INTRODUCTION

WATER CHEMISTRY

Water is surely God's greatest gift to mankind. The very existence of life cannot be imagined without water. One can live without food, shelter or any other thing but life without water is just not possible. Even our body contains around 70% water in it. From an engineer's point ofview, water is no less important. It is required in boilers for production of steam, which acts as a source of energy, as a coolant in many power and chemical plants, in steel, paper, testile, ice and many other such industries. Despite its incredible importance, water is receiving least attention and is getting contaminated in ways beyond description.

Water (H_2O) is a polar inorganic compound which is a tasteless, odorless liquid and colorless compound at room temperature. It is the most abundant substance on earth and hte only common substance ot exist as a solid, liquid, and gas on earth's surface. It si also thr third most abundant molecule in the universe.

Water molecules form hydrogen bonds with each other and are strongly polar. Its hydrogen bonding imparts many unique properties, such as having a solid form less dense than its liquid form, alternatively high boiling point of 100°C for its molar mass, and a high heat capacity.

1. Composition of water
2. Structure, bonding and shape of water molecule
3. Physical properties
4. Hardness of water
5. Polarity and hydrogen bonding of water and ice
6. Density ofwater is maximum at 4 degree Celsius
7. Autoionization of water
8. Levelling effect of water and acid base character
9. Amphiprotic nature
10. Chemical properties of water
11. Water as a solvent

COMPOSITION OF WATER

Water contains only hydrogen and oxygen. Both the elements have natural, stable and radioactive isotopes. Hydrogen has three isotopes namely hydrogen ('H), Ductirum (^{2}D) and Tritum (^{3}T), whereas opxygen exist ni the form of five isotopes i.c. ^{14}O, ^{15}O, ^{16}O, ^{17}O, ^{18}O Due ot these isotopes water molecule can exist as H_2O with molecular mass of 18 and D_2O with molecular mass of 20. There are some other forms HDO, HTO etc.

The most common form is H_2O (99.78%), D_2O exist only small amount (0.022%) and other forms exists in traces only.

D_2O is called heavy water and it is produced by enrichment from natural waters. It has importance because it is used in nuclear technology as a moderate.

STRUCTURE, BONDING AND SHAPE OF H_2O MOLECULE

In water, the central atom is oxygen is bonded to two hydrogen atoms. The electronic configuration of H-atom is Is' and that of oxygen atom in the ground state is $1s^2 2s^2 2p^4$ represented in Fig. 5.1.
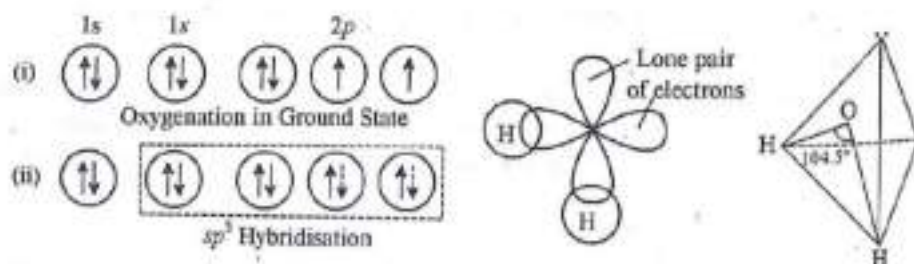

Fig. 5.1. Tetrahedral (V-shaped) molecule of water formed by sp³ hybridisation.

In Figure 5.1., the dotted arrows represent electrons supplied by hydrogen atoms. The underlying 3-orbitals are not shown. Note-that the shape of the orbital containing lone pair of electrons is different from the shape of the orbital containing a bond pair of electrons. Thus,there are two unpaired electrons which can form two bonds with hydrogen atom, without involving any excitation of the oxygen atom. But, in that case, the water molecule involving only two orbitals, should have been linear and nonpolar like BeF_2. This is not so actually. Water molecule is known to have a bent structure and it is highly Polar. This is explained on the basis of hybridisation. The central oxygen atom in water molecule has four orbitals, the two containing lone pairs, and the other two containing bond pairs. These orbiters undergo sp^3 Hybridisation to give four sp^3 Hybrid orbitals of equivalent energy. According to Sidwick Powell theory, these hybridised orbital give rise to a tetrahedron structure with two corners, occupied by hydrogen atoms, and two corners occupied by lone pair of electrons.

Since the force of repulsion between the two lone pairs of electrons among themselves is more than the force of repulsion between a lone pair and a bond pair which in turn is more than the force of repulsion between to bond pairs of electron, the two electron will press the two bond pairs inwards, resulting the bond of water reduced from 109.5° to 104.5°.

PHYSICAL PROPERTIES

Most of the unique properties of water are due to presence of H-bonding between its molecules. Some of the important properties are discussed below:

1. Freezing and Boiling Point of Water

Water freezes at 0°C and boils at 100°C. In fact, water's freezing and boiling points are the baseline with which temperature is measured. Water is unusual ni that the solid form, ice, is less dense than the liquid form, that is why ice floats on water. It is due ot the property of H-bonding in water that has been explained in next article.

