

KCE Society's COEIT, Jalgaon

Department of First Year Engineering (Basic Science)

Engineering Chemistry

Unit-I

Water Treatment

Chapter: 1. Water Treatment

Water is nature's most wonderful, abundant and useful compound. Of the many essential elements for the existence of human beings, animals and plants (wiz. air, water, food, shelter, etc.), water is rated to be of the greatest importance. Without food, human can survive for a number of days, but water is such an essential thing that without it one cannot survive.

Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. Probably, its most important use as an engineering material is in the 'steam generation '.

Water is also used a coolant in power and chemical plants. In addition to it, water is widely 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, fire-fighting, etc.

SOURCES OF WATER:

Surface waters:

(i). Rain water is probably the purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards through the atmosphere, it dissolves a considerable amount of industrial gases (like CO_2 , SO_2 , NO_2 , etc.) and suspended solid particles, both of organic and inorganic origin.

(ii). River water: Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers.

In general, the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

Underground waters:

A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it meet a hard rock, when it retreads upwards and it may even come out in the form of 'spring'.

Spring and well water (or underground water):

In general, is clearer in appearance due to the filtering action of the soil, but contain more of dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

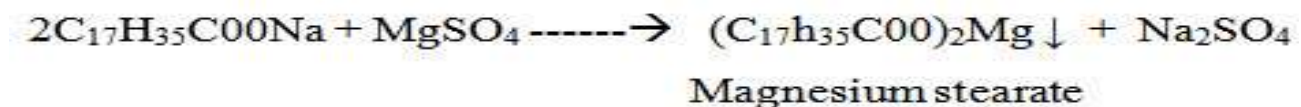
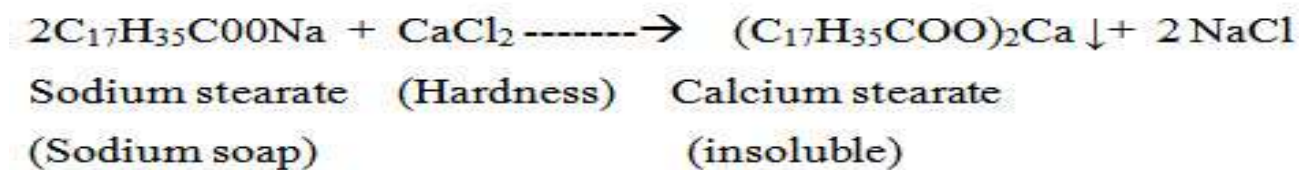
HARDNESS OF WATER:

Hardness in water is that characteristic, which prevents the lathering of soap.

This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it.

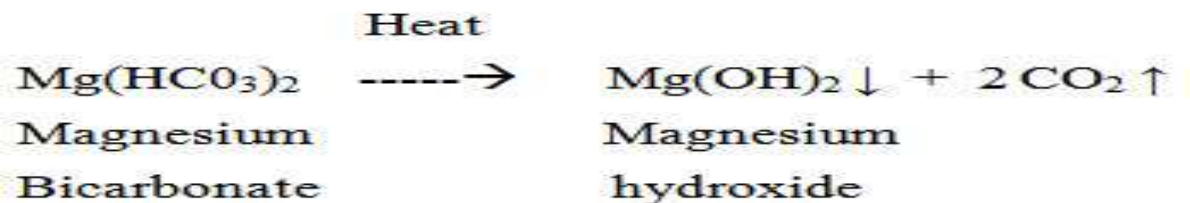
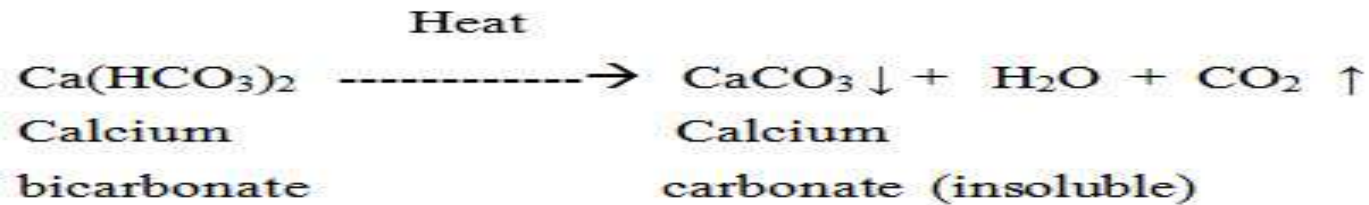
A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms a white scum or precipitate.

