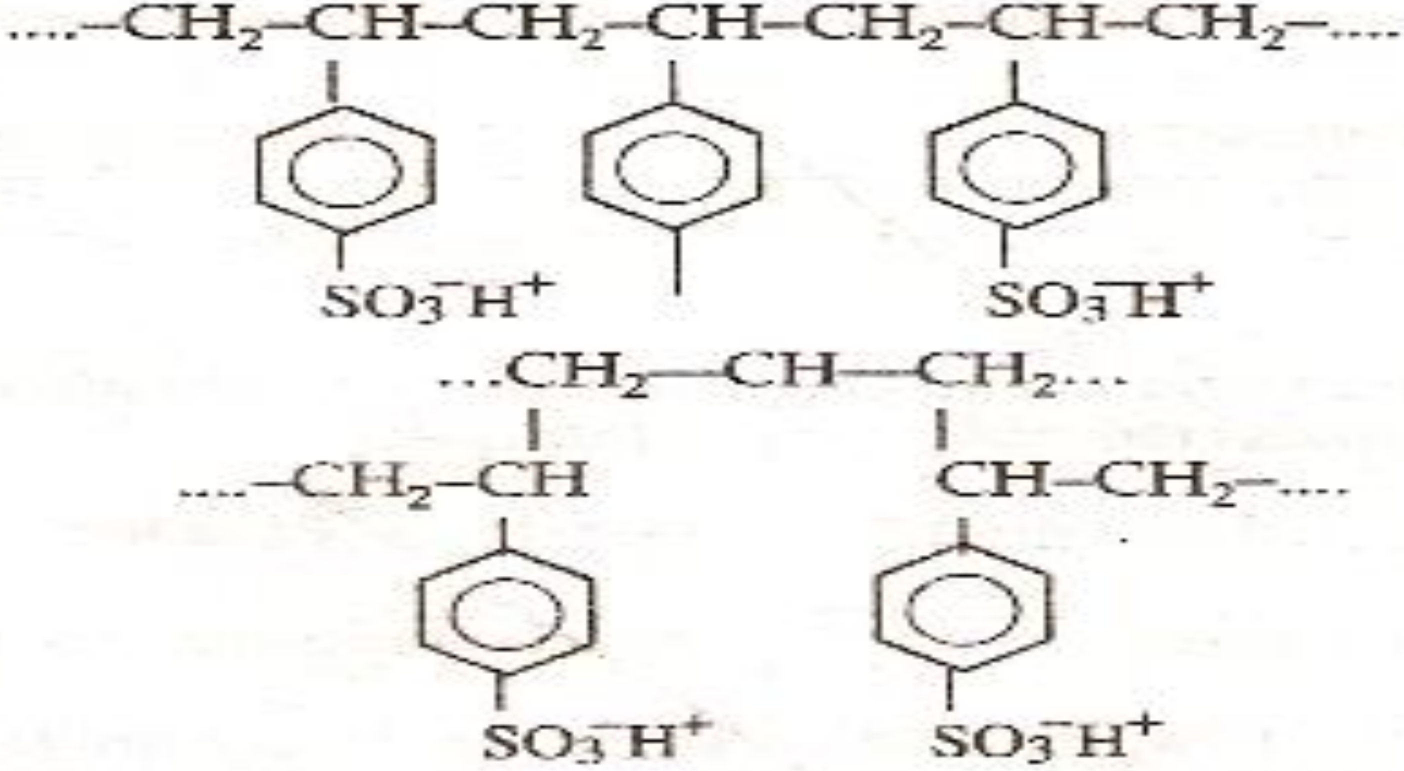
Comparison of permutit process with lime-soda process.

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, coagulation, filtration and removal of the sludges and precipitates.	It involves difficulty in settling, coagulation, 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.