2. Specific heat of water

Water has high specific heat value. This means that water can absorb a lot of heat before it begins ot get hot That is why water is used in industries and in car radiator as a coolant. The highest specific heat value of wateralsohelpniregulatinghterateatwhcihair changes temperature. The temperature change in between seasons is gradual rather than sudden, especially near the oceans because of high specific heat value of water.

3. Viscosity and surface tension

The substance which contain hydrogen bonding exist as associated molecules. So, there flow becomes comparatively difficult In other words,they have higher viscosity and high surface tension.

Water has a very hgih surface tension. In other words, water is sticky and elastic intends to clamp together and drops rather than spread out in a thin. Film surface tension is responsible for capillary action which allows the water to move through the roots of plants and through the tiny blood vessels in our bodies.

4. Polar Characteristics

Due to its polar character, Ionic salt dissolved in it and are ionised in it. Other polar substances such as alcohols and acids also get dissolved in it. Water is a very good solvent, it is rarely pure, and some of the properties of impure water can vary from those of the pure substance. There aare also many compounds which are insoluble in water, such as fats, oils and other non-polar substances.

5. Amphoteric Nature

Water is amphoteric, meaning that it is both an acid and a base- it produces H+ and OH- ions by self-ionization. This means the product of the concentrations of H+ and OH- is constant at a given temperature. the pH value of pure water is 7, which means it contains equal number of H+ ions and OH- ions in it and is neutral in nature. Based on the above mentioned physical properties of water, the following conclusions are important:

1. The freezing point, boiling point, heat of fusion and heat of vaporization of water are abnormally higher than those of the hydrides of the other elements of the same group 16 such as H2S, H2Se, H2Te, etc. This is due to the presence of intermolecular hydrogen bonding in H2O molecules which is, however, absent among the molecules of H2S,, H2Se, H2Te, etc.

2. Water has a higher specific heat, thermal conductivity and surface tension than most other liquids. These properties allow water to play a vital role in the biosphere. For example, the high heat of vaporization and the high heat capacity of water are responsible for moderation of the climate and body temperature of living organisms.

3. Water because of its high dielectric constant (78.39) has the ability to dissolve most of the inorganic (ionic) compounds and is, therefore, regarded as a universal solvent. Whereas solubility of ionic compounds takes place due ot ion-dipole interactions (i.e. salvation of ions), the solubility of covalent compounds such as alcohols, amines, urea, glucose, sugar, etc. takes place due to the tendency of these molecules to form hydrogen bonds with water.

4. Heavy water (D2O) has slightly higher values of phvsical constants because of its higher molecular mass as compared to that of ordinary water (H2O).

HARDNESS OF WATER

Water which does not produce lather with soap solution readily, but forms a white scum or precipitate is called hard water.

It is due to the presence of some dissolved salts in it. Soaps are sodium and potassium salts of higher fatty like steric acid, oleic acid and palmitic acid. When hard water is treated with soap, it does not produce lather, rather soap gets precipitated in the form of souls of calcium and magnesium. No lather is formed until all these ions are completely removed and hence a large amount of soap gets wasted in the process.

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

(Calcium chloride from hard water)   Sodium stearate (Soap)   Calcium stearate (Insoluble ppt.)

Search precipitates are not formed with detergents, which our cell phone needs of long chained alcohols. Water, easily forms lather which show is called soft water. Such water does not contain calcium and magnesium salts in it. The process of removing hardness from water is called softening of water.

The main difference between the two types of water are:

Hard Water	Soft Water
1. Water which does not produce lather with soap solution readily, but forms a white scum or precipitate is called "Hard Water".	1. Water which lathers easily on shaking with soap solution, is called "Soft Water".
2. Hard water contains dissolved salts of calcium and magnesium in it.	2. Soft water does not contain dissolved calcium and magnesium salts in it.
3. In hard water, cleansing quality of soap is lowered and a lot of it is washed during washing and bathing.	3. In soft water, cleansing quality of soap s not lowered and so soap is not wasted during washing and bathing.
4. Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking.	4. Less fuel and time are required for cooking in soft water.

Types of Hardness
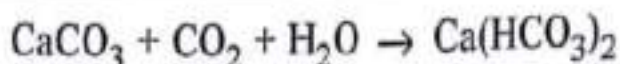
Hardness of water is of two types :
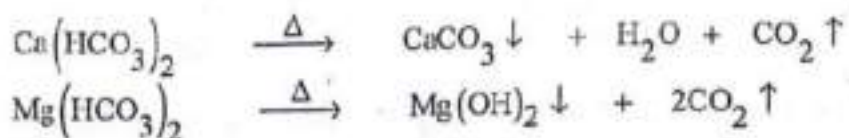
(A) Temporary hardness

(B) Permanent hardness

Temporary hardness (Carbonate Hardness or Alkaline Hardness):

It is caused due to the presence of bicarbonates of calcium and magnesium. It is called temporary hardness because it can be removed easily by boiling.

The presence of bicarbonates ni water is due to dissolution of insoluble carbonates in the presence of atmospheric carbon dioxide.