This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are depicted as follows:



Thus, water which does not produce lather with soap solution readily, but forms a white curd, is called hard water. On the other hand, water which lathers easily on shaking with soap solution, is called soft water. Such water, consequently, does not contain dissolved calcium and magnesium salts in it.

(1) Temporary or carbonate hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel. Thus;



(2) Permanent or non-carbonate hardness is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

EQUIVALENTS OF CALCIUM CARBONATE

The concentration of hardness as well as non-hardness constituting ions are, usually expressed in terms of equivalent amount of CaCO_3 , since this mode permits the multiplication and division of concentration, when required. The choice of CaCO_3 in particular is due to its molecular weight is 100 (equivalent weight = 50) and moreover, it is the most insoluble salt that can be precipitated during water treatment.

The equivalents of CaCO_3 ,

The equivalents of CaCO_3 ,

[Mass of hardness producing-substance] x [Chemical equivalent of CaCO_3]

=- $\frac{\text{Mass of hardness producing-substance}}{\text{Chemical equivalent of hardness-producing substance}}$

= $\frac{\text{Mass of hardness-producing substance} \times 50}{\text{Chemical equivalent of hardness-producing substance}}$

UNITS OF HARDNESS:

(1) Parts per million (ppm) is the parts of calcium carbonate equivalent per 10^6 parts of water, i.e., $1 \text{ ppm} = 1 \text{ part of CaCO}_3 \text{ eq.}$

(2) Milligrams per liter (mg/L) are the number of milligrams of CaCO_3 equivalent hardness present per liter of water. Thus;
 $1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ eq. hardness of 1 L of water}$

But 1 L of water weighs

$= 1 \text{ kg} = 1,000 \text{ g} = 1,000 \times 1,000 \text{ mg} = 10^6 \text{ mg.}$

(3) Clarke's degree ($^\circ\text{Cl}$) is number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon(10lb) of water. Thus:

$1^\circ \text{ Clarke} = 1 \text{ grain of CaCO}_3 \text{ eq. hardness per gallon of water.}$

$1^\circ \text{ Cl} = 1 \text{ part of CaCO}_3 \text{ eq. hardness per 70,000 parts of water.}$

(4) Degree French ($^\circ\text{Fr}$) is the parts of CaCO_3 equivalent hardness per 10^5 parts of water. Thus: $1^\circ \text{ Fr} = 1 \text{ part of CaCO}_3 \text{ hardness eq. per } 10^5 \text{ parts of water.}$

(5) Mille equivalent per liter (meq/L) is the number of mill equivalents of hardness present per liter. Thus; $1 \text{ meq/L} = 1 \text{ meq of CaCO}_3 \text{ per L of water}$
 $= 10^{-3} \times 50 \text{ g of CaCO}_3 \text{ eq. per liter}$
 $= 50 \text{ mg of CaCO}_3 \text{ eq. per liter}$
 $= 50 \text{ mg/L of CaCO}_3 \text{ eq.} = 50 \text{ ppm.}$

Relationship between various units of hardness:

1 ppm	= 1 mg/L	= 0.1° Fr	= 0.07° Cl	= 0.02
meq/L				
1 mg/L	= 1 ppm	= 0.1° Fr	= 0.1° Fr	= 0.02
meq/L				
1° Cl	= 1.433° Fr	= 14.3 ppm	= 14.3 mg/L	= 0.286
meq/L				
1° Fr	= 10 ppm	= 10 mg/L	= 0.07° Cl	= 0.2 meq/L
1 meq/L	= 50 mg/L	= 50 ppm	= 5° Fr	= 0.35° Cl

(iii). Lake water has a more constant chemical composition. It, usually, contains much lesser amount of dissolved minerals than well water, but quantity of organic matter present in it is quite high.

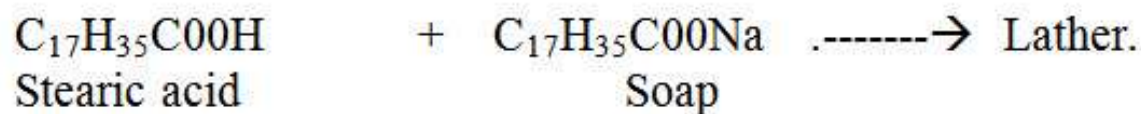
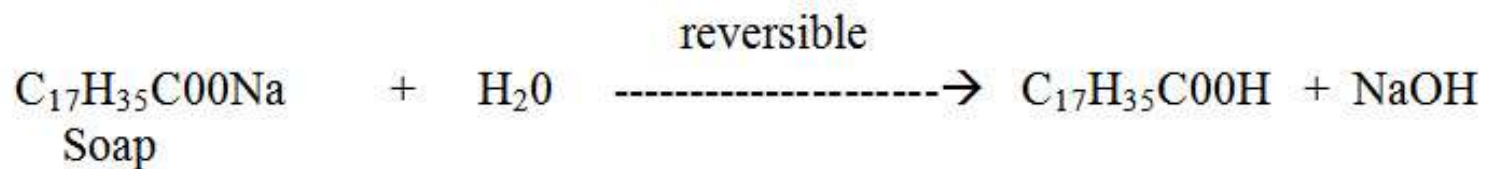
(iv). Sea water is the most impure form of the water. Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium; bicarbonates of potassium magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

