## WATER PURIFICATION
## METHODS- ZEOLITES ION-EXCHANGE RESINS,

### Introduction:

Water is nature's most wonderful, abundant, useful compound and is an essential without it one cannot survive.

It occupies a unique position in industries. Its most important use is as an engineering material in the *steam generation.*

Water is also used as c*oolant* in power and chemical plants.

It is also 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, etc.

### Occurrence:

Water is widely distributed in nature. It has been estimated that about 75% matter on earth's surface consists of water. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90-95% of water.

### Sources of Water:

Different sources of water are:

*1. Surface Waters:* Rain water (purest form of natural water), River water, Lake Water, Sea water (most impure form of natural water).

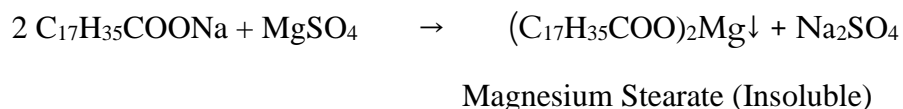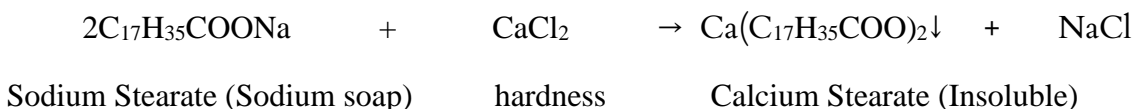*2. Underground Waters:* Spring and Well water. Underground waters have high organic impurity.

### What is hardness of

### water? Hardness:-

Hardness of water is a characteristic property by which water "*prevents lathering of soap".* It is defined as the soap consuming capacity of water.

**Causes:**

- The hardness of water is due to presence of certain salts (mainly bicarbonates, sulphates and Chlorides) of Ca, Mg and few other heavy metal salts dissolved in water.

- A sample of hard water when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) do not produce lather with soap, but on the other hand forms a white scum or precipitate.

- The precipitate is formed due to insoluble soaps of Ca and Mg.

Reactions:-

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

Sodium Stearate (Sodium soap) \qquad hardness \qquad Calcium Stearate (Insoluble)

$$2\ C_{17}H_{35}COONa + MgSO_4 \quad \rightarrow \quad (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$$

Magnesium Stearate (Insoluble)

Thus the water which does not produce lather with soap solution readily is called **HARD WATER** and water which lathers easily on shaking with soap solution is called **SOFT WATER**.
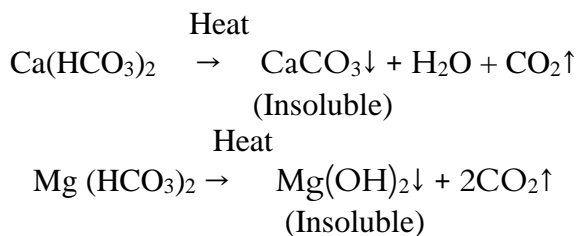
**Carbonate and non-carbonate hardness of water**

**Types of hardness**:

1. **Temporary** or **carbonate hardness**:-

- It is caused by the presence of dissolved bicarbonates of Ca, Mg and other heavy metals and carbonate of Iron.

- Temporary hardness is mostly destroyed by mere boiling of water i.e., when bicarbonates are decomposed, they yield insoluble carbonates or hydroxides, which are deposited as *'crust'* at the bottom of the vessel.

Reactions:-

$$Ca(HCO_3)_2 \quad \xrightarrow{Heat} \quad CaCO_3\downarrow + H_2O + CO_2\uparrow$$
(Insoluble)

$$Mg\ (HCO_3)_2 \xrightarrow{Heat} \quad Mg(OH)_2\downarrow + 2CO_2\uparrow$$
(Insoluble)

## 2. PERMANENT or NONCARBONATE HARDNESS:-

- It is due to presence of chlorides and sulphates of Ca, Mg, Fe and other heavy metals.
- It is not destroyed upon boiling.
- It can be eliminated by different techniques like, Lime Soda process, Ion exchange process, Zeolite process, etc.

*Total Hardness= Temporary Hardness + Permanent Hardness.*

**Expression of hardness of water**

**Equivalents of CaCO₃:-**

- The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of $CaCO_3$.

CaCO₃ is chosen as a standard because,

i) Its molecular weight (100) and ii) equivalent weight (50) is a whole

number, so the Calculations in water analysis can be simplified.

$$\text{Amount equivalent to } CaCO_3 = \frac{x \times 100}{\text{Molecular weight of hardness producing salt}}$$

**Where x $\longrightarrow$ Mass of hardness producing salt**

**Calculation of equivalents of CaCO₃:**

| Salt/ion | Molar mass | Chemical Equivalent Or Equivalent Weight | Multiplication factor for converting 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 |

**Units of hardness**:-

1. Parts Per Million (ppm):- is the parts of $CaCO_3$ equivalent hardness per $10^6$ parts of water i.e., 1ppm= 1 part of $CaCO_3$ equivalent hardness in $10^6$ parts of water.