,
$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

On boiling, bicarbonates of calcium and magnesium, get decomposed to give insoluble, carbonates or hydroxides. These cabinets or hydroxide is being insoluble or removed in form of precipitates and thus temporary hardness is removed.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$
$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

Temporary hardness is also called carbonate, hardness or alkaline hardness. It is due to the presence of bicarbonates of calcium and magnesium, carbonates of iron and other heavy metals to small extent and hydroxides of the hardness producing metal ions. It can be determined by titration and standard acid solution using methyl orange as an indicator.

Permanent hardness (non-carbonate or non-alkaline hardness):

It is due to the presence of chlorides and sulphates of calcium and magnesium. It is called permanent hardness, since it cannot be removed by boiling.

However, it can be removed by using various chemical agents. Calcium and magnesium salts are not the only salts responsible for hardness. They are mentioned because they are most commonly present. However, all soluble salts of heavy metals cause hardness. It is also called non-carbonate or non-alkaline hardness. It can be determined by subtracting the alkaline hardness from the total hardness.

Hard water has to softend before it is used for domestic or industrial purpose, because hard water not only consumes more soap or detergent used for washing clothes but it shortens the life of fabrics and clothes. Hard water can damage the equipments used in industries.

Hard water can damage the equipments used in industries. Water is used in boilers for generating steam, but hard water, if used, will form scales and sludges in the pipelines which give rise many harmful effects. So, hard water must be converted to soft water before using it for domestic or industrial purpose.

Disadvantages of Hard Water:

Hard water contains large amounts of bicarbonates, sulphates and chlorides of calcium and magnesium dissolved in it. These dissolved salts cause undesirable effects both in houses and industries. Hard water causes number of problems in domestic use, industrial use and in boilers. These problems are explained below:

1. **Problems in domestic use**
Hard water causes many undesirable efects when used ofr domestic purposes. mSoe instances are given below:
A. Wastage of Soap: a large amount of soap is wasted when hard water is used for washing purpose as it does not produce lather with soap readily.
B. Spoiling clothes: soap reacts with hard water to form insoluble calcium and magnesium soap which sticks to the clothes in the form of scum.These scum are not easy to remove and make dirty marks on the clothes.
C. Deposition in kettles: calcium and magnesium salts form a solid precipitate inside the kettles if hard water is boiled in it. It is due to the formation of carbonate and hydroxide in boiling water.
D. Cooking: pulses and other vegetables do not cook well in hard water.

2. **Problems in Industrial use:**
A. Paper industry: In paper industry, water is used along with soap for sizing the paper. If hard water is used, calcium and magnesium source present in it, waste a good amount of soap by forming insoluble precipitate.
B. Textile industry: Water is used in textile industry for cleaning, washing and whitening of yarn. For such purposes soap is required. If hard water is used much soap is wasted.
C. Dyeing: if hard water is used for dyeing purposes, salts of calcium and magnesium spoil the desired shade and thus the dyed clothes do not give a homogenous look.
D. Choking and clogging problem: Water pipes are blocked due to the precipitation of source, during boiling of hard water. This involves extra cost for maintenance and repair of water pipes.

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3. Problems in Boilers: huge quantity of water is used in boiler for generation of steam. If hard water is used in the boiler a number of difficulties arise which are listed as:

A. scale and sludge formation

B. Boiler corrosion.

C. Priming and foaming

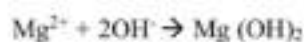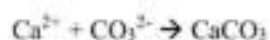D. Caustic embrittlement.

WATER SOFTENING METHODS

Softening of Water

Water used for industrial purposes should be pure. ie., It should be free from hardness, scale forming substances and corrosive agents like dissolved O_2 etc., The process of removing hardness producing salts from water is known as softening of water.

CLARK 'S PROCESS

It is the process of liming hard water. It is used to decreases the alkalinity of water. During lime treatment the following reactions occur.

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

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$

Softening of Water can be done by the following two ways

1. External conditioning or External treatment
2. Internal conditioning or Internal treatment.

EXTERNAL CONDITIONING

It involves the removal of hardness producing salts from the water before feeding into the boiler. The external treatment can be done by the following methods.

a) Lime soda process

b) Zeolite or Permutitprocess

c) Demineralisation (or) Deionization.

The above said processes are the examples of ionexchange process of water softening. In an ion-exchange process, a reversible exchange of ions taking place between a stationary solid phase and an external liquid mobile phase.

a) **Lime-Soda Process**

Lime-Soda process is a very important method used for the softening of water.
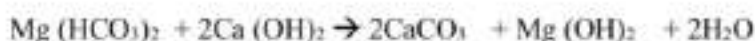
[i] **Principle**

The lime-soda process involves the chemical conversion of all the soluble hardness-causing salts by the addition of soda and lime into insoluble precipitates which could easily be removed by settling and filtration.