Surface water, generally, contains suspended matter, which often contains the disease-producing (or pathogenic) bacteria's. Hence, such waters as such are not considered to be safe for human consumption.

HARD WATER

In domestic use:

(i) Washing: Hard water, when used for washing purposes, does not lather freely with soap. On the other hand, it produces sticky precipitates of calcium and magnesium soaps. The formation of such insoluble, sticky precipitated continues, till all calcium and magnesium salts present in water are precipitated. After that, the soap (e.g., sodium stearate) gives lather with water. Thus;



This causes wastage of soap being used. Moreover, the sticky precipitate (**of calcium and magnesium soaps**) adheres on the fabric/cloth giving spots and streaks. Also presence of iron salts may cause staining of cloth.

(ii) Bathing: Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is depressed and a lot of it is wasted.

(iii) Cooking: 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 certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an unpleasant taste and muddy-looking extract. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

(iv) Drinking: Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

Industrial use:

(i) Textile industry: Hard water causes much of the soap (used in washing yarn, fabric etc.) to go as waste, because hard water cannot produce good quality of lather. Moreover, precipitated of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed latter on, do not produce exact shades of color. Iron and manganese salts-containing water may cause colored spots on fabrics, thereby spoiling their beauty.

(ii) Sugar industry: Water containing sulphates, nitrates, alkali carbonated, etc., if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(iii) Dyeing industry: The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitated, which yields impure shades and give spots on the fabrics being dyed.

(iv) Paper industry: Calcium and magnesium salts tend to react with chemicals and other materials employed to provide a smooth and glossy (i.e., shining) finish to paper. Moreover, iron salts may even affect the color of the paper being produced.

(v) Laundry: Hard water, if used in laundry, causes much of the soap used in washing to go as waste. Iron salts may even cause coloration of the clothes.

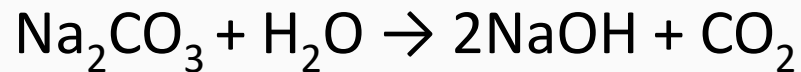
(vi) Concrete making: Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(vii) Pharmaceutical industry: Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.) may produce certain undesirable products in them.

In steam generation in boilers: For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as: (i) scale and sludge formation, (ii) corrosion, (iii) priming and foaming and (iv) caustic embrittlement.

CAUSTIC EMBRITTLEMENT:

Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. During softening process by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide,



and this makes the boiler water basic ["caustic"]. The NaOH containing water flows into the minute hair-cracks, always present in the inner side of boiler, by capillary action. Here, water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate this causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.

PRIMING AND FOAMING

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation is called priming. Priming is caused by;

- 1.the presence of a large amount of dissolved solids;
- 2.high steam velocities,
- 3.sudden boiling ;
- 4.improper boiler design
- 5.sudden increase in steam-production rate.

Foaming is the production of persistent foam or bubbles in boilers, which do not break easily. Foaming is due to presence of substances like oils (which greatly reduce the surface tension of water).

Priming and foaming, usually, occur together.

They are objectionable because;

- (i) dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency,
- (ii) dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery;
- (iii) actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

Priming can be avoided by: (i) fitting mechanical steam purifiers; (ii) avoiding rapid changing steaming rate; (iii) maintaining low water levels in boilers, and (iv) efficient softening and filtration of the boiler-feed water.

Foaming can be avoided by: (i) adding anti-foaming chemicals like castor oil, or (ii) removing oil from boiler water by adding compounds like sodium aluminates.

