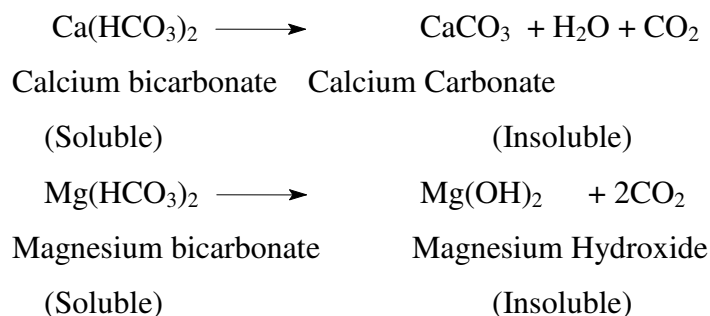**Q. What is temporary and permanent hardness and write the differences between them**

Hardness of water is of two types. Temporary hardness and Permanent hardness:
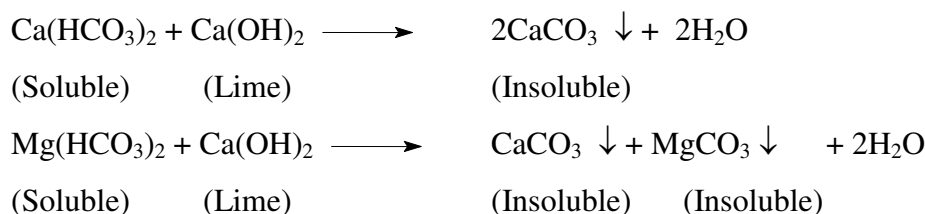
i)   Temporary hardness*:* It is due to the presence of soluble bicarbonates of calcium and magnesium. Such water is also said to possess **carbonate hardness**. The term temporary indicates that most of the hardness can be removed by simply boiling the water.

The methods employed for removing temporary hardness are the following.

1. By boiling*:* Temporary hard water contains calcium and magnesium bi-carbonates. These salts are decomposed on boiling the water, forming insoluble calcium and magnesium carbonates which can easily be removed by filtration.
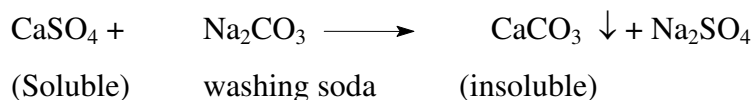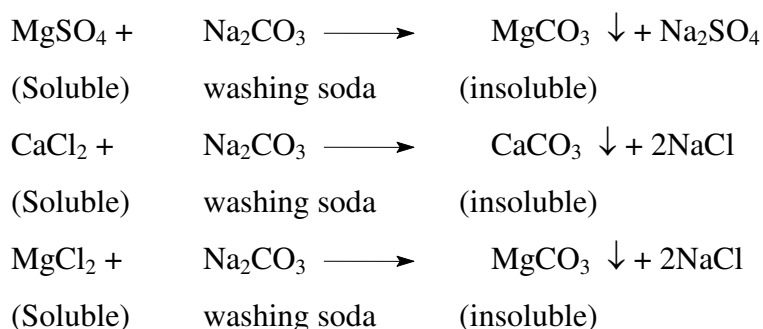
$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

Calcium bicarbonate   Calcium Carbonate

(Soluble)   (Insoluble)

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CO_2$$

Magnesium bicarbonate   Magnesium Hydroxide

(Soluble)   (Insoluble)

2. Clark's Method*:* This is the cheapest method for removing temporary hardness of water and is therefore widely used. In this method sufficient amount of lime (Calcium hydroxide) is added to the water which converts all the soluble bicarbonates into insoluble carbonates as shows below:

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

(Soluble)   (Lime)   (Insoluble)

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + MgCO_3 \downarrow + 2H_2O$$

(Soluble)   (Lime)   (Insoluble)   (Insoluble)

ii) Permanent Hardness*:* It is due to the presence of chlorides and sulphates of calcium and magnesium. Such water is said to possess "**Non-Carbonate Hardness**". The term permanent indicates that such type of hardness cannot by removed by simple boiling of water.

