Calculation of lime-soda requirement.

Constituent	Reaction	Need
Ca^{2+} (Perm. Ca)	$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	S
Mg^{2+} (Perm. Mg)	$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$	
HCO_3^- (e.g., $NaHCO_3$)	$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
	$2HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + CO_3^{2-}$	L – S
$Ca(HCO_3)_2$ (Temp. Ca)	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$	L
$Mg(HCO_3)_2$ (Temp. Mg)	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow$ $2CaCO_3 + Mg(OH)_2 + 2H_2O$	2L
CO_2	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$	L
H^+ (free acids, HCl, H2SO4, etc.)	$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
Coagulants : $FeSO_4$	$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2 + Ca^{2+}$ $2Fe(OH)_2 + H_2O + O_2 \longrightarrow 2Fe(OH)_3$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
$Al_2(SO_4)_3$	$2Al^{3+} + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3Ca^{2+}$ $3Ca^{2+} + 2Na_2CO_3 \longrightarrow 3CaCO_3 + 6Na^+$	L + S
$NaAlO_2$)	$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$ $2NaOH$ is eq to $Ca(OH)_2$	–L

Notes : (1) If $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are considered as ions $(Ca^{2+} + 2HCO_3^-)$ and $(Mg^{2+} + 2HCO_3^-)$ respectively, then calculation results will be same.

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

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

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

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

Now 100 parts by mass of $CaCO_3$ are equivalent to : (i) 74 parts of $Ca(OH)_2$, and (ii) 106 parts of Na_2CO_3.

∴ Lime requirement for softening

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

∴ Soda requirement for softening

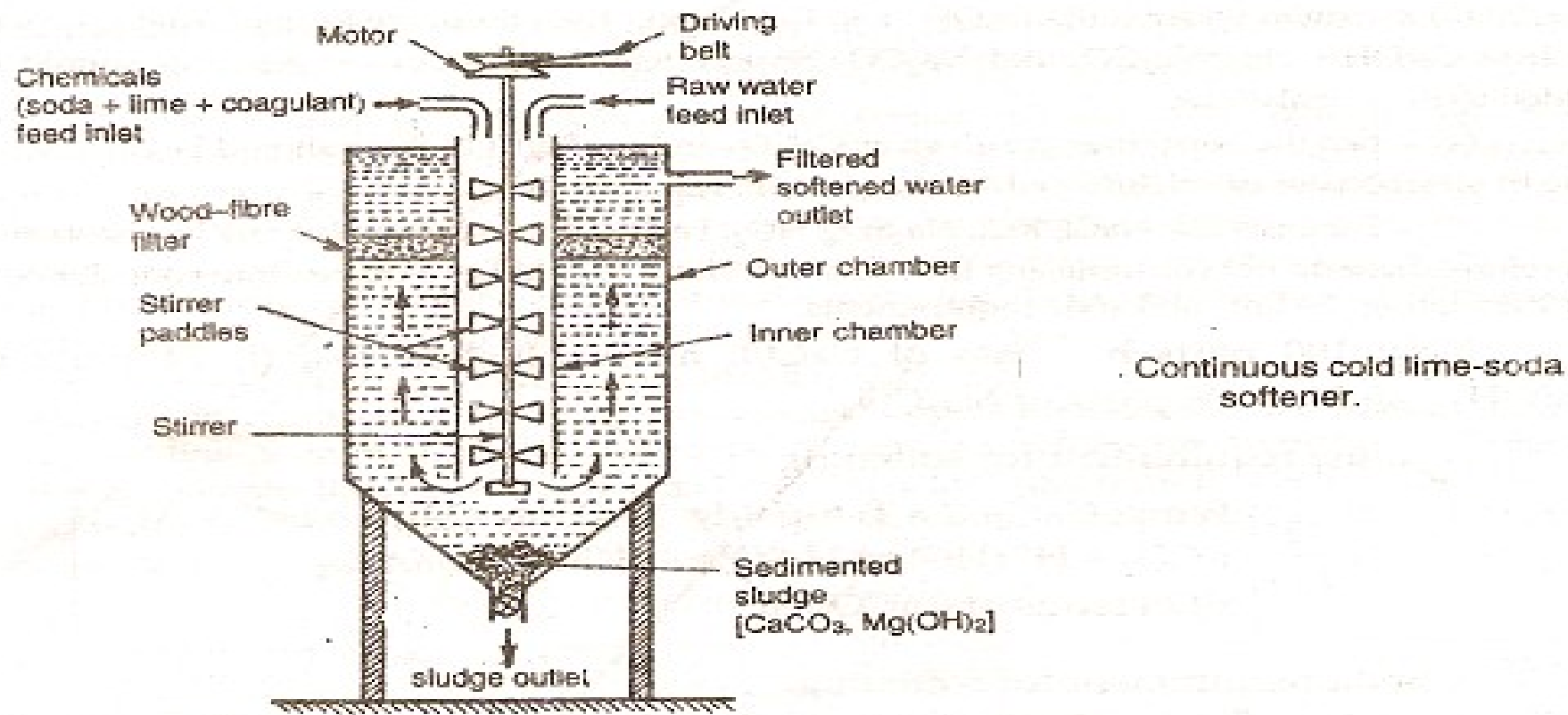$$= \frac{106}{100}\left[\begin{array}{l} \text{Perm. }(Ca^{2+} + Mg^{2+} + Al^3 + Fe^{2+}) + H^+ (HCl \text{ or } H_2SO_4) - HCO_3^- \\ \text{all in terms of } CaCO_3 \text{ eq} \end{array}\right]$$