In this process, water to be softened is treated with calculated amounts of lime $Ca(OH)_2$ and soda Na_2CO_3. For quick completion of reactions, the reagents may be used in 10 % excess. The functions of lime and soda are as follows.
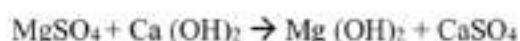
Functions of lime

Lime removes temporary hardness, permanent magnesium hardness, dissolved iron and aluminium salts, dissolved CO_2 and H_2S gases and free mineral acids present in water. The reactions involved are as follows 1. Removal of temporary calcium and magnesium hardness
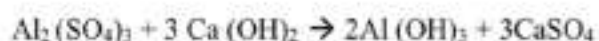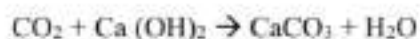
$$Ca\,(HCO_3)_2 + Ca\,(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

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

Removal of permanent magnesium hardness

$$MgCl_2 + Ca\,(OH)_2 \rightarrow Mg\,(OH)_2 + CaCl_2$$

$$MgSO_4 + Ca\,(OH)_2 \rightarrow Mg\,(OH)_2 + CaSO_4$$

Removal of dissolved iron and magnesium salts

$$Al_2\,(SO_4)_3 + 3\,Ca\,(OH)_2 \rightarrow 2Al\,(OH)_3 + 3CaSO_4$$

$$FeSO_4 + Ca\,(OH)_2 \rightarrow Fe\,(OH)_2 + CaSO_4$$

$$2Fe\,(OH)_2 + H_2O + 1/2O_2 \rightarrow 2Fe\,(OH)_3$$

Removal of dissolved CO_2 and H_2S

$$CO_2 + Ca\,(OH)_2 \rightarrow CaCO_3 + H_2O$$

$$H_2S + Ca\,(OH)_2 \rightarrow CaS + 2H_2O$$

Removal of free mineral acid

$$2HCl + Ca\,(OH)_2 \rightarrow CaCl_2 + 2H_2O$$

$$H_2SO_4 + Ca\,(OH)_2 \rightarrow CaSO_4 + 2H_2O$$
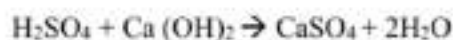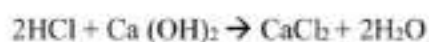
## Functions of soda

During the removal of Mg^{2+}, Fe^{2+}, Al^{3+}, HCl and H_2SO_4 by lime, permanent calcium hardness is introduced in the water due to formation of calcium salts. The permanent calcium hardness thus introduced on account of the treatment of water with lime and the permanent calcium hardness already present in water before lime treatment are removed by soda. The reactions involved are as follows,

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
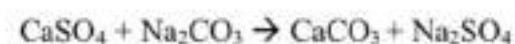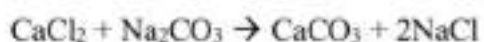
The chemical reactions involved in the lime-soda process are quite slow. Moreover, the precipitates formed [particularly of $CaCO_3$ and $Mg(OH)_2$ are fine and have a tendency to form super-saturated solutions. This results in after deposition of these precipitates later in the pipes and boiler tubes leading to their clogging and corrosion. These drawbacks of the process can be overcome by

o thorough mixing of chemicals and water.
o allowing proper time for the completion of reactions. o the use of accelerators such as active charcoal and
o the use of coagulants such as alum or $NaAlO_2$.

[ii] Process
The lime-soda process can be carried out both at room temperature as well as at higher temperatures. The process carried out at room temperature is called cold lime-soda process and that carried out at 94°-100°C is called hot lime-soda process.

1. Cold Lime-Soda Process

In this method, water to be softened is treated with calculated quantities of lime and soda at room temperature. Small amounts of a coagulant such as alum, aluminium sulphate, sodium aluminate etc., are also added.

The coagulant helps the finely divided precipitate formed in the process to flocculate. Sodium aluminate also helps in the removal of silica and oil present in water.

Method

The mixture of water, calculated quantities of lime and soda and a small amount of a coagulant is fed from the top into inner chamber of a vertical circular tank (Fig.1).

The chamber is provided with a vertical rotating shaft carrying a number of paddles to ensure vigorous stirring and continuous mixing of water with the chemicals added.
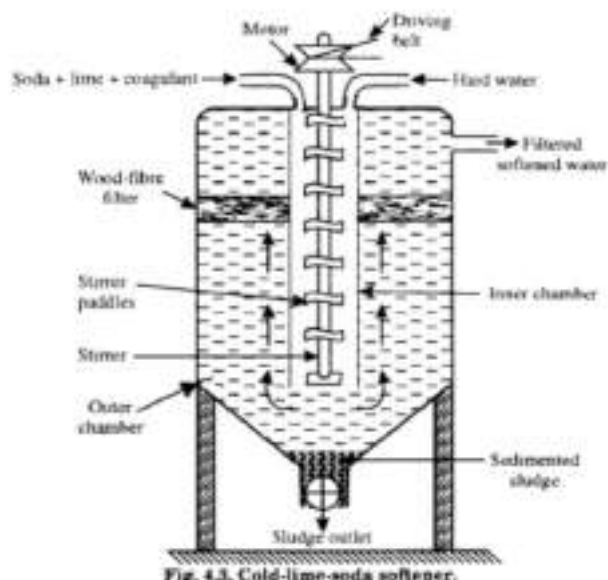
Fig. 4.3. Cold-lime-soda softener.