The permanent hardness can be removed by addition of calculated quantity of sodium carbonate (washing soda) by which calcium and magnesium carbonates are precipitated as shows below*:*

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$

(Soluble)   washing soda   (insoluble)

$$MgSO_4 + \quad Na_2CO_3 \longrightarrow \quad MgCO_3 \downarrow + Na_2SO_4$$

(Soluble)   washing soda   (insoluble)

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

(Soluble)   washing soda   (insoluble)

$$MgCl_2 + \quad Na_2CO_3 \longrightarrow \quad MgCO_3 \downarrow + 2NaCl$$

(Soluble)   washing soda   (insoluble)

Q. what are the Units of Hardness And its Inter conversion.

The hardness causing ions are usually expressed in terms of an equivalent amount of $CaCO_3$.

Units of Expression of Hardness*:*

1) Parts per million (ppm)

2) Milligram per litre

3) Degree French (^0Fr)

4) Clarke's degree (^0Cl)

$$1ppm = 1mg / litre = 0.07\,^0Cl = 0.1\,^0Fr$$
$$1\,^0Cl = 1.43\,^0Fr = 14.3\ ppm = 14.3\ mg/litre$$
$$1\,^0Fr = 0.7\,^0Cl = 10ppm = 10\ mg/litre$$

Q. Problem:

Calculate the carbonate hardness and non carbonate hardness of sample water containing the dissolved salts in one litre of hard water as given below. Also calculate total hardness. $Ca(HCO_3)_2 = 32.4$ mg; $Mg(HCO_3)_2 = 14.6$mg; $CaSO_4 = 13.6$mg; $MgSO_4 = 11.1$mg; $CaCl_2 = 12.0$mg; $MgCl_2 = 9.5$mg.

Solution:

Hardness producing salt	Amount	Multiplication factor	Equivalents of $CaCO_3$
$Ca(HCO_3)_2$	32.4	100/162	20
$Mg(HCO_3)_2$	14.6	100/146	10
$CaSO_4$	13.6	100/136	10
$MgSO_4$	22.2	100/120	20
$CaCl_2$	12.0	100/111	10
$MgCl_2$	9.5	100/95	10

Temparary hardness due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2 = 20 + 10 = 30$ppm

Permanent hardness due to $CaSO_4$, $MgSO_4$, $CaCl_2$ and $MgCl_2$ =10+20+10+10= 50ppm
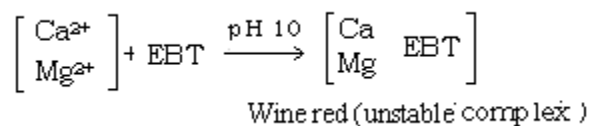
Total hardness = 30ppm + 50ppm = 80ppm or mg/l

Q. Estimation of Hardness by EDTA Method:

Disodium salt of Ethylene Diamine Tetra Acetic acid is used as the permanent complexing agent with Ca^{2+} and Mg^{2+} ions of hard water in the EDTA method.
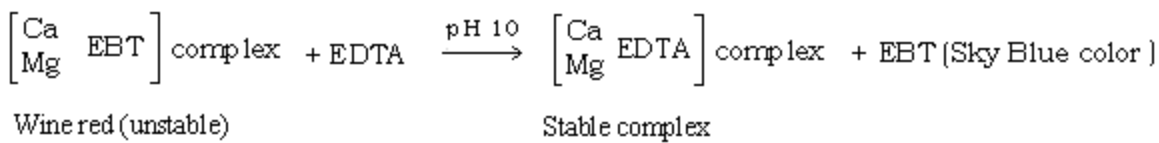
The structure of EDTA is given below.

$$NaOOCH_2C \diagdown \atop HOOC\,H_2C \diagup N-CH_2-CH_2-N \diagup CH_2\,COOH \atop \diagdown CH_2\,COONa$$
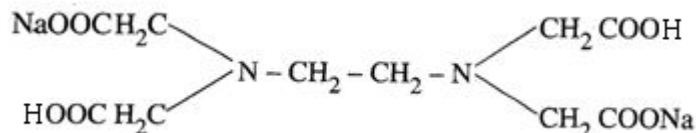
Before starting the titration, to the hard water ammonium buffer (to maintain pH 10) and EBT indicator are added which form an unstable complex of wine red color.

$$\begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} + EBT \xrightarrow{pH\ 10} \begin{bmatrix} Ca \\ Mg \end{bmatrix} EBT \end{bmatrix}$$

Wine red (unstable complex)

After the titration, the sodium salt of EDTA form Stable complex with water containing Ca^{2+} and Mg^{2+} ions replacing the unstable complex. The completion of the complex formation is indicated by EBT indicator giving a sky blue color. + EDTA

$$\begin{bmatrix} Ca \\ Mg \end{bmatrix} EBT \end{bmatrix} complex + EDTA \xrightarrow{pH\ 10} \begin{bmatrix} Ca \\ Mg \end{bmatrix} EDTA \end{bmatrix} complex + EBT (Sky Blue color)$$

Wine red (unstable)   Stable complex

Procedure:

1. **Preparation of standard hard water:** 1g of pure dry $CaCO_3$ should be dissolved in small quantity of dilute HCl and then evaporated to dryness on a water bath. The residue is dissolved in distilled water and make up to 1L. 1 ml of this solution contains 1 mg of $CaCO_3$ equivalent hardness.

