ppm	100/60

$\therefore$ 1,000 mL of water

$= (15/50) \times 10$ mL of N–$Na_2CO_3 = 3$ mL of N–Na_2CO_3

$= \dfrac{3 \times 50}{1,000}$ g of $CaCO_3$ eq $= 0.150$ g of $CaCO_3$ eq

$\therefore$ Hardness of water $= 0.150$ g/L or 150 mg/L or **150 ppm.**

Since sodium carbonate removes permanent hardness causing ions, so the above result represents permanent hardness of water.

Example 16. *50 mL of a sample water consumed 15 mL of 0.01 M-EDTA before boiling and 5 mL of the same EDTA after boiling. Calculate the degree of total hardness, permanent hardness and temperature hardness.*

(Anna, Nov. 2K)

Solution. 50 mL of water sample $\equiv$ 15 mL of 0.01 M–EDTA

$= \dfrac{15 \times 1000}{50}$ mL of 0.01 M–EDTA $= 300$ mL of 0.01 M–EDTA

$= 2 \times 300$ mL of 0.01 N–EDTA

($\because$ Molarity of EDTA $= 2 \times$ Normality of EDTA)

$\equiv 600$ mL (or 0.6 L) of 0.01 eq $CaCO_3$

$\equiv 0.6 \times 0.01 \times 50$ g $CaCO_3$ eq

Hence, total hardness $= 0.30$ g or 300 mg of $CaCO_3$ eq

$= 300$ mg/L or **300 ppm.**

Now 50 mL of boiled water $\equiv 5$ mL of 0.01 M–EDTA

$\therefore$ 1,000 mL of boiled water $= \dfrac{5 \times 1,000}{50}$ mL of 0.01 M–EDTA

$= 100$ mL of 0.01 M–EDTA

$= 200$ mL (or 0.2 L) of 0.01 N–EDTA

$= 0.2 \times 0.01 \times 50$ g of $CaCO_3$ eq

$= 0.1$ g or 100 mg of $CaCO_3$ eq

Hence, permanent hardness $= 100$ mg/L or ppm

$\therefore$ Temporary hardness $= (300 - 100)$ ppm $= 200$ **ppm.**

Example 17. *0.5 g of CaCO₃ was dissolved in HCl and the solution made upto 500 mL with distilled water. 50 mL of the solution required 48 mL of EDTA solution for titration. 50 mL of hard water sample required 15 mL of EDTA and after boiling and filtering required 10 mL of EDTA solution. Calculate the hardness.*

(Anna, May 04)

Solution. 500 mL of SHW $\equiv 0.5$ g or 500 mg $CaCO_3$ eq

$\therefore$ 1 mL SHW $\equiv 1$ mg $CaCO_3$

Now 48 mL of EDTA soln. $= 50$ mL SHW $\equiv 50$ mg $CaCO_3$ eq

$\therefore$ 1 mL of EDTA soln. $\equiv 50/48$ mg $CaCO_3$ eq.

(i) *Calculation of the total hardness of water :*

50 mL hard water $\equiv 15$ mL EDTA $\equiv 15 \times (50/48)$ mg $CaCO_3$ eq

$= 15.625$ mg $CaCO_3$ eq.

$\therefore$ 1,000 mL of hard water $\equiv \dfrac{15.625 \times 1,000}{50}$ mg $CaCO_3$ eq.

$= 312.5$ mg/L $CaCO_3$ eq.

Hence,   total hardness $= 312.5$ mg/L or 312.5 ppm

(ii) *Calculation of non-carbonate hardness*

50 mL boiled hard water $\equiv$ 10 mL EDTA soln.

$$\equiv 10 \times (50/48) \text{ mg } CaCO_3 \text{ eq.}$$
$$= 10.417 \text{ mg } CaCO_3 \text{ eq.}$$

$\therefore$ 1,000 mL boiled hard water $= \dfrac{10.417 \times 1000}{50}$ mg $CaCO_3$ eq.

$$= 208.3 \text{ mg } CaCO_3 \text{ eq.}$$

$\therefore$ Non-carbonate hardness = 208.3 mg/L or **208.3 ppm**

Hence, carbonate hardness = (312.5 – 208.3) = **104.2 ppm.**

Example 18. *The hardness of 50,000 litres of a sample was removed by passing it through a zeolite softener The softener then required 200 litres of NaCl solution, containing 125 g/litre of NaCl for regeneration. Calculate the hardness of the sample of water.*

<div align="right">(UPT, Dec. 03)</div>

Solution. 200 L of NaCl solution

$$\equiv 200 \text{ L} \times 125 \text{ g/L} = 25,000 \text{ g NaCl} = (25,000 \times 50)/585 \text{ g } CaCO_3 \text{ eq.}$$
$$= 21,368 \text{ g } CaCO_3 \text{ eq.}$$

$\therefore$ Hardness of 50,000 L water $\equiv$ 21,368 g $CaCO_3$ eq.

or hardness of 1 L water $\equiv \dfrac{21,368}{50,000} = 0.4274$ g $CaCO_3$ eq.

$$= 427.4 \text{ mg } CaCO_3 \text{ eq.}$$

Hence, hardness of water   = **427.4 mg/L (or ppm).**

Example 19. *50 mL of water sample during each time of titration against soap solution gave the following results :*

(i) *Lather factor = 0.5 mL.*   (ii) *Total hardness volume = 15.5 mL.*

(iii) *Permanent hardness volume = 12.5 mL.*   (iv) *Standard hard water volume = 40.5 mL,*

Standard hard water is prepared by dissolving 0, 2 g of CaCO₃ per litre. Calculate total, temporary and permanent hardness of water sample in ppm.