Caustic embrittlement can be avoided :

1. by using sodium phosphate as softening agent, instead of sodium carbonate ;
2. by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these;
3. by adding sodium sulphate to boiler water. Na_2SO_4 also blocks hair-cracks, thereby preventing infiltration of caustic soda solutions. It has been observed that caustic cracking can be prevented, if Na_2SO_4 is added to boiler water so that the ratio :
is kept as 1:1:2:1 and 3:1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

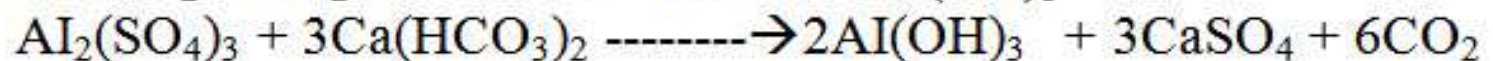
SOFTENING METHODS:

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. It should, therefore, be freed from hardness-producing salts before put to use. The process of removing hardness-producing salts from water, is known as softening of water. In industry, main three methods employed for water softening. Like;

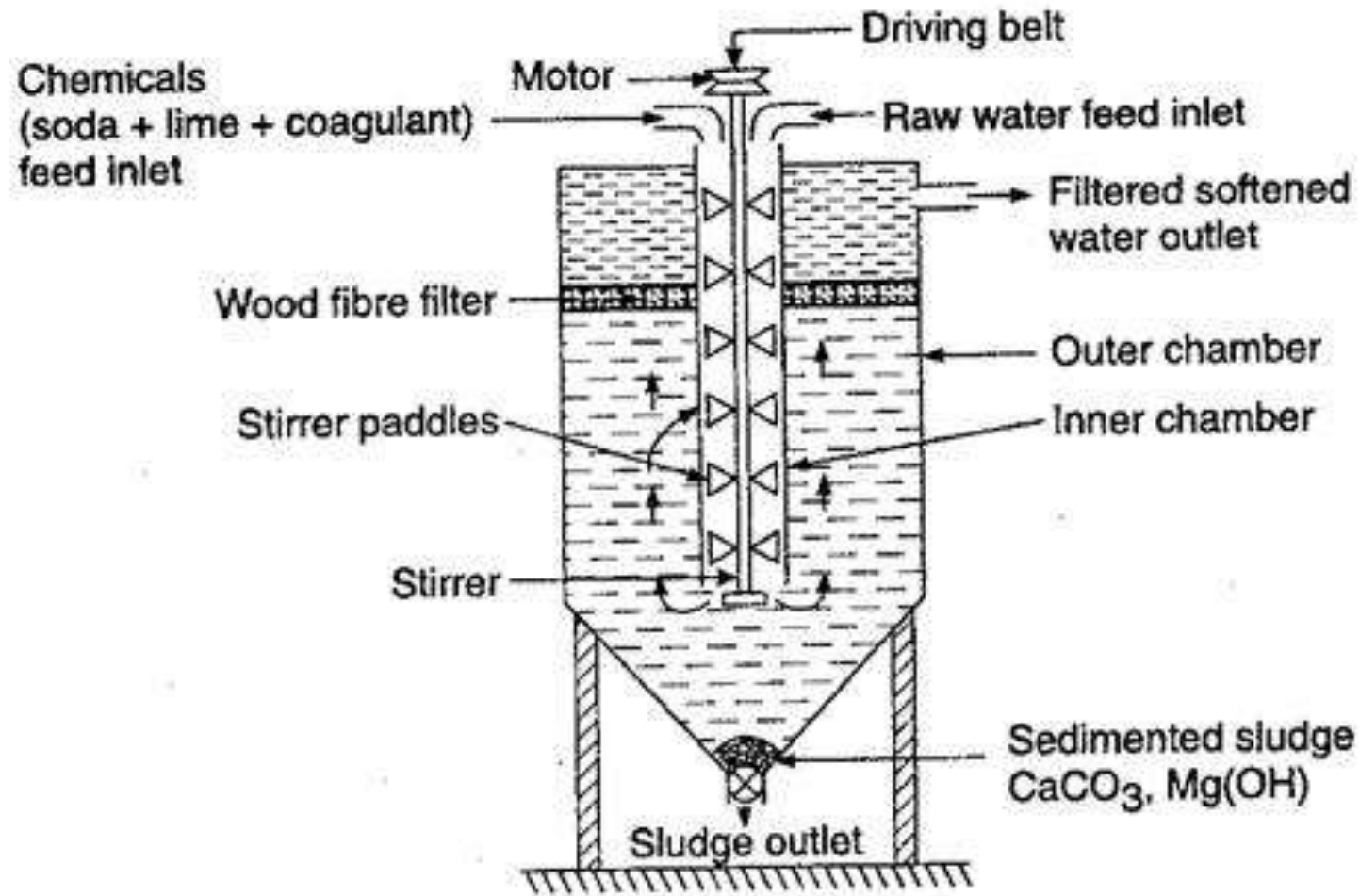
Lime-soda process: In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime (Ca(OH)_2) and soda (Na_2CO_3). Calcium carbonate (CaCO_3) and Magnesium hydroxide (Mg(OH)_2) are precipitated and are filtered off.