Fig 1 Cold Lime-Soda Process

The chemical reactions take place and the hardness producing salts get converted into insoluble precipitates which accumulate in the form of a heavy sludge.

As the softened water reaches the outer coaxial chamber, it rises upwards and is filtered by a wood-fibre filter and finally taken out from an outlet provided at the top of the outer cylinder.

The heavy sludge settles down at the bottom of the outer chamber and is taken out through an outlet. The softened water obtained from this process contains a residual hardness of about 50- 60 ppm.

2. Hot Lime-Soda Process

In this process, water is treated with the softening chemicals at a temperature of 94°-100°C. Since the process is carried out at a temperature close to the boiling point of the solution, the reaction proceeds faster and the softening capacity of the process increases several times.
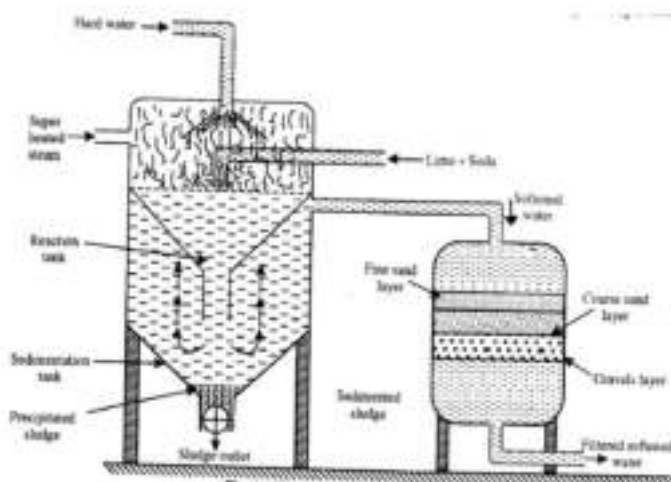

Fig.2 Hot Lime-Soda Process

At this temperature, the viscosity of water is much less than that at room temperature. Hence, rate of aggregation of particles increases and there is hardly any need of adding any coagulant. Moreover, the dissolved gases also escape to some extent at the temperature of the process.

Method

A typical hot lime-soda water softening plant is shown in Fig.2. It consists of
> a reaction tank
> a conical sedimentation vessel and
> a sand filter.
Raw water is fed from the top into the reaction tank where it is thoroughly mixed with calculated quantities of softening chemicals and is agitated with superheated steam. The reactions take place and water gets softened. The softened water containing sludge then enters into the sedimentation vessel where sludge settles down.

The softened water rises up in the vessel, while precipitated sludge is taken out through an outlet provided at the bottom of the vessel. The softened water is then taken to a sand filter which ensures the complete removal of the sludge from softened water.

The softened water obtained from this process contains a residual hardness of 15-30 ppm.

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Advantages of the process

The hot lime-soda process has the following advantages.

>> The process is much faster as compared to the cold sodalime process.

>> It is very economical.

>> Lesser amounts of coagulants are needed.

>> The process increases the pH value of the treated water, thereby reducing the corrosion of distribution pipes.

>> To certain extent, iron and manganese are also removed from water.

>> Much of dissolved gases in water are also removed.

>> Due to an increase in the pH, the amount of pathogenic bacteria in treated water also gets reduced.

Disadvantages of the process

The hot lime-soda process has the following disadvantages.

>> Disposal of large amounts of sludge formed in the process poses problems.

>> The treated water obtained by this process is not completely softened. It still contains a residual hardness of about 15-30 ppm, which is not good for boilers.

Table 1.4 Difference between cold and hot lime soda process

Cold L-S Process	Hot L-S Process
Done at room temperature.	Done near the boiling point of water.
Reactions are slow and takes hours to complete.	Fast and takes only 15 minutes.
Precipitate is finely divided and therefore coagulants are needed.	Coarse precipitate coagulants not needed.
Tank size is large.	Small and compact.
Residual hardness 50 to 60 ppm.	15 to 30 ppm
Chemicals are consumed by dissolved gas,CO_2 etc.,	CO_2 and temporary hardness are automatically removed.

b) Zeolite (or) Permutit Process

Zeolites are naturally occuring hydrated sodium aluminium silicate, $Na_2O.Al_2O_3.x SiO_2yH_2O$ where $x = 2$ to 10 and $y = 2$ to 6. The synthetic form of zeolite is known as permutit. Synthetic zeolite is represented by Na_2Ze. The sodium ions which are loosely held in Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water. Natural zeolites are non-porous.

Synthetic zeolites are porous and gelly structure. They are prepared by heating together china clay, feldspar and soda ash. These zeolites are higher exchange capacity per unit weight than natural zeolites.

Process

In this process, the hard water is passed through a bed of sodium zeolite (Na_2Ze). The hardness causing ions (Ca^{2+}, Mg^{2+}) in hard water is replaced by loosely held sodium ions in zeolite bed(Fig.3.7). The outgoing soft water contains only sodium ions.