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

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3 \downarrow$$
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)
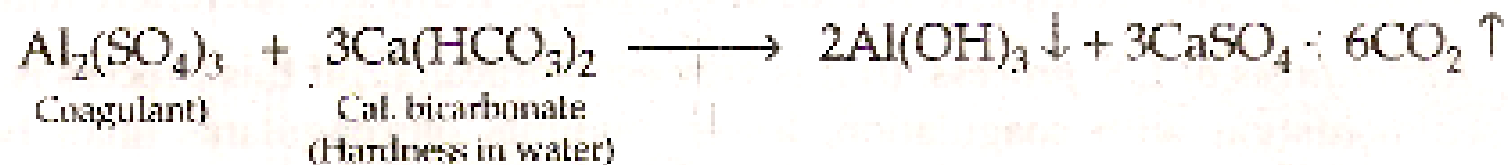
Method : Raw water and calculated quantities of chemicals (lime + soda + coagulant) are fed from the top into the inner vertical circular chamber, fitted with a vertical rotating shaft carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous 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

complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top (see Fig.   ) Sludge settling at the bottom of the outer chamber is drawn off occasionally.

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.
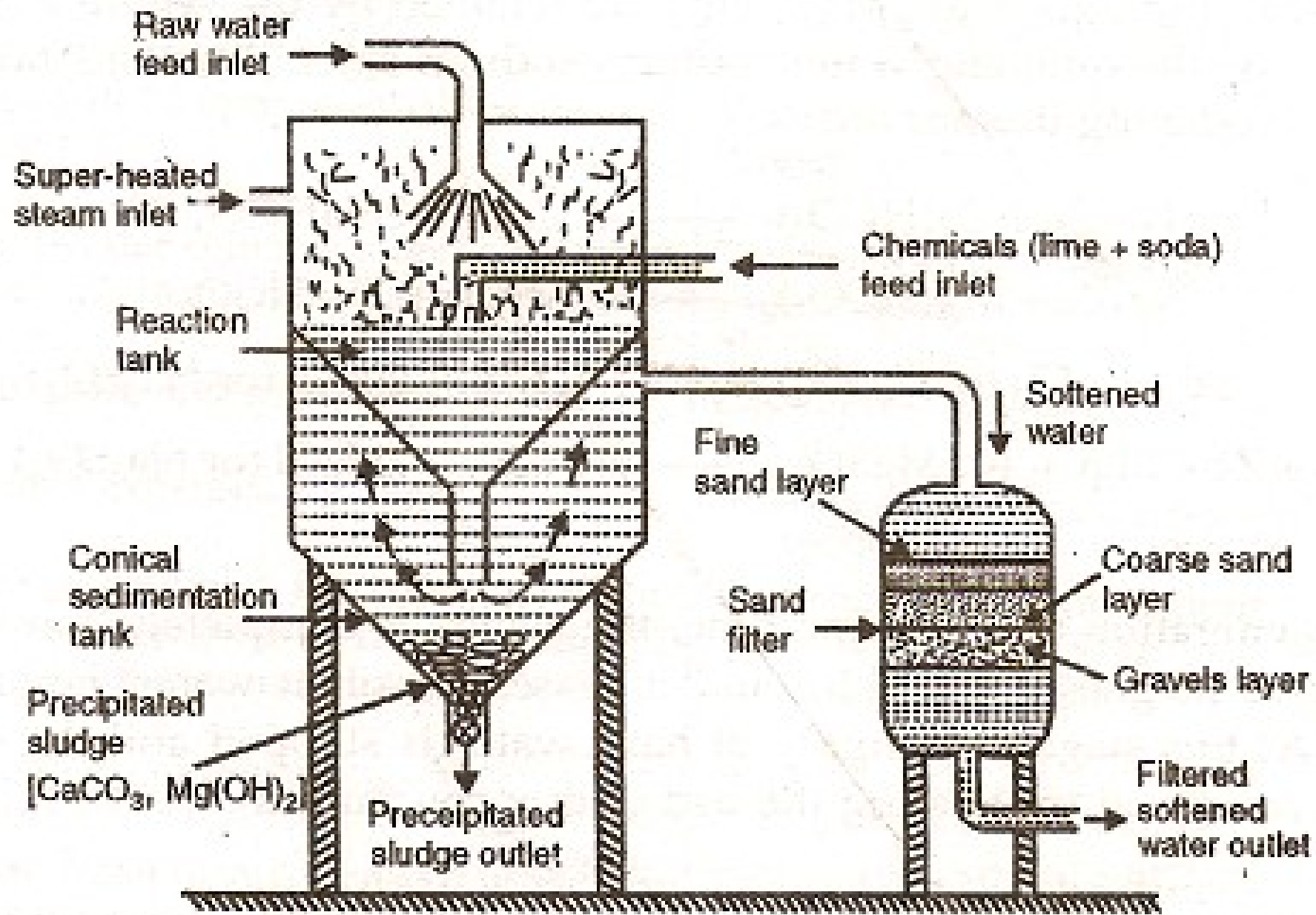
(ii) **Hot lime-soda process** involves in treating water with softening chemicals at a temperature of 80 to $150°C$. Since hot process is operated at a temperature close to the boiling point of the solution, so : (a) the reaction proceeds faster ; (b) the softening capacity of hot process is increased 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.) of three parts: (a) a 'reaction tank' in which raw water, chemicals and steam are thoroughly mixed ; (b) a "conical sedimentation vessel" in which sludge settles down, and (c) a "sand filter" which ensures complete removal of sludge from the softened water.