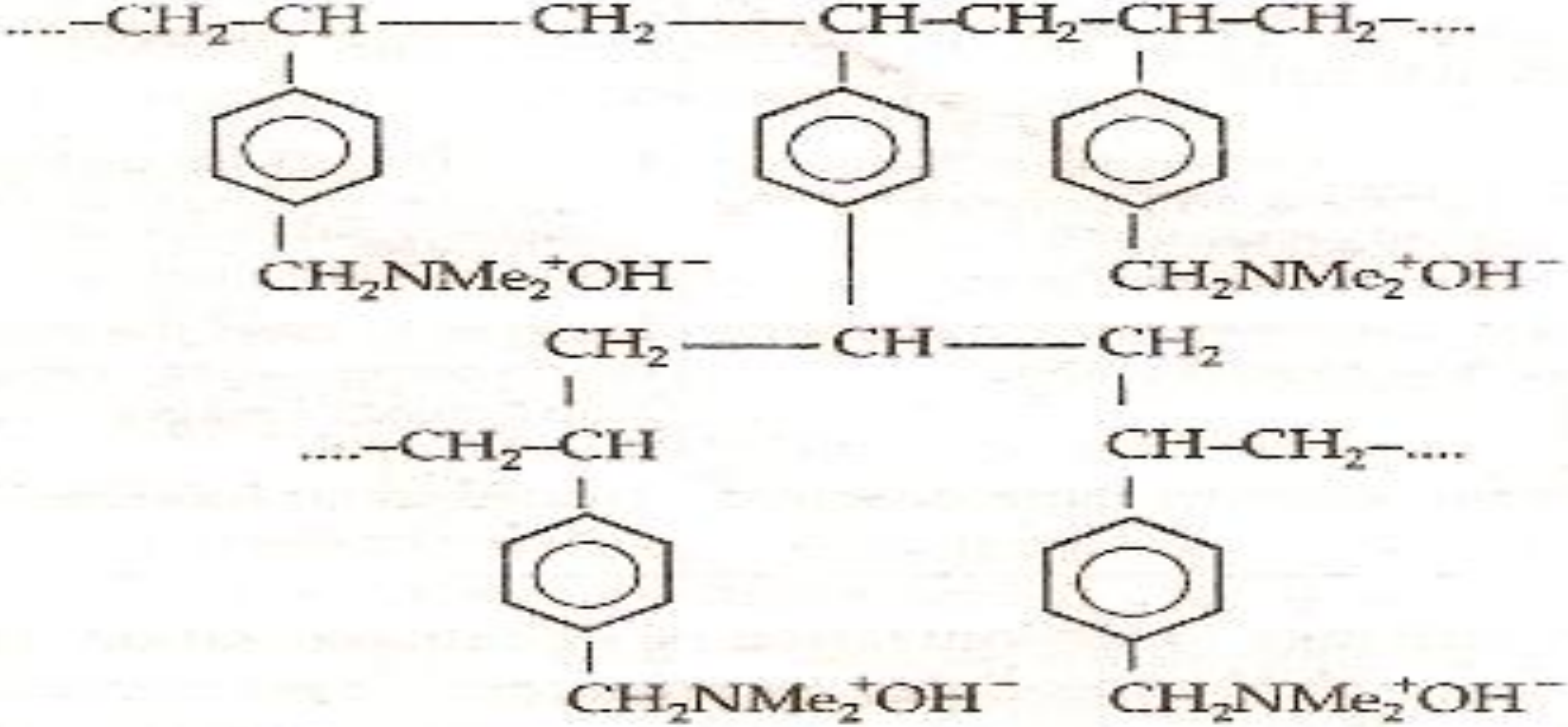
(3) **Ion exchange** or **de-ionization** or **de-mineralization process** : *Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the "functional groups" attached to the chains are responsible for the ion-exchanging properties.* Resins containing 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.



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.