1 Cold lime-soda process:

In this method, calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finally divided, so they do not settle down easily and can not be filtered easily. It is essential to add small amount of coagulants which hydrolyze to flocculent, gelatinous precipitate of aluminum hydroxide, and entraps the fine precipitates. Use of sodium aluminates 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.



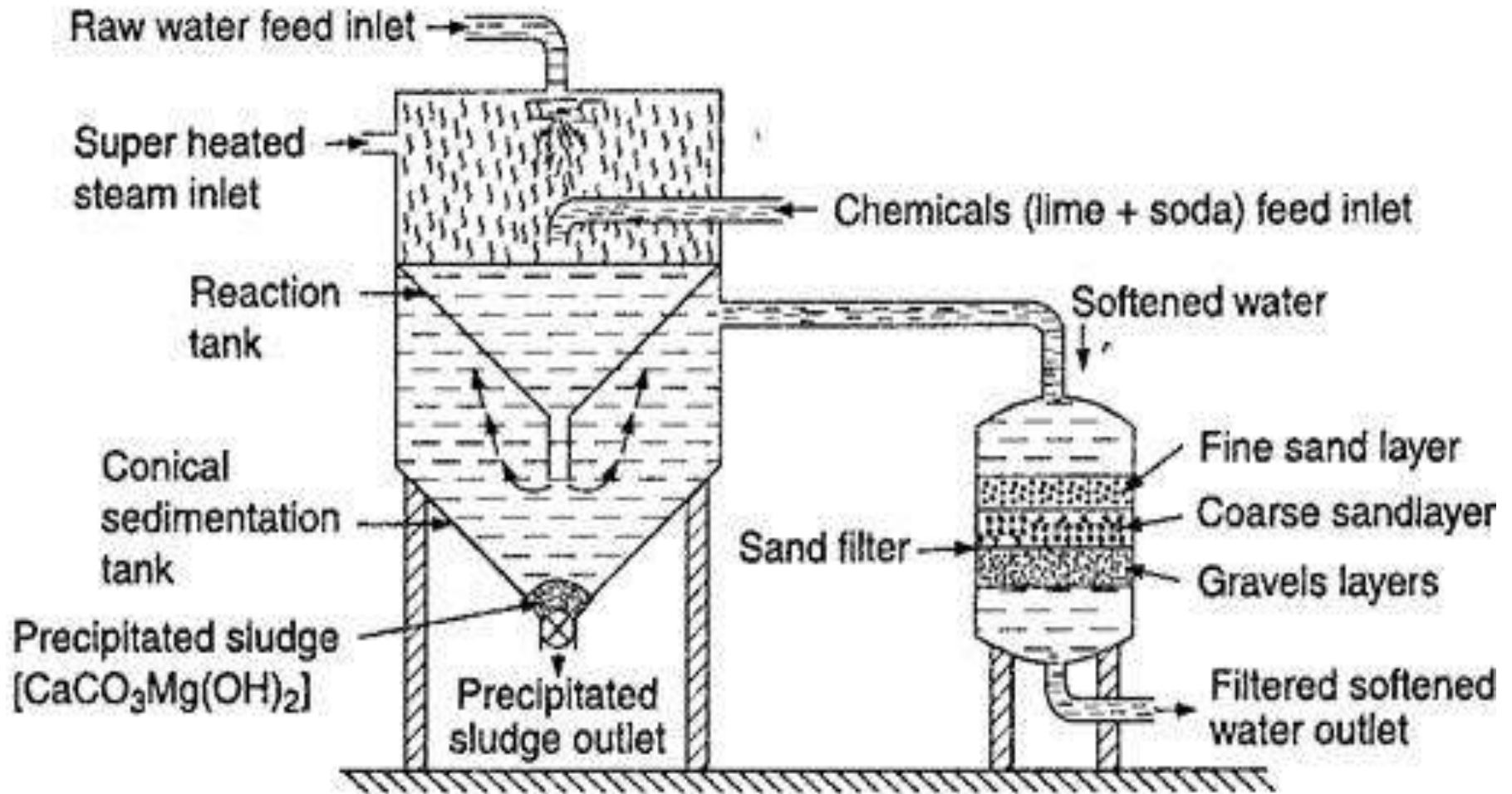
1 Cold lime-soda process



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 flock settles down in the outer chamber by the time the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn off occasionally.