Advantages of L.S. process: (i) It is very economical. (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed. (iii) The process increases the pH value of the treated-water, thereby corrosion of the distribution pipes is reduced. (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced. (v) To certain extent, iron and manganese are also removed from the water. (vi) Due to alkaline nature of treated-water, amount of pathogenic 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.

Raw water feed inlet

Super-heated steam inlet

Chemicals (lime + soda) feed inlet

Reaction tank

Softened water

Fine sand layer

Conical sedimentation tank

Sand filter

Coarse sand layer

Gravels layer

Precipitated sludge [$CaCO_3$, $Mg(OH)_2$]

Precipitated sludge outlet

Filtered softened water outlet

Continuous hot lime-soda softener.

(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 it's 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.   ). The
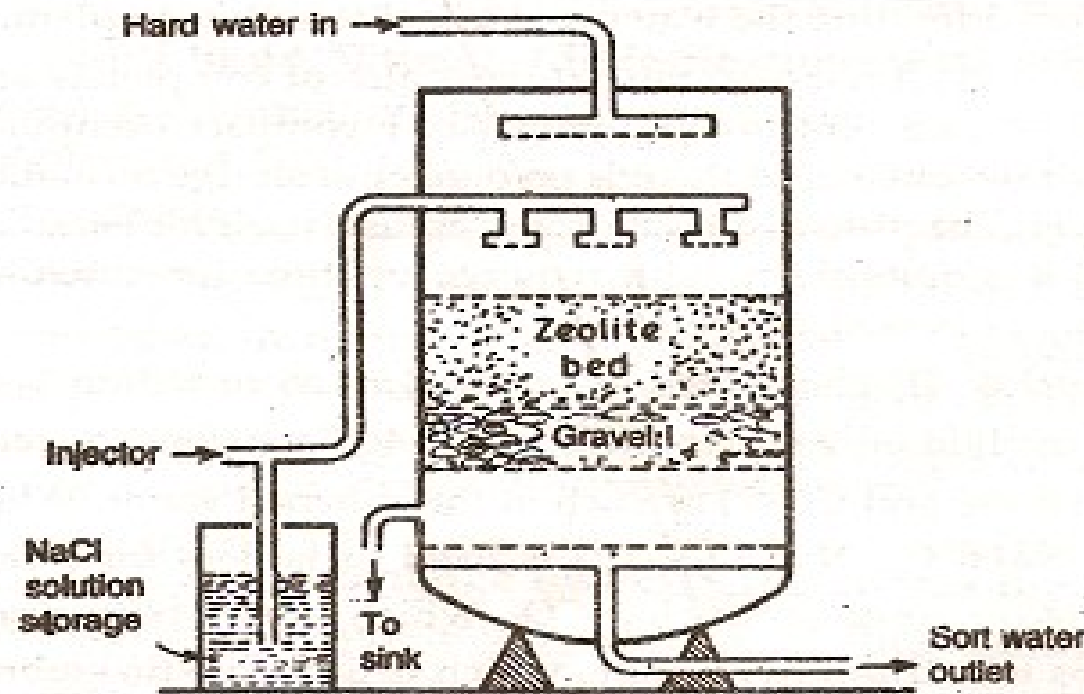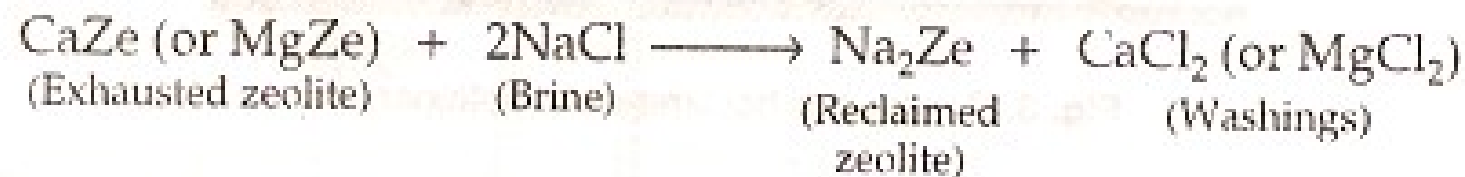