2. **Preparation of EDTA solution:** 3.72 grams of pure sodium salt of EDTA crystals should be dissolved in 1L of water (0.01 M).

3. **Preparation of Indicator:** 0.5g of EBT should be dissolved in 100mL of alcohol.

4. **Preparation of buffer solution:** It can be prepared by mixing 67.5g of NH_4Cl in 570mL of liquid ammonia and then diluted to 1L with water.

5. **Standardization of EDTA solution:** The burette is filled with the EDTA solution. 50 ml standard hard water pipette out into a clean conical flask. Add 10-15 ml of buffer solution and few drops of Erichrome black – T indicator. The wine red solution in the conical flask is titrated against the burette EDTA solution till the wine red color changes to sky blue color. Let the volume of EDTA consumed be V_1 ml.

6. **Titration of unknown hard water or Estimation of total hardness:** 50 ml sample hard water pipette out into a clean conical flask. Add 10-15 ml of buffer solution and few drops of Erichrome black – T indicator. The wine red solution in the conical flask is titrated against the burette EDTA solution till the wine red color changes to sky blue color. Let the volume of EDTA consumed be V_2 ml.

7. **Estimation of Permanent hardness:** Take 250ml of water sample in a large beaker, boil it till volume is reduced to about 50ml [when all bicarbonates are decomposed to insoluble $CaCO_3$ + $Mg(OH)_2$]. The temporary salts settle down. Filter and wash thoroughly and make up solution again to 250 ml. pipette out 50 ml 0f made up solution into clean conical flask and titrate it against EDTA solution in the burette to get the end point. Let the volume of EDTA consumed be V_3 ml

Calculations:

	V_1 ml of EDTA	=	50 ml of standard hard water
$\therefore$	V_1 ml of EDTA	=	50 mg of $CaCO_3$
$\therefore$	1ml of EDTA	=	$50/V_1$ mg of $CaCO_3$ equivalent
	Now 50ml of given hard water	=	V_2 ml of EDTA
		=	$V_2 \times 50/V_1$ mg of $CaCO_3$ equivalent
$\therefore$	1L (1000ml) of given hard water	=	1000 V_2/V_1 mg of $CaCO_3$ equivalent
$\therefore$	Total hardness of water	=	$1000V_2/V_1$ mg/L=$1000V_2/V_1$ ppm
	Now 50ml of boiled water	=	V_3 ml of EDTA
		=	$V_3 \times 50/V_1$ mg of $CaCO_3$ equivalent
	$\therefore$ 1000 (mL)	=	(1L) of boiled water
	Permanent hardness	=	1000 V_3/V_1 mg of $CaCO_3$ equivalent
$\therefore$	Permanent hardness	=	1000 V_3/V_1 ppm
And	Temporary hardness	=	Total hardness – Permanent hardness
		=	$1000\left[\dfrac{V_2}{V_1} - \dfrac{V_3}{V_1}\right]ppm$

$$= \frac{1000(V_2 - V_3)}{V_1} \, ppm$$

Q. Explain Electro dialysis method for Desalination of Brakish Water:

Ans.