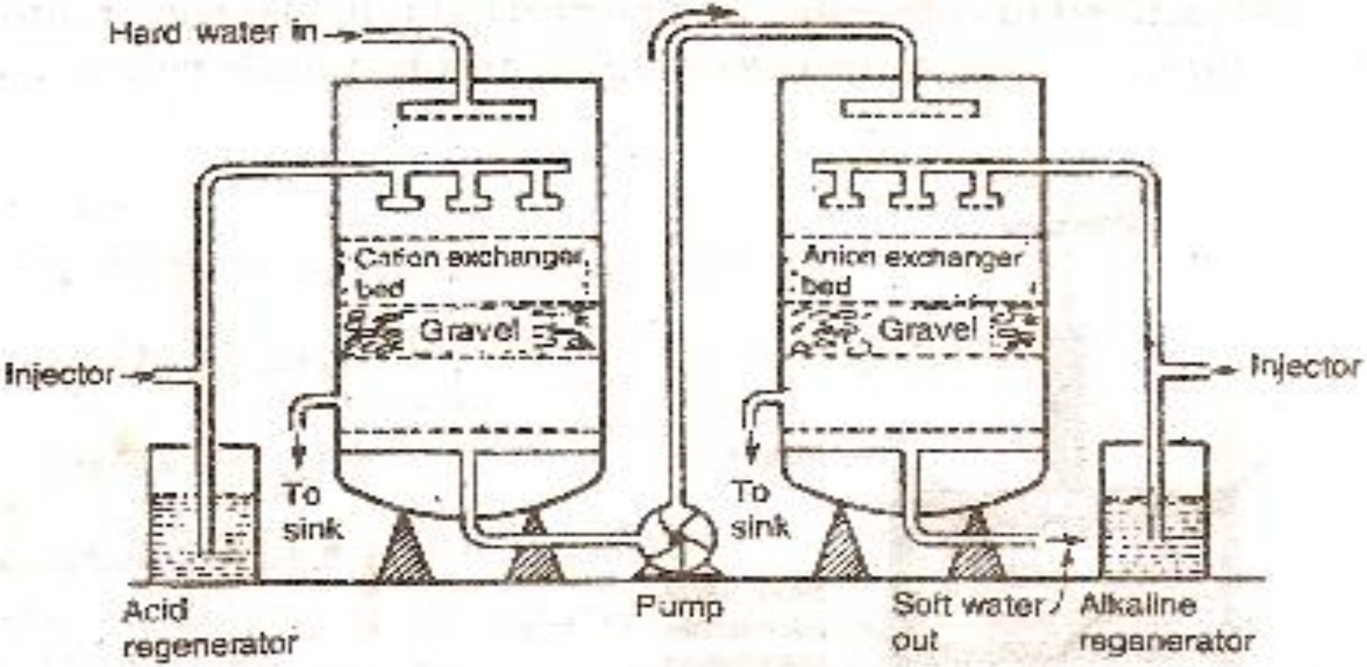
Basic or anion exchange resin (hydroxide form).

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



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.

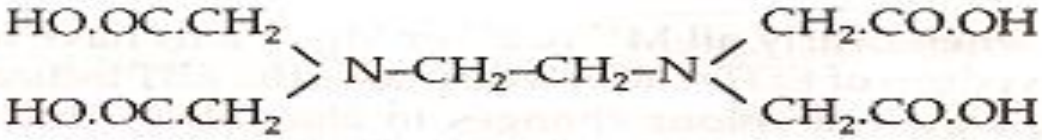
Advantages : (1) The process can be used to soften highly acidic or alkaline waters. (2) It produces water of very low hardness (say 2 ppm). So it is very good for treating water for use in high-pressure boilers.

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.