. Zeolite softener.

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)

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.

$$\underset{\text{(Exhausted zeolite)}}{CaZe \text{ (or MgZe)}} + \underset{\text{(Brine)}}{2NaCl} \longrightarrow \underset{\substack{\text{(Reclaimed} \\ \text{zeolite)}}}{Na_2Ze} + \underset{\text{(Washings)}}{CaCl_2 \text{ (or MgCl}_2)}$$

The washings (containing CaCl2 and MgCl2) 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.
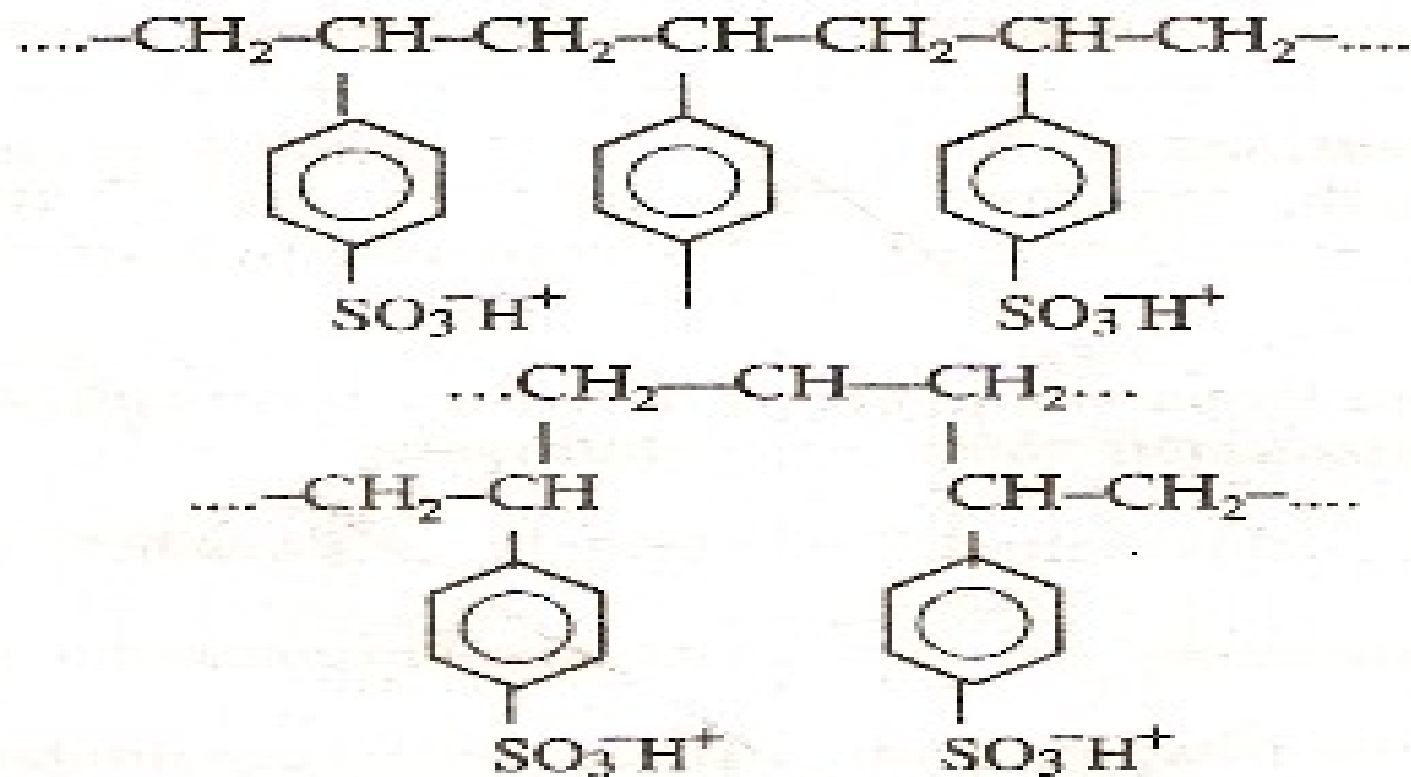
Disadvantages of zeolite process : (1) The treated-water contains more sodium salts than in lime-soda process. (2) The method only replaces Ca^{2+} and Mg^{2+} ions by Na^+ ions, but leaves all the acidic ions (like HCO_3^- and CO_3^{2-}) as such in the softened water. When such softened water (containing $NaHCO_3$, 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.