2. Hot lime-soda process



2.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 :

- (i) the reaction proceeds faster.
 - (ii) the softening capacity of hot process is increased to many fold.
 - (iii) the precipitate & sludge formed settle down rapidly & hence, no coagulants are needed.
 - (iv) much of the dissolved gases (such as CO₂ and air) driven out of the water
 - (v) viscosity of softened water is lower, so filtration of water becomes much easier.
- This in-turn increases the filtering capacity of filters.
- (vi) hot lime-soda process produces water of comparatively lower residual hardness of 15 to 30 ppm.

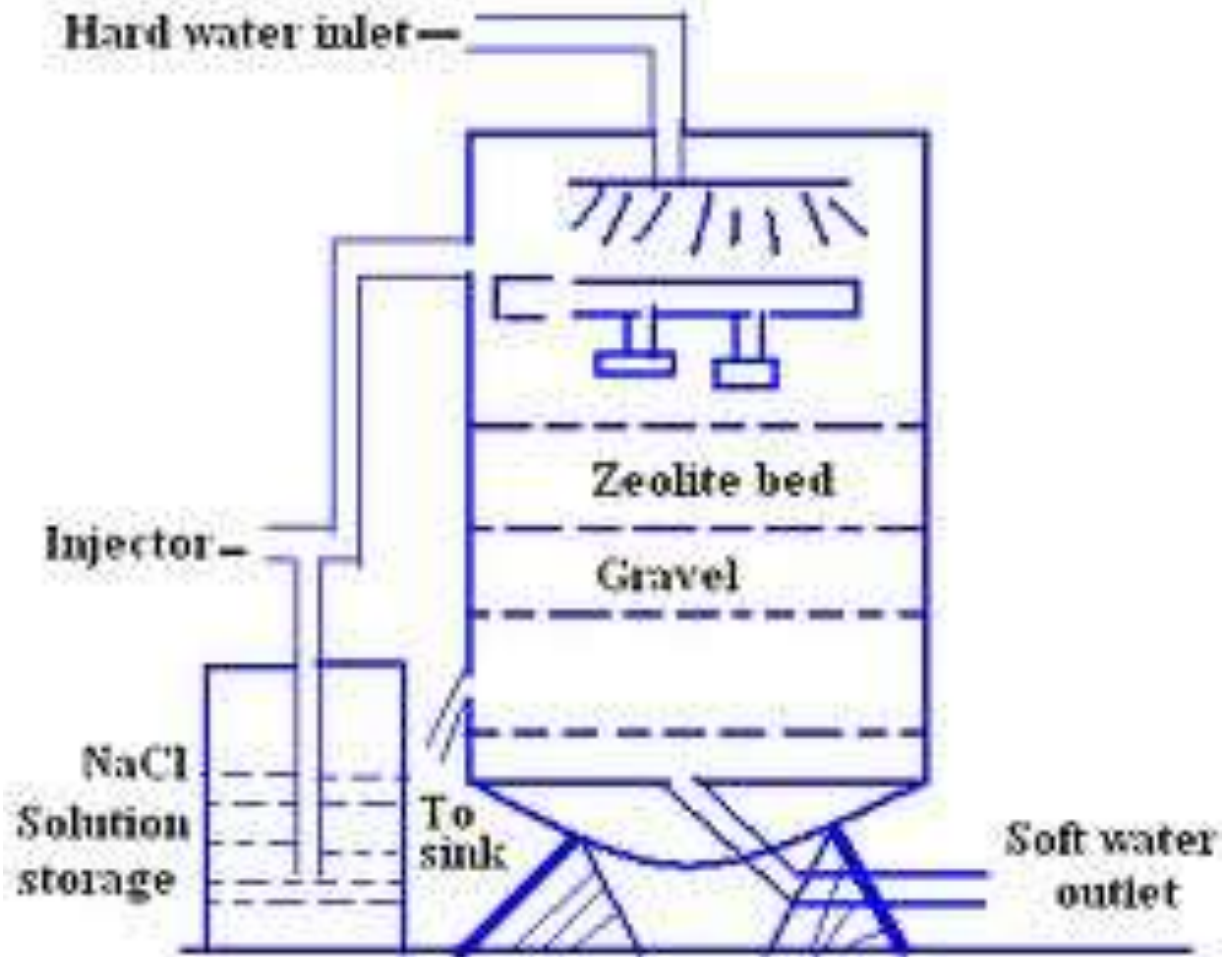
Advantages of Lime-Soda process :

- (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 is reduced.
- (v) To certain extent, iron & manganese are also removed from the H₂O.
- (vi) Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced.