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

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$$

$$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl$$

$$Na_2Ze + MgCl_2 \rightarrow MgZe + 2NaCl$$

$$Na_2Ze + CaSO_4 \rightarrow CaZe + Na_2SO_4$$

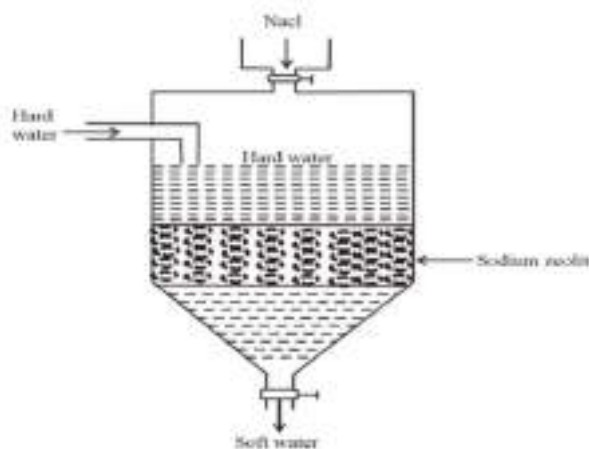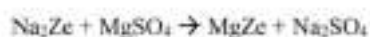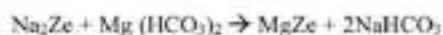$$Na_2Ze + MgSO_4 \rightarrow MgZe + Na_2SO_4$$

Fig. 3 Zeolite process

Regeneration

After the softening process, the zeolite is completely converted into calcium and magnesium zeolites and it gets exhausted. At this stage the hard water supply is stopped and the exhausted bed is regenerated by treating with a concentrated 10% brine (NaCl) solution.

$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$$
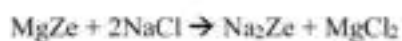
Exhausted	Regenerated
Zeolite	Zeolite

Advantages of the process

>> This process removes hardness upto 10ppm.
>> Operational cost is less
>> The equipment used is compact No sludge formation.
>> The plant can be connected to water supply line as it avoids double pumping. Requires less time for softening
>> Maintenance and operation is easy
>> The process automatically adjusts itself to waters of different hardness.

Limitations of the process

>> The process exchanges only Ca^{2+} and Mg^{2+} ions with Na ions. It does not remove the acidic ions like HCO_3^-, CO_3^{2-}.
>> Water containing such ions is not much suitable for boilers as it may cause corrosion of boilers. Turbid water, if used clogs the pores of the Zeolite bed, making it inactive.
>> Highly acidic or alkaline water will destroy the Zeolite bed.
>> Coloured ions (Fe^{2+} and Mn^{2+}) if present in water should be removed first and then the water is sent to the bed, as these ions convert sodium Zeolite into their respective Zeolites (FeZe, MnZe) which are difficult to be regenerated.
>> High capital cost

c) Demineralization (or) Deionization Process

In this method ion exchange resins are used as softening material. In this process cations like Ca^{2+}, Mg^{2+} and anions like Cl^-, SO_4^{2-} which are responsible for hardness are removed respectively by cation exchange resins and anion exchange resins. Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure. The functional groups attached to the chains are responsible for the ionexchanging properties.

Cation exchange resins (RH+)

Resin containing acidic functional groups (-COOH, -SO3H) are capable of exchanging their H^+, ions with cations of hard water.

 Example: (i) Sulphonated coals.
(ii) Sulphonated polystyrene.
R-SO3H ; R-COOH ≡ RH2
Anion exchange resins (ROH-)
Resins containing basic functional groups (-NH2, -OH) are capable of exchanging their OH- ions with the anions of hard water.
Example: (i) Cross-linked quaternary ammonium salts. (ii) Urea-formaldehyde resin

R-NR₃OH ; R-OH ; R-NH₂ ≡ R(OH)₂

Process
The hard water first passed through a cation exchange column (Fig.1.8) which absorbs all the cations like Ca^{2+}, Mg^{2+}, Na^+, K^+ etc., present in the hard water.

$$2RH^+ + CaCl_2 \rightarrow R_2Ca + 2HCl$$

$$2RH^+ + MgSO_4 \rightarrow R_2Mg + H_2SO_4$$

$$RH^+ + NaCl \rightarrow RNa + HCl$$
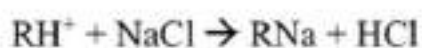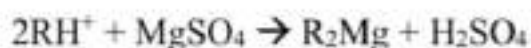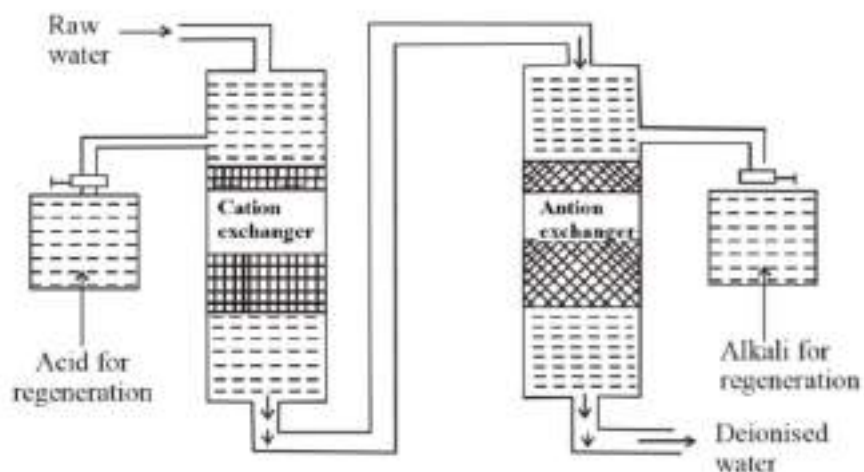
Fig.4 Demineralisation process