Comparison of permutit process with lime-soda process.

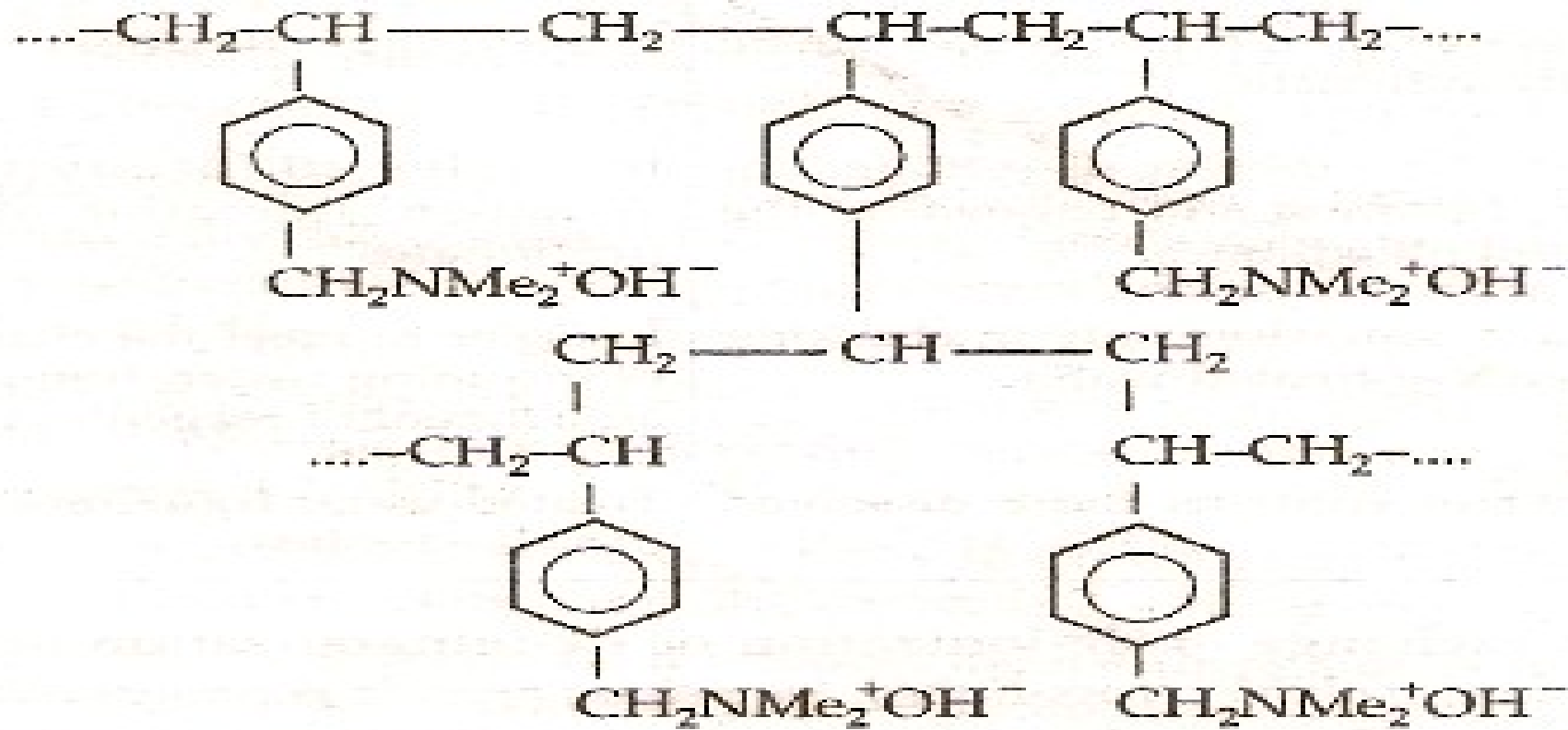| Permutit method	Lime-soda method
1. Water of 10-15 ppm residual hardness is obtained.	Water of, generally, 15-50 ppm hardness is obtained.
2. Treated-water contains larger amount of sodium salts than in original raw water.	Treated-water contains lesser amount of sodium salts.
3. Cost of plant and material 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 amount of 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.