Disadvantage of Lime-Soda process:

- (i) For efficient and economical softening, careful operation and skilled supervision is 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 up to 15 ppm, which is not good for boilers.

Zeolite or Pmutits process



Zeolite or permutits process :

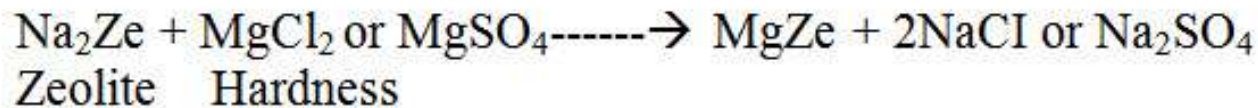
Chemical structure of sodium zeolite may be represented as : $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x = 2-10$ and $y = 2-6$. Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness-producing ions in water.

Zeolites are also known as permutits.

Zeolites are of two types : (a) **Natural zeolites** are non-porous. For example, natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_3\text{OS}_4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. (b) **Synthetic zeolites** are porous and possess gel structure. They are prepared by heating together china clay, feldspar 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. The 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;



Regeneration:

After some time, the zeolite is completely converted into calcium and magnesium zeolites and it stops 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.



The washings containing CaCl_2 and MgCl_2 are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.

Limitation of zeolite process:

- (i) 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.
- (ii) if water contains large quantities of coloured ions such as Mn^{2+} and Fe^{2+} , they must be removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.
- (iii) Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralized with soda, before admitting the water to the zeolite softening plant.

Advantages of zeolite process:

- (i) it removes the hardness almost completely and water of about 10 ppm hardness is produced.
- (ii) The equipment used is compact, occupying a small space.
- (iii) No impurities are precipitated, so there is no danger of sludge formation in the treated-water at a later stage.
- (iv) The process automatically adjusts itself for variation in hardness of incoming water.
- (v) it is quite clean.
- (vi) it requires less time for softening.
- (vii) it requires less skill for maintenance as well as operation.

Disadvantages of zeolite process:

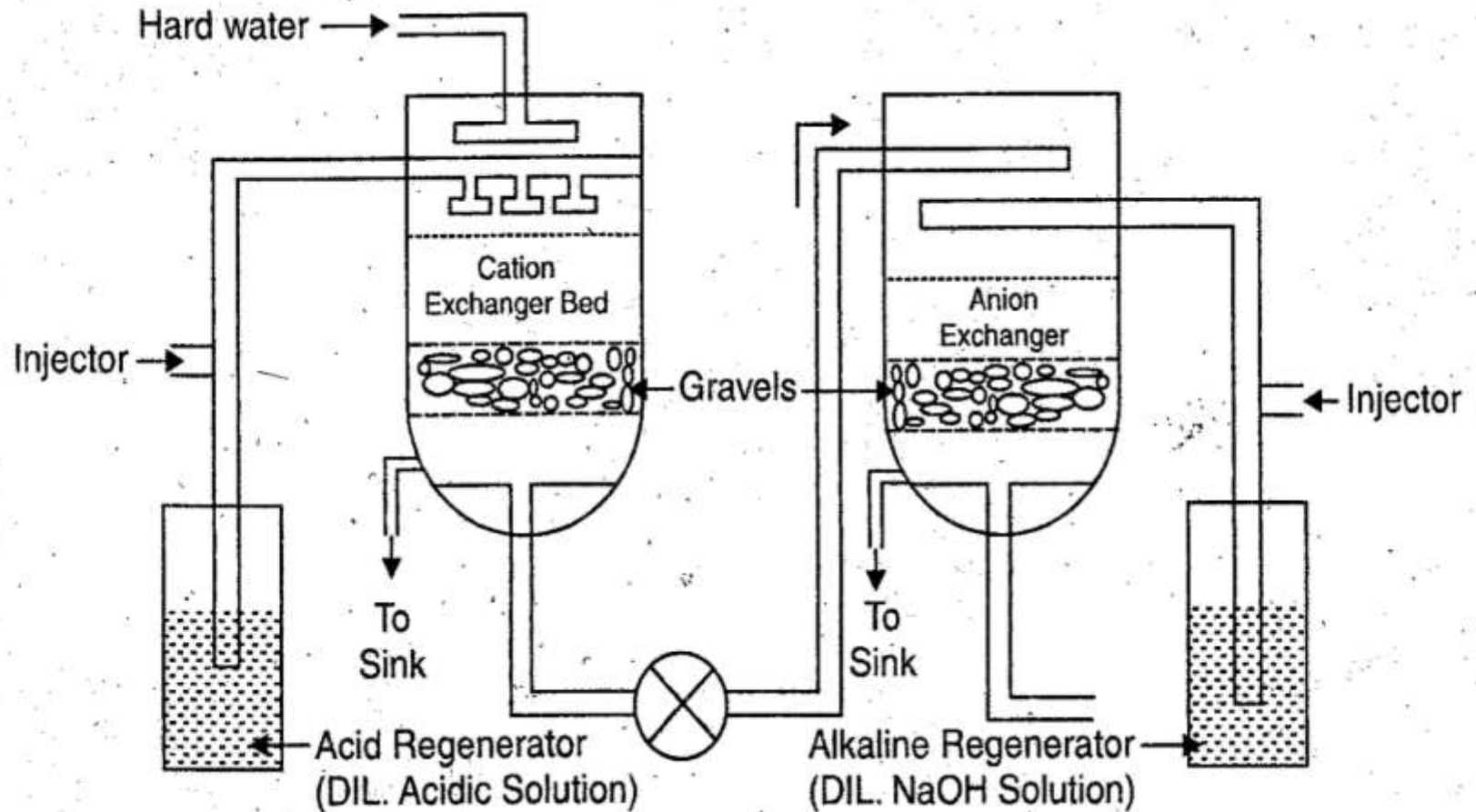
- (i) The treated-water contains more sodium salts than in lime-soda process.
- (ii) The method only replaces Ca^{2+} and Mg^{2+} ions by Na^{+} ions, but leaves all the acidic ions like HCO_3^{-} and CO_3^{2-} as such in the softened water. When such softened water (containing NaHCO_3 , Na_2CO_3 etc.) is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2 , which causes corrosion ; and sodium carbonate hydrolysis to sodium hydroxide, which causes caustic embrittlement.
- (iii) 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.