Electrodialysis: Electrodialysis is based on the principle that the ions present in saline water migrate towards their respective electrodes through ion selective membranes under the influence of applied e.m.f.
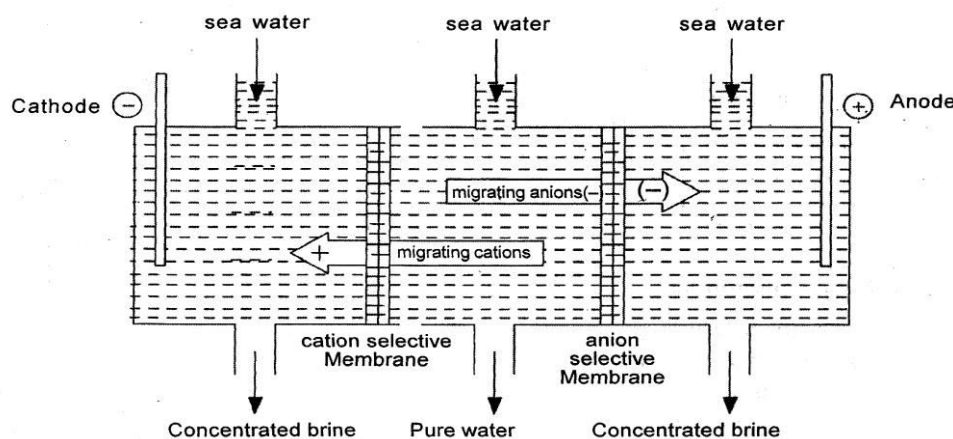
The unit consists of a chamber, two electrodes (the cathode and the anode). The chamber is divided into three compartments with the help of thin, rigid, ion-selective membranes which are permeable to either cation or anion. The anode is placed near anion selective membrane. While the cathode placed near cation selective membrane. The anion selective membrane is containing positively charged functional groups such as R_4N^+ and is permeable to anions only. The cation selective membrane consists of negatively charged functional groups such as RSO_3^- and is permeable to cations only. Under the influence of applied e.m.f. across the electrodes the cations move towards cathode through the membrane and the anions move towards anode through the membrane. The net result is depletion of ions in the central compartment while it increases in the cathodic and anodic compartments. Desalination water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.

Advantages of Electrodialysis:

1) The unit is compact.

2) The process is economical as far as capital cost and operational expenses are concerned.

Q. Explain Reverse Osmosis method for desalination of brakish water.

Ans.

Reverse Osmosis: When two solutions of unequal concentration are separated by a semi permeable membrane which does not permit the passage of dissolved solute particles. Flow of

solvent takes place from the dilute solution to concentration solution, this is called Osmosis. If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent is forced to move from higher concentration to lower concentrated side across. Thus the solvent flow is reversed hence this method is called reverse osmosis. Thus, in reverse osmosis pure water is separated from the contaminated water. This membrane filtration is also called super filtration or hyper-filtration.
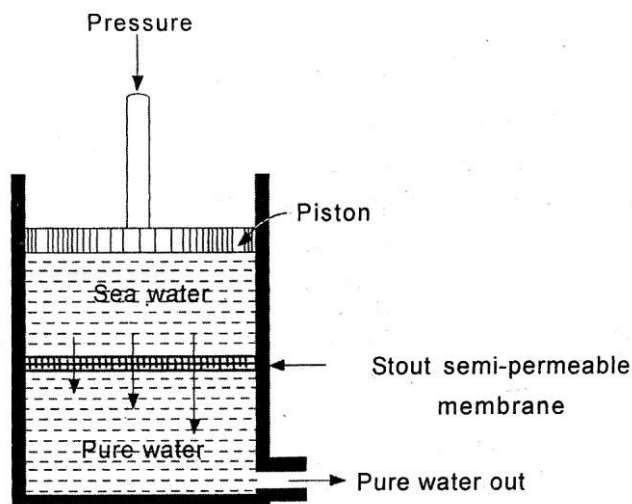
Method of purification: The reverse osmosis cell consists of a chamber fitted with a semi permeable membrane, above which sea water / impure water is taken and a pressure of 15 to 40 kg/cm^2 is applied on the sea water/impure water. The pure water is forced through the semi permeable membrane which is made of very thin films of cellulose acetate. However, superior membrane made of polymethylmethacrylate and polyamide polymers have come to use.
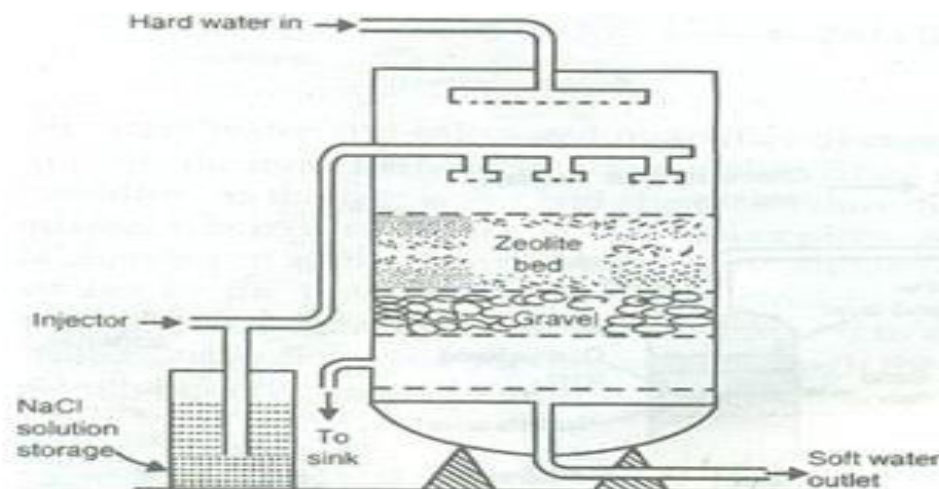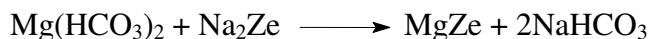
Advantages of Reverse Osmosis:

1) Ionic and non-ionic, colloidal and high molecule weight organic matter is removed from the water sample.
2) It removes colloidal silica
3) The maintenance cost is almost entirely on the replacement of membrane.
4) The life time of the membrane is quite high, about 2 years
5) The membrane can be replaced with in few minutes.
6) Low capital cost, low operational cost and high reliability method.
7) This water can be used for high pressure boilers.

Q. Explain ZEOLITE PROCESS (OR) PERMUTIT PROCESS for treatment of industrial water.

Ans.

Process:

The hard water is passed through a zeolite bed fixed in a cylinder at a specific rate. The hardness causing ions, Ca^{2+}, Mg^{2+} etc., are retained by the zeolite as CaZ and MgZ respectively. An equivalent amount of sodium salts were introduced into water. The reaction taking place during the softening process is:

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$
$$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$$
$$CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$$
$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$
$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$
$$MgCl_2 + Na_2Ze \longrightarrow MgZe + 2NaCl$$

Regeneration:

After sometime, the zeolite bed is completely converted to calcium and magnesium zeolites and no purification of raw water takes place i.e., the zeolite bed gets exhausted. At this stage the purification of hardwater is stopped and the zeolite bed is regenerated by treating the bed with 10% brine (NaCl) solution.

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$
$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

The washings containing $CaCl_2$ and $MgCl_2$ are discarded.

Limitations of zeolite process:

1) Raw water should not contain turbidity. Turbidity will block clog the process of zeolite bed and makes it inactive. Turbidity of water must be removed by coagulation, filtration etc.,

2) Raw water must be not contain any coloured ions like Mn^{2+} and Fe^{2+}, because they form manganese zeolite and ferrous zeolite which cannot be regenerated.

3) Mineral acids if present in water will destroy the zeolite bed permanently. Water must be neutralized with soda before it is fed into the zeolite bed.

Advantages of Zeolite process:

1) It reduces hardness up to 10 ppm.

2) No precipitation of the products takes place. Hence no disposal of sludge is required.

3) The equipment is quite compact

4) Requires less skilled assistance.

5) It requires less time for softening.

Disadvantages of Zeolite process:

1) The treated water contains more sodium salts than in lime-soda process.

2) The method replaces only Ca^2+ and Mg^2+ ions by Na+ ions, leaves acidic ions like HCO_3^- and CO_3^{2-} as $NaHCO_3$ and Na_2CO_3.

3) These $NaHCO_3$ salt decompose and liberate CO_2 which causes corrosion.

4) The Na_2CO_3 salt produced in water decomposed due to the high temperature maintained in the boiler to NaOH, which causes caustic embrittlement.

Q. Explain ION-EXCHANGE PROCESS for treatment of industrial water.

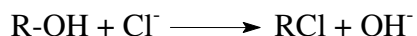**Ans.**

Process: This process involves the following steps.

Step-1: The hard water is passed through a bed of cation-exchange resin ($RCOOH$ or $R-SO_3H$) of tank 'A'. The Ca^{2+} and Mg^{2+} ions are exchanged with H^+ ions of the resin.

$$2RCOOH + Ca^{2+} \longrightarrow (RCOO)_2Ca + 2H^+$$
$$2RCOOH + Mg^{2+} \longrightarrow (RCOO)_2Mg + 2H^+$$
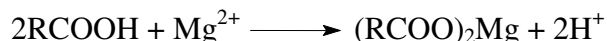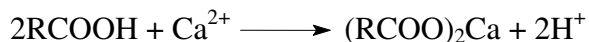
Thus, hardness producing cations (Ca2+ & Mg2+) are removed. The water coming out contains H^+, Cl^-, SO_4^{2-} and HCO_3^- ions.