...–CH$_2$–CH–CH$_2$–CH–CH$_2$–CH–CH$_2$–....

SO$_3^-$H$^+$ SO$_3^-$H$^+$

...CH$_2$—CH—CH$_2$...

....–CH$_2$–CH   CH–CH$_2$–....

SO$_3^-$H$^+$ SO$_3^-$H$^+$

Acidic or cation exchange resin (sulphonate form).

(ii) **Anion exchange resins** (R'OH$^-$) are styrene-divinyl benzene or amine-form-aldehyde 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.

$$....-CH_2-CH \underline{\qquad} CH_2 \underline{\qquad} CH-CH_2-CH-CH_2-....$$

CH_2NMe_2^+OH^-

CH_2NMe_2^+OH^-

$$CH_2 \underline{\qquad} CH \underline{\qquad} CH_2$$

$$....-CH_2-CH \qquad\qquad CH-CH_2-....$$
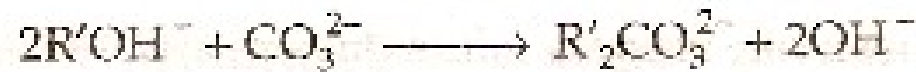
CH_2NMe_2^+OH^-   CH_2NMe_2^+OH^-

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. H2SO4. The regeneration can be represented as :

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+} \text{ (washing)}$$

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

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

$$R'_2SO_4^{2-} + 2OH^- \longrightarrow 2R'OH^- + SO_4^{2-} \text{ (washing)}$$
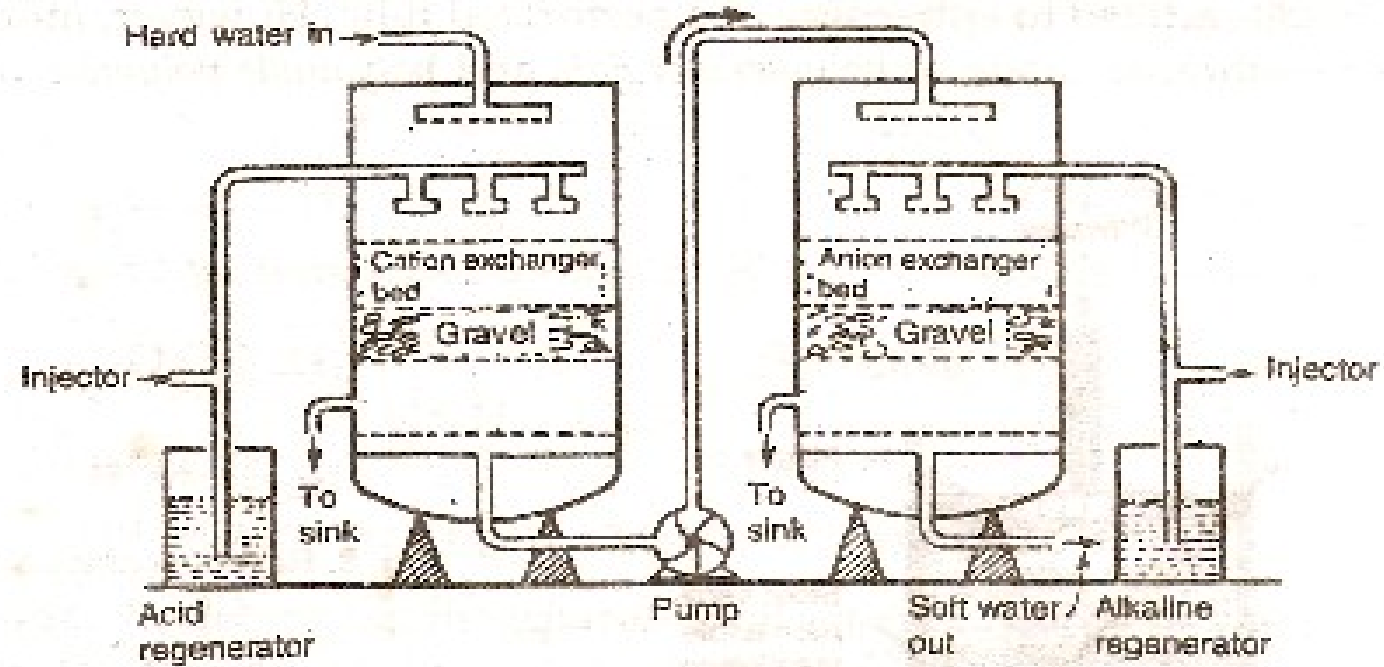
Demineralization of water.