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 ($-\text{COOH}$, $-\text{SO}_3\text{H}$ etc.) are capable of exchanging their H^+ ions with other cations, which comes in their contact; whereas those containing basic functional groups ($-\text{NH}_2 = \text{NH}$ as hydrochloride salt) are capable of exchanging their anions with other anions, which comes in their contact. The ion-exchange resins may be classified as:

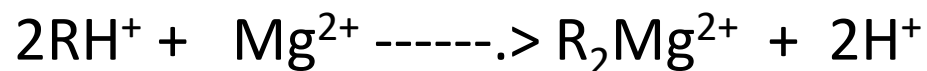
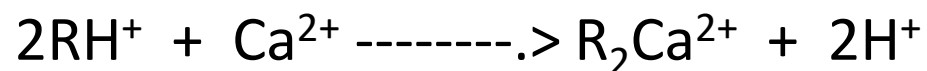
3. Ion exchange or De-ionization or De-mineralization process



(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.

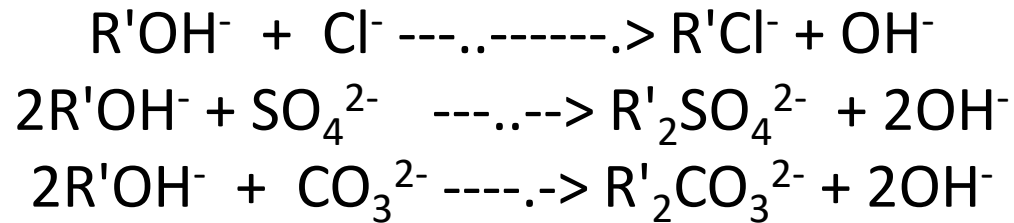
(ii) Anion exchange resins ($\text{R}'\text{OH}^-$) are styrene-divinyl benzene or amine formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH^- anions with anions in water.

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;

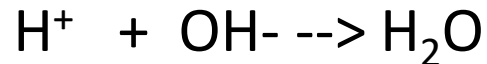


After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- , etc. present in the water and equivalent amount of OH^- ions are released from this column to water.

Thus:



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



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 H_2SO_4 . The regeneration can be represented as :



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 :



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:

- (i) The process can be used to soften highly acidic or alkaline waters.
 - (ii) 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:

- (i) The equipment is costly and more expensive chemicals are needed.
- (ii) 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 then by filtration.