The cation free water is then passed through an anion exchange column, which absorbs all the anions like Cl^-, SO_4^{2-} etc., present in the water.

$$2ROH^- + 2HCl \rightarrow 2RCl + 2H_2O$$

$$2ROH^+ + H_2SO_4 \rightarrow R_2SO_4 + 2H_2O$$
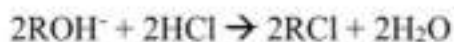
Thus the water coming out from the anion exchange is free from both cations and anions. This water is known as ionfree water (or) deionised (or) demineralised water.

Regeneration

When the cation exchange column is exhausted, it can be regenerated by passing a solution of dil.HCl (or) dil.H2SO4.

$$R_2Ca + 2HCl \rightarrow 2RH^+ + CaCl_2$$

$$R_2Mg + H_2SO_4 \rightarrow 2RH^+ + MgSO_4$$

$$RNa + HCl \rightarrow RH^+ + NaCl$$
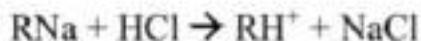
When the anion exchange column is exhausted, it can be regenerated by passing a solution of dil. NaOH.

$$2RCl + 2NaOH \rightarrow 2ROH^- + 2NaCl$$

$$R_2SO_4 + 2NaOH \rightarrow 2ROH^- + Na_2SO_4$$

Dr. Nancy's Chemistry Notes

Advantages

>> The process can be used to soften highly acidic (or) alkaline water.

>> It produces water of very low hardness (2ppm). Disadvantages:

>> The equipment is costly and more expensive chemicals are needed.

>> If the water contains turbidity, the output is low due to clogging.

MIXED BED DEIONIZER

This comprises of a single cylinder. This contains a bed of intimate mixture of cation exchanger resin and anion exchanger resin. When water is passed through this bed it comes in contact many times with both cation and anion exchangers alternatively. The effect of mixed bed exchanger is equivalent to passing through a series of several cation and anion exchangers (multiple cycle). The outgoing water from the mixed bed contains even less than 1ppm of dissolved salts.

Regeneration

When the resins are exhausted, the mixed bed is back washed by forcing water in the upward direction. The lighter anion exchanger gets displaced to form an upper layer. The heavier cation exchanger forms the lower layer. There after the anion exchanger is regenerated by passing caustic soda solution from the top and then rinsed and reused. The lower cation exchanger bed is then regenerated by passing sulphuric acid solution and rinsed and then reused. The two beds are then mixed again by forcing compressed air. The bed is then reused.

Table 1.5 Comparison of Zeolite & Demineralization process

Zeolite (or) Permutit Process	Demineralization (or) Deionization Process
It exchanges only cations.	Both the cation and anoin exchanges are available.
Residual hardness 1-5 ppm.	Residual hardness 0-2 ppm.
Cost of plant and material high.	Cost higher.
Operating expenses are low.	Operating expenses high.
Acidic water cannot be treated.	Even highly acidic or highly alkaline water can be treated.
Treated water contains more dissolved solids	No dissolved solids.

Characteristics of Soft, Deionised and Distilled Water

Soft Water
>> It does not contain hardness producing ions like Ca , Mg
>> It may contain Na , K , SO_4, Cl ions and microorganisms.

Deionised water (mineral water)
>> It does not contain any ions including hardness producing cations.
>> It may contain some amount of micro-organisms.

Distilled Water
>> It does not contain any ions and micro-organisms, because it is prepared by condensing the vapour of boiling water.

Hard Water
It contains all hardness producing ions.

Specification for Drinking water

>> The common specifications recommended by the US Public health for Drinking water are given below.
>> Water should be clear and odourless.
>> It should be cool.
>> It should be pleasant to taste.
>> Turbiditiy of water should not exceed 10 ppm.
>> pH of the water should be in the range of 7.0 – 8.5.
>> Chloride and sulphate contents should be less than 250 ppm.
>> Total hardness of the water should be less than 500 ppm.
>> Total dissolved solids should be less than 500 ppm.
>> Fluoride content of the water should be less than 1.5 ppm.
>> The water must be free from disease producing bacteria.
>> Water should be free from objectionable dissolved gases like H_2S.
>> Water should be free from objectionable minerals such as lead, chromium, manganese and arsenic salts.

Estimation of Hardness of Water by EDTA Method

The hardness of water can be estimated by EDTA method. This is a reliable method because of its greater accuracy. In this method hardness is estimated by forming complexes. EDTA is Ethylene diamine tetra aceticacid.