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

The regenerated ion exchange resins are then used again.

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

Disadvantages : (1) The equipment is costly and more expensive chemicals are needed. (2) If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.
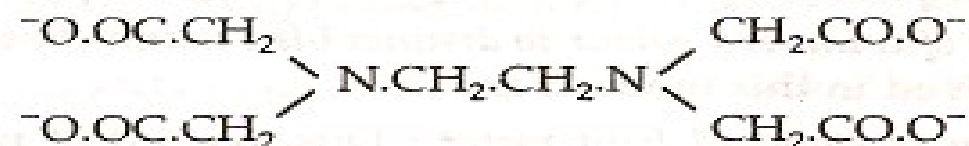
high, about 2 years. (*v*) The membrane can be replaced within a *few minutes*, thereby providing nearly uninterrupted water supply. (*vi*) Due to low capital cost, simplicity, low operating cost and high reliablility, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high-pressure boilers.

ESTIMATION OF HARDNESS OF WATER

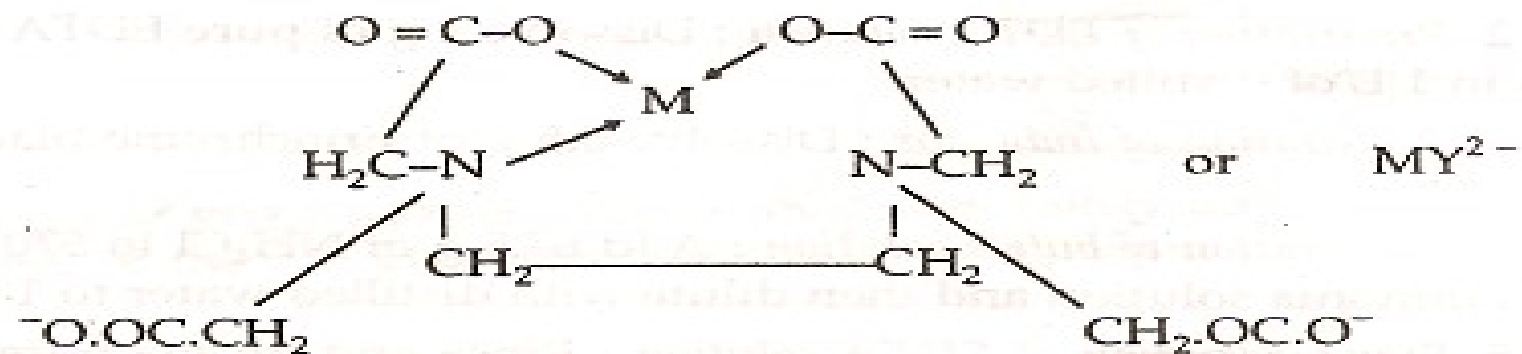**EDTA method :** This is a *complexometric method*. Ethylene diamine tetraacetic acid (EDTA),

$$HO.OC.CH_2 > N-CH_2-CH_2-N < CH_2.CO.OH \\ HO.OC.CH_2 \qquad\qquad CH_2.CO.OH$$
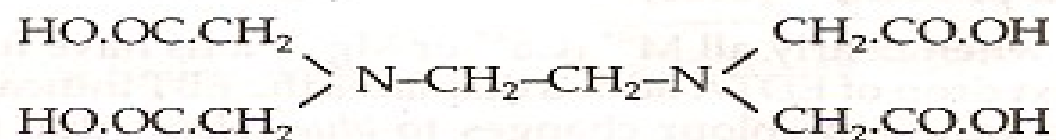
in the form of its sodium salt yields the *anion* ;

$$^-O.OC.CH_2 > N.CH_2.CH_2.N < CH_2.CO.O^- \\ ^-O.OC.CH_2 \qquad\qquad CH_2.CO.O^-$$

which *forms complex ions* with Ca^{2+} and Mg^{2+}.