<div align="right">(Amravati, Dec. 2K)</div>

Solution. 1 L of SHW   = 200 mg $CaCO_3$ eq

$\therefore$ 50 mL of SHW = 200 × (50/1,000) mg $CaCO_3$ eq

$$= 20 \text{ mg } CaCO_3 \text{ eq.}$$

Now 50 mL SHW $\equiv$ 20 mg$CaCO_3$ eq $\equiv$ 40.5 – 0.5 = 40 mL soap soln.

$\therefore$ 40 mL soap solution $\equiv$ 20 mg $CaCO_3$ eq.

or 1 mL soap solution $\equiv$ 20/40 or 0.5 mg $CaCO_3$ eq.

(i) Calculation of total hardness of water :

50 mL HW $\equiv$ 15.5 – 0.5 or 15 mL of soap soln.

$$\equiv 15 \times 0.5 \text{ mg } CaCO_3 \text{ eq} = 7.5 \text{ mg } CaCO_3 \text{ eq.}$$

$\therefore$ 1 L HW $\equiv$ 7.5 × 1,000/50 or 150 mg $CaCO_3$ eq.

Hence, total hardness = 150 mg/L or **150 ppm**

(ii) Calculation of permanent hardness of water :

50 mL BHW   = (12.5 – 0.5) or 12 mL soap soln.

$$\equiv 12 \times 0.5 \text{ or } 6 \text{ mg } CaCO_3 \text{ eq}$$

$\therefore$ 1 L BHW   = 6 × 1,000/6020 mg $CaCO_3$ eq

$\therefore$ Permanent hardness   = **120 mg/L or 120 ppm.**

Hence, temporary hardness   = (150 – 120) = **30 ppm.**

(35)

Example 20. *100 mL of water sample on titration with N/50 HCl requires 8.0 mL of the acid to phenolphthalein end-point and 9.0 mL of the acid to methyl orange end point. Calculate the type and extent of alkalinity present in the water sample* (RGT, June 04)

Solution. 100 mL of water upto phenolphthalein end-point $\equiv$ 8.0 mL of N/50 HCl

$$100 \text{ mL} \times N_P = 8.0 \text{ mL} \times (N/50)$$

or   normality, $N_P = \dfrac{8.0 \text{ mL}}{100 \text{ mL}} \times \dfrac{N}{50} = 0.0016 \text{ N}$

Strength of alkalinity upto phenolphthalein end-point as $CaCO_3$ eq,

$$P = 0.0016 \times (50 \text{ g/L}) = 0.08 \text{ g/L} = 80 \text{ mg/L} = 80 \text{ ppm}$$

Now 100 mL of water upto methyl orange end-point

$$\equiv 9.0 \text{ mL of N/50 HCl}$$

$$100 \text{ mL} \times N_M = 9.0 \text{ mL} \times (N/50)$$

or   normality, $N_M = \dfrac{9.0 \text{ mL}}{100 \text{ mL}} \times \dfrac{N}{50} = 0.0018 \text{ N}$

Strength of alkalinity upto methyl orange end-point as $CaCO_3$ eq,

$$M = 0.0018 \times (50 \text{ g/L}) = 0.09 \text{ g/L} = 90 \text{ mg/L} = 90 \text{ ppm}$$

$\therefore$ Now $P\ (= 80 \text{ ppm}) > \dfrac{1}{2}M \left(= \dfrac{1}{2} \times 90 \text{ ppm} \right)$

so the *alkalinity is due to* OH^- *and* CO_3^{2-}.

Now alkalinity due to CO_3^{2-} ions = 2 (M – P) = 2 (80 – 80) ppm = **20 ppm.**

and   alkalinity due to OH^- ions   = (2P – M) = (2 × 80 – 90) ppm = **70 ppm.**

Example 21. *100 mL water sample required 4 mL of N/50 H_2SO_4 for neutralization to phenolphthalein end-point. Another 16 mL of the same acid was needed for further titration to methyl orange end-point. Determine the type and amount of alkalinity.* (Ku, Jan. 04)

Solution. 100 mL of water upto phenolphthalein end-point

$$\equiv 4 \text{ mL of N/50 } H_2SO_4$$

$\therefore$ $100 \text{ mL} \times N_P = 4 \text{ mL} \times (N/50)$

or   normality, $N_P = \dfrac{4 \text{ mL} \times N}{100 \text{ mL} \times 50} = 0.0008 \text{ N}$

$\therefore$ Strength of alkalinity upto phenolphthalein end-point at $CaCO_3$ eq,

$$P = 0.0008 \times (50 \text{ g/L}) = 0.04 \text{ g/L} = 40 \text{ mg/L} = 40 \text{ ppm}$$

Now 100 mL of water upto methyl orange end-point,

$$\equiv (4 + 16) \text{ mL of N/50 } H_2SO_4$$

$\therefore$ $100 \text{ mL} \times N_M = 20 \text{ mL} \times N/50$

or   normality, $N_M = \dfrac{20 \text{ mL} \times N}{100 \text{ mL} \times 50} = 0.0040 \text{ N}$

$\therefore$ Strength of alkalinity upto methyl orange end-point as $CaCO_3$ eq,

$$M = 0.004 \times (50 \text{ g/L}) = 0.2 \text{ g/L} = 200 \text{ mg/L}$$

Now $P\ (= 40 \text{ ppm}) < \dfrac{1}{2}M \left(\dfrac{1}{2} \times 200 \text{ ppm} = 100 \text{ ppm} \right),$

so *carbonate and bicarbonate are present.*

Now alkalinity due to CO_3^{2-} = 2P = 2 × 40 ppm = **80 ppm**

Alkalinity due to HCO_3^- = (M – 2P) = (200 – 2 × 40) = **120 ppm.**