Molecular structure of EDTA

$$HOOC-H_2C, HOOC-H_2C \diagdown N-CH_2-CH_2-N \diagup CH_2-COOH, CH_2-COOH$$

In this complexometric method, disodium salt of ethylene diamine tetra acetic acid is actually used.

Structure of disodium salt of EDTA

$$NaOOC-H_2C, HOOC-H_2C \diagdown N-CH_2-CH_2-N \diagup CH_2-COOH, CH_2-COONa$$

Principle

1. Disodium salt of EDTA forms complex with calcium and magnesium ions present inwater.
2. The indicator used in this titration is Eriochrome Black–T (EBT) which also form unstable complex with calcium and magnesium ions present in water, at pH value about8–10.
3. In order to maintain the pH, buffer solution [NH4Cl–NH4OH] mixture is added. Only at this pH such a complexation is possible.
4. pH=8–10

$$Ca^{2+}/Mg^{2+} + EBT \xrightarrow{} [Ca / Mg - EBT]$$

Indicator   Unstable complex (Bluecolour)
(Wine red)

This wine red colour solution is titrated against EDTA, EDTA replaces EBT indicator from [Ca / Mg - EBT] complex. The colour of the solution changes from wine red to steel blue at the end point.

pH=8-10

$$[Ca / Mg - EBT] + EDTA \longrightarrow [Ca / Mg - EDTA] + EBT$$

Unstablecomplex   Stablecomplex   (Steel blue)

(Winered)   (Colorless)
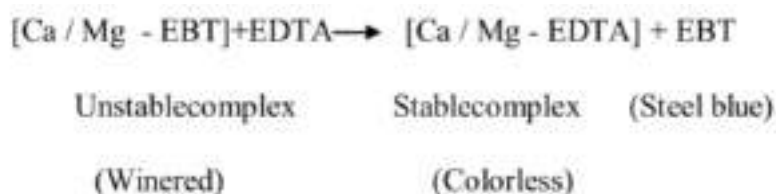
Reagents Required :

EDTA solution

It is prepared by dissolving 4 gms of EDTA in 1000 ml of distilled water.

Standard hardwater

1 gm of pure $CaCO_3$ is dissolved in minimum quantity of HCl and then made upto 1000 ml using distilled water.

1 ml of standard hardwater = 1mg of $CaCO_3$ equivalent hardness.

EBT indicator

0.5 gms of EBT is dissolved in 100 ml of alcohol.

Buffer solution:

67.5 gms of NH_4Cl and 570 ml of NH_3 are dissolved and the solution is made upto 1000 ml using distilled water.

Procedure

1) Standardisation of EDTA solution

20ml of Std. hard water is taken in a conical flask. 5 ml of buffer solution and a few drop of EBT indicator are added. The solution is titrated against EDTA taken in burette. The endpoint is the colour change from wine red to steel blue colour. Let the volume of EDTA consumed be V1 ml.

Calculation:

1ml of std.hard water = 1mg of CaCO$_3$

20 ml of std. hard water = 20 mgs of CaCO$_3$

20 ml of std. hard water consumes = V$_1$ml of EDTA V$_1$ml of EDTA consumes= 20 ml of Std hardwater.

$$= 20 \times 1 \text{ mg of CaCO}_3\text{eq. hardness}$$

1 ml of EDTA = 20/ v$_1$ mg / L CaCO$_3$ eq. hardness

2) Estimation of Total Hardness

20ml of sample hard water is pipetted out into a conical flask and titrated against EDTA taken in burette by adding the buffer and the indicator to get the end point. Let the volume of EDTA consumed be V2 ml.

Calculation

20 ml of sample hardwater = V$_2$ml of EDTA

$$= V2 \times 20/V1 \text{ mg of CaCO3 eq. Hardness}$$

In 1000 ml of water sample   = V2 $\times$ 20/ V1 $\times$ 1000/20 mg of CaCO3 eq.hardness

Total hardness= 1000 x V2/ V1 mg / L (or) ppm.

3) Estimation of Permanent Hardness

250ml of water sample is boiled off to a volume of 50 ml in a beaker to remove temporary hardness. The temporary hard salts settle down. Filter and wash thoroughly and make up the solution again to 250 ml. 20 ml of this solution which isfree from carbonate hardness is titrated against the EDTA as done before. Let the volume of EDTA consumed be V3 ml.

Calculation:

20 ml of boiled sample hard water consumes $= V_3$ ml of EDTA

$= V_3 \times 20 / V_1$ mg of $CaCO_3$ eq. hardness

In 1000 ml of water sample

$= V_3 \times 20 / V_1 \times 1000 / 20$ mg of $CaCO_3$ eq. hardness

$= 1000 \times V_3 / V_1$ mg/L (or) ppm.

Permanent hardness $= 1000 \times V_3 / V_1$ mg/L (or) ppm.

Estimation of Temporary Hardness

This can be calculated by using the following methods. Temporary Hardness = Total Hardness – Permanent Hardness

Temporary Hardness = $1000 \times V_2 - V_3 / V_1$ mg/L (or) ppm.

Advantages of EDTA method

>> This method is more accurate in the estimation of hardness of water than other methods rapid process.

>> It is convenient and more rapid process.