2. Milligrams Per Litre (mg/L):- number of milligrams of $CaCO_3$ equivalent hardness present per liter of water.

   1mg/L=1mg of $CaCO_3$ equivalent hardness of 1L of water= $1kg=1000g=10^6mg$.

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

3. Clarke's degree ($^0Cl$):- the no. of grains (1/7000lb) of $CaCO_3$ equivalent hardness per gallon (10lb) of water or it is parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

   $\therefore$1 $^0Cl$= 1 grain of $CaCO_3$ eq hardness per gallon of water

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

4. Degree French ($^oFr$):- parts of $CaCO_3$ equivalent hardness per $10^5$ parts of water.

   $\therefore$$1^0$ Fr= 1 part of $CaCO_3$ equivalent hardness per $10^5$ parts of water.

5. Milli-equivalent per liter (meq/L):- is the number of milli-equivalents of hardness present per liter. 1meq/L= 1meq of $CaCO_3$ per liter of water

   = $10^{-3}$x 50 g of $CaCO_3$ eq. per liter

   = 50 mg of $CaCO_3$ eq. per liter = 50 mg/L of $CaCO_3$ eq. = 50ppm.

**Relationship between various units of hardness**:

1 ppm = 1 mg/L = 0.1$^o$ Fr = 0.07 $^oCl$ = 0.02 meq/L

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1 $^oCl$ = 1.433 $^oFr$ = 14.3 ppm = 14.3 mg/L = 0.0286meq/L

1 $^oFr$ = 10 ppm = 10 mg/L = 0.7 $^oCl$ = 0.2 meq/L

1 meq/L = 50 mg/L = 50 ppm = 5 $^oFr$ = 0.35 $^oCl$

**Ion exchange/deionization/demineralization:-**

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure and the functional groups attached to the chains are responsible for ion exchanging properties.
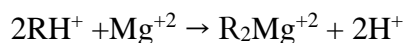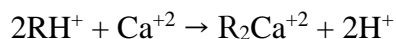
Resins containing acidic functional groups (-COOH, $-SO_3H$) are capable of exchanging their cations; those containing basic functional groups ($-NH_2=NH-$) as HCl are capable of exchanging their anions with other anions, which comes in their contact.
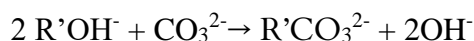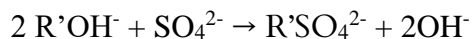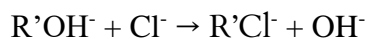
The ion exchange resins may be classified as :-

1)      **Cation Exchange Resins ($RH^+$):-** are mainly styrene-divinyl benzene co-polymers which on sulphonation or carboxylation become capable to exchange their $H^+$ ions with cations in the water.

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

**Process:-**

Raw water is first passed through cation exchanger and the removal of cations take place like $Ca^{+2}$, $Mg^{+2}$ etc takes place and equivalent amount of $H^+$ ions are released from this column to water. Thus,

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

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

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.

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

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

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

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

$H^+ + OH^- \rightarrow H_2O$

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

**Regeneration:**

After the deionization of certain amount of raw water the cation and anion exchangers will be exhausted.

Regeneration of cation exchanger is carried out by passing dil. HCl or $H_2SO_4$ solution into the bed.

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

The column is washed with deionized water and the washings ($Ca^{+2}$, $Mg^{+2}$ etc and $Cl^-$ or $SO_4^{2-}$) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH.

$$R_2 SO_4^{2-} + 2 OH^- \rightarrow 2R'OH^- + SO_4^{2-} \text{ (washing)}$$

The column is washed with deionized water and washings containing $Na^+$ and $SO_4^{2-}$ or $Cl^-$ ions is passed to sink or drain.

The regenerated ion exchange resins are then used again.