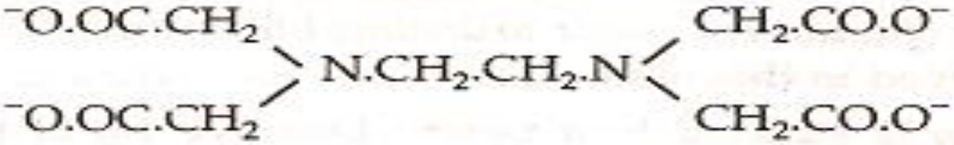
high, about 2 years. (*v*) The membrane can be replaced within a *few minutes*, thereby providing nearly uninterrupted water supply. (*vi*) Due to low capital cost, simplicity, low operating cost and high reliablility, the reverse osmosis is gaining ground at present for converting sea water into drinking 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),

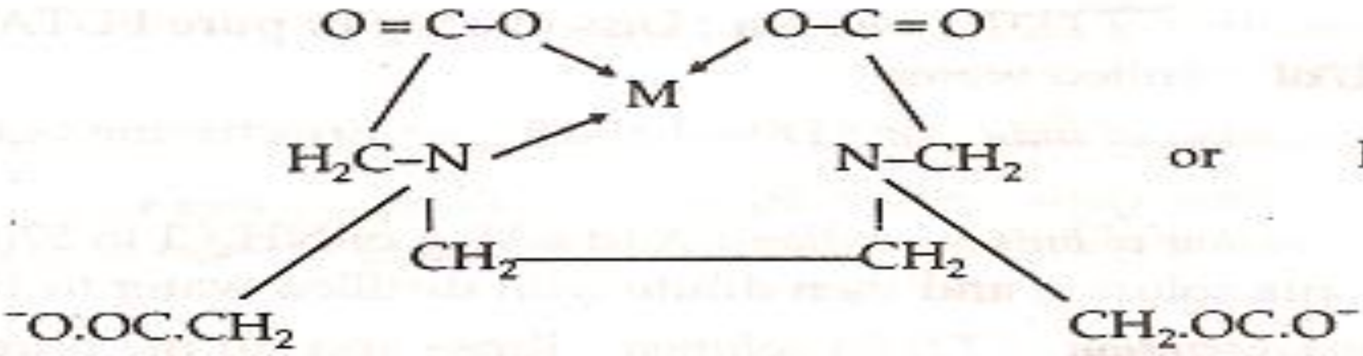


in the form of its sodium salt yields the *anion* ;



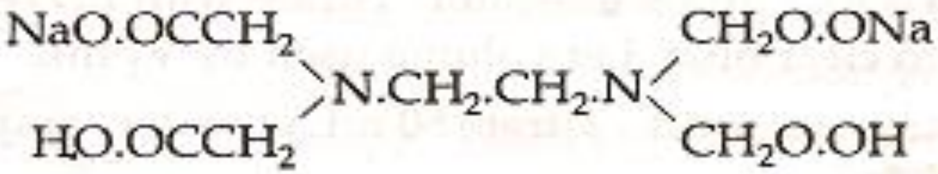
which *forms complex ions* with Ca^{2+} and Mg^{2+}.

Thus :



or MY^{2-}

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



$$\begin{matrix} \mathrm{NaO.OCCH_2} & & \mathrm{CH_2O.ONa} \\ & \rangle\mathrm{N.CH_2.CH_2.N}\langle & \\ \mathrm{HO.OCCH_2} & & \mathrm{CH_2O.OH} \end{matrix} \qquad (\text{or } \mathrm{Na_2H_2Y})$$

(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 :

$$\underset{(Ca^{2+} \text{ or } Mg^{2+} \text{ of hard water})}{M^{2+}} + \text{EBT} \xrightarrow{pH = 10} \underset{\text{Wine-red}}{[\text{M–EBT}] \text{ complex}}$$

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 :

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

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

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,

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

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

$= V_1$ mL of EDTA

∴ 50 × 1 mg of $CaCO_3$ $= V_1$ mL of EDTA

∴ 1 mL of EDTA $= 50/V_1$ 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 $= 1{,}000\ V_2/V_1$ mg/L

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

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 $\qquad \ldots(ii)$

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

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

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

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.