Thus :

$$O=C-O \qquad\qquad O-C=O \\ \diagdown \qquad\qquad\quad \diagup \\ M \\ H_2C-N \qquad N-CH_2 \qquad or \qquad MY^{2-} \\ | \qquad\qquad\qquad | \\ CH_2 \qquad\qquad\qquad CH_2 \\ ^-O.OC.CH_2 \qquad\qquad\qquad CH_2.OC.O^-$$

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

$$\begin{matrix} NaO.OCCH_2 \\ \\ HO.OCCH_2 \end{matrix} \Big\rangle N.CH_2.CH_2.N \Big\langle \begin{matrix} CH_2O.ONa \\ \\ CH_2O.OH \end{matrix} \quad (\text{or } Na_2H_2Y)$$
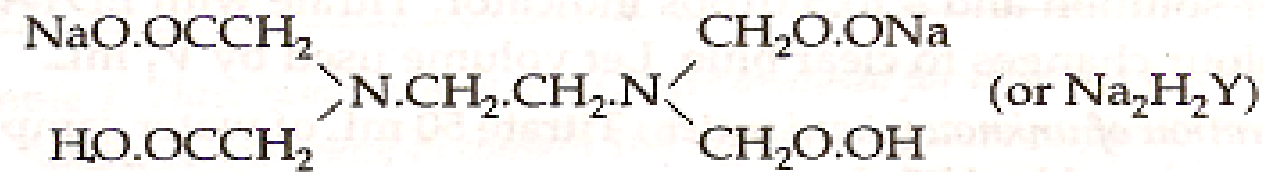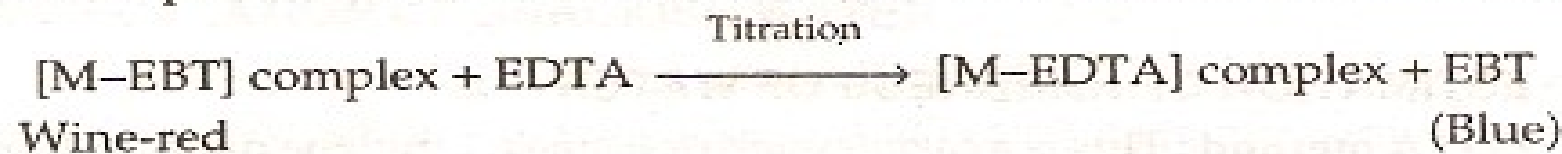
(Mol. wt. = 372.24 ; Eq. wt. = 186.14), *i.e.,* M soln. = 2 N soln.)

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 :

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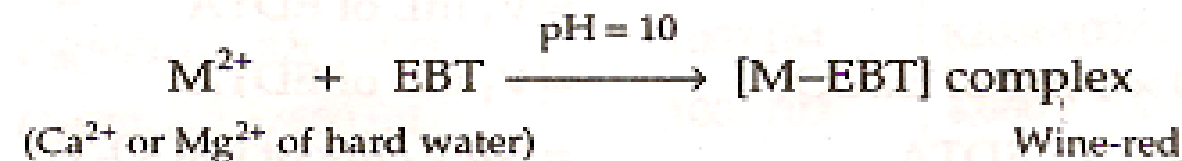
So initially a wine-red coloured is obtained. During the course of titration against EDTA solution, EDTA combines with M^{2+} (or Ca^{2+} or Mg^{2+}) ions from *stable complex*, M-EDTA and releasing free EBT, which instantaneously combines with M^{2+} ions still present in the solution, thereby wine-red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

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

$$\underset{\substack{(Ca^{2+} \text{ or } Mg^{2+} \text{ still present})}}{M^{2+}} + \underset{\text{(Blue)}}{EBT} \xrightarrow{\hspace{1cm}} \underset{\text{Wine-red}}{[M-EBT] \text{ complex}}$$

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,

$$[M-EBT] \text{ complex} + EDTA \longrightarrow [M-EDTA] \text{ complex} + EBT \text{ (blue)}$$

Thus, change of wine-red colour to distinct blue marks the end-point of titration.

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.

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

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 washings 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

$$= V_1 \text{ mL of EDTA}$$

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

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

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

$$= \frac{V_2 \times 50}{V_1} \text{ mg of CaCO}_3 \text{ eq}$$

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

$$= 1,000 \ V_2/V_1 \text{ mg of CaCO}_3 \text{ eq}$$

$\therefore$ Total hardness of water $= 1,000 \ V_2/V_1 \text{ mg/L}$

$$= \boxed{1,000 \ V_2/V_1 \text{ ppm}} \qquad \qquad ...(i)$$

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 $= 1,000 \ V_3/V_1 \text{ mg of CaCO}_3 \text{ eq}$

$\therefore$ Permanent hardness $= 1,000 \ V_3/V_1 \text{ ppm} \qquad \qquad ...(ii)$

and temporary hardness $= [\text{Total} - \text{Permanent}] \text{ hardness}$

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

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

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.