Fig. Deionisation of water
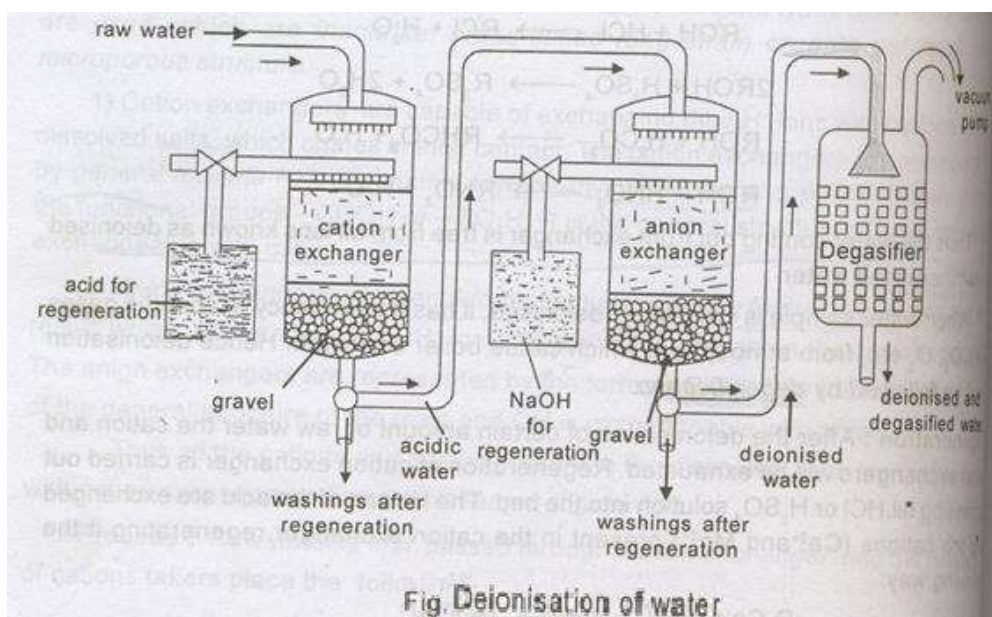
**Advantages:**

1) Highly acidic or alkaline water samples can be purified by this process.

2) The hardness possessed by the deionised water is 2ppm.

3) The deionised water is most suitable for high pressure boilers.

**Disadvantages**:

1) The ion exchanging resins are expensive hence the cost of purification is high.

2) Raw water should contain turbidity below 10ppm. Otherwise pores in the resin will be blocked and output of the process is reduced.

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## MIXED-BED DEIONIZER:

- In mixed-bed deionizers the cation-exchange and anion-exchange resins are intimately mixed and contained in a single pressure vessel. The thorough mixture of cation-exchangers and anion-exchangers in a single column makes a mixed-bed deionizer equivalent to a lengthy series of two-bed plants. As a result, the water quality obtained from a mixed-bed deionizer is appreciably higher than that produced by a two-bed plant.

## Permutit or Zeolite Process

Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly its sodium ions for $Ca^{2+}$ and $Mg^{2+}$, having the general formula $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. Common zeolite is $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$ and is known as natrolith. Others gluconites, green sand etc. are used for water softening. Zeolites are represented as $Na_2Ze$

Artificial Zeolite used for softening purpose is permutit. These are porous and glassy and have greater softening capacity than green sand. They are prepared by heating together with china clay, feldspar and soda ash.

**Method of Softening**: Hard water is passed through a bed of zeolite at a specific rate at ordinary temperature; the hardness causing cations i.e., $Ca^{2+}$ and $Mg^{2+}$ are exchanged for $Na^+$ and it is converted to $CaZe$ and $MgZe$.

The reactions taking place the softening process are as follows-

$Ca(HCO_3)_2 + Na_2Ze \rightarrow CaZe + 2NaHCO_3$

$MgSO_4 + Na_2Ze \rightarrow MgZe + Na_2SO_4$

$CaCl_2 + Na_2Ze \rightarrow CaZe + 2NaCl$
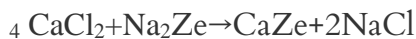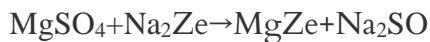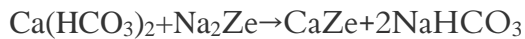
After some time, when the zeolite is completely changed into calcium and magnesium zeolites, then it gets exhausted (saturated with $Ca^{2+}$ and $Mg^{2+}$ ions) and it ceases to soften water. It can be regenerated and reused by treating it with a 10% brine (sodium chloride) solution. Regeneration reactions are

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$
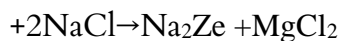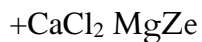
**Advantages-**

It removes the hardness almost completely (about 10 ppm hardness). The process automatically adjust itself for variation in hardness of incoming water.

This process does not involve any type of precipitation, thus, no problem of sludge formation occurs.

**Limitations-**

1) Raw material must be free from turbidity and suspended impurities.

2) Highly acidic water is not suitable as it affects mineral.