Step-2: The hardwater is then passed through a bed of anion exchange resin ($R-OH$ or $R-NH_2$) of tank 'B'. The Cl^-, SO_4^{2-} and HCO_3^- ions are exchanged with OH^- ions of the resin.

$$R-OH + Cl^- \longrightarrow RCl + OH^-$$
$$2R-OH + SO_4^{2-} \longrightarrow R_2SO_4 + 2OH^-$$
$$R-OH + HCO_3^- \longrightarrow RHCO_3 + OH^-$$

Thus, hardness producing anions (Cl^-, SO_4^{2-} & HCO_3^-) are removed.

Step-3: The H^+ ions produced in tank 'A' combine with OH^- ions produced in tank 'B' to form water.

$$H^+ + OH^- \longrightarrow H_2O$$
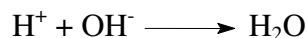
Thus, this process removes all types of hardness producing cations and anions present in water. The resulting water is known as demineralized or deionized water.

Demineralization of water.
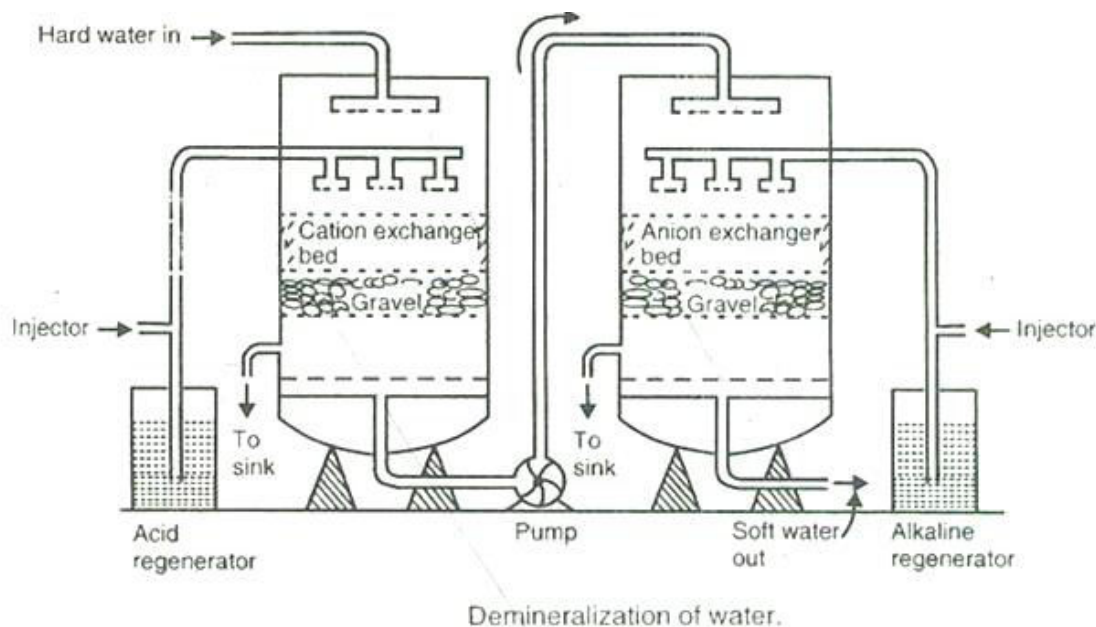
Regeneration of Resins: With constant use, the resins get exhausted. This can be regenerated as follows:

i) The exhausted cation-exchange resin can be regenerated by passing dilute HCl.

$$(RCOO)_2Ca + 2HCl \longrightarrow 2RCOOH + CaCl_2$$
$$(RCOO)_2Mg + 2HCl \longrightarrow 2RCOOH + MgCl_2$$

$CaCl_2$ and $MgCl_2$ are removed as wash.

ii) The exhausted anion-exchange resin can be regenerated by passing dilute NaOH.

$$RCl + NaOH \longrightarrow R\text{-}OH + NaCl$$
$$R_2SO_4 + 2NaOH \longrightarrow 2R\text{-}OH + Na_2SO_4$$
$$RHCO_3 + NaOH \longrightarrow R\text{-}OH + NaHCO_3$$

NaCl, Na_2SO_4 and $NaHCO_3$ are removed as wash.

Advantages:

1. It produces very pure water of hardness nearly 2 ppm.

2. Highly acidic and alkaline water can be treated by this process.

3. It is very good fit for use as boiler feed water.

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Disadvantages:

1. The equipment is costly and more expensive.

2. Highly turbidity water cannot be treated by this process.

3. The turbidity must below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.