3) Zeolites of iron and manganese cannot be easily regenerated by passing NaCl solution. Hence iron and manganese impurities in the water to be treated must be minimum.
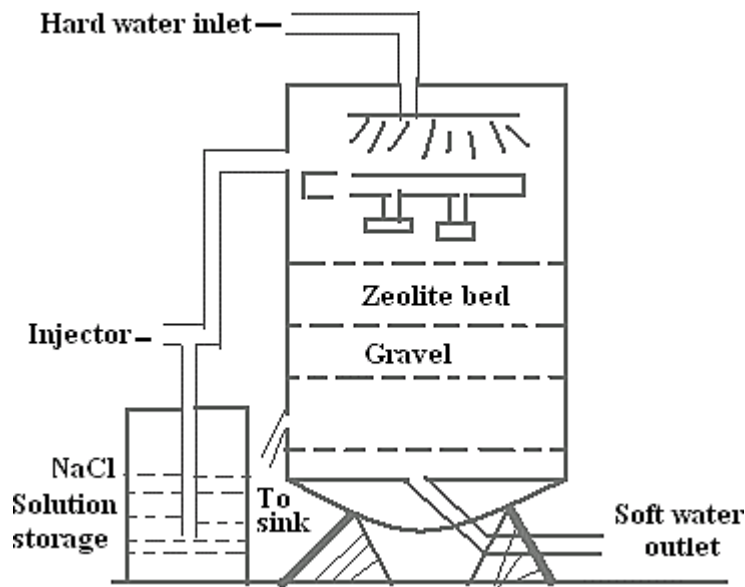


Fig: Zeolite process

# 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".** Ex. Sea water (contains an average of about 3.5% salts) is an example of brackish water.

It is totally unfit for drinking purpose.

Commonly used methods for desalination of brackish water are:-

1)   Electro dialysis

2)   Reverse Osmosis

## *Reverse osmosis:-*

When two solutions of unequal concentrations are separated by a semipermeable membrane (which does not permit selectively the passage of dissolved solute particles i.e., molecules, ions etc) flow of solvent takes place from dilute to concentrated sides, due to Osmosis.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses i.e., solvent is forced to move from concentrated side to dilute across the membrane. This is the principle of reverse osmosis.

Thus, in reverse osmosis, pure solvent (water) is separated from its contaminants, rather than removing contaminants from water. This membrane filtration is also called **"Super/ Hyper filtration".**

*Method:*

In this process, pressure (15-40 kg/cm$^2$) is applied to sea water/impure water (to be treated) to force its pure water through the semi-permeable; leaving behind the dissolved solids (both ionic and non-ionic). The principle of reverse osmosis as applied for treating saline/sea water is as follows: given in fig above.

The membrane consists of very thin film of cellulose acetate, affixed to either side of a perforated tube. Superior membranes recently developed are made of polymethacrylate and polyamide polymers have come into use.

**Advantages:**

1) Reverse osmosis process has distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.

2) It removes colloidal silica, which is not removed by demineralization.

3) The life time of membrane is quite high, about 2 years.

4) The membrane can be replaced within a few minutes thereby providing nearly uninterrupted water supply.

5) Low capital cost, simplicity, low operating cost and high reliability.

6) The reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.
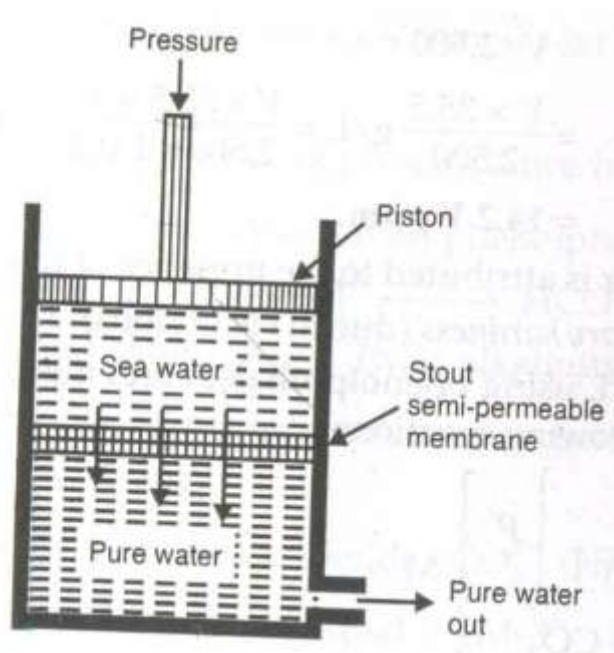


**Diagram for Reverse Osmosis**

**References:**

1. S. S. Dara, A Text book of Engineering Chemistry, S. Chand & Co Ltd., New Delhi, 20th Edition, 2013.

2. Teh.Fu.Yen, Chemistry for Engineers, Imperial College Press, 2008.

3. O.V. Roussak and H.D. Gesser, Applied Chemistry-A Text Book for Engineers and Technologists, Springer Science Business Media, New York, 2nd Edition, 2013.