D. INDUSTRIAL CHEMISTRY

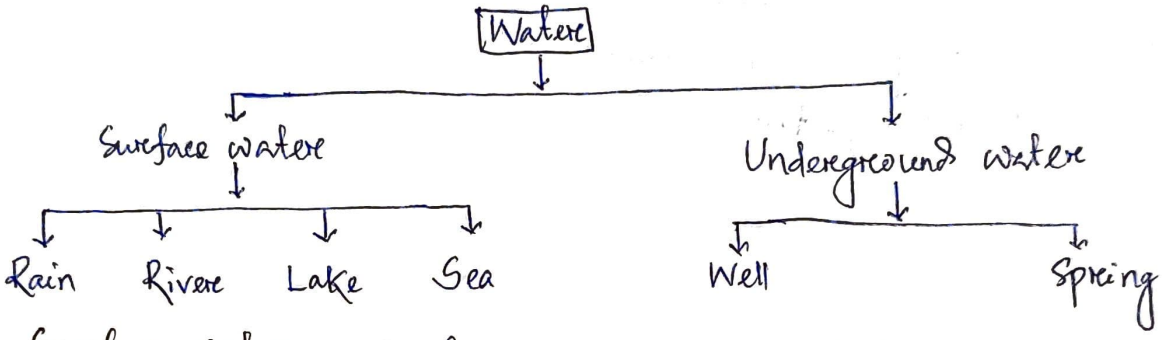
Chapter - 10 Water Treatment

* Water :-

Next to air, water is the most important constituent of life-support systems. Water is one of the most plentiful and readily available of all chemicals. It is called Universal Solvent because it can dissolve more substances than any other liquid. Although it is most often perceived as a liquid at normal atmospheric pressure, water exists as a solid below 0°c and as a gas above 100°c.

* Sources of water :

The sources of water can be classified as follows.



A. Surface water :- Surface water is just what the name implies; it is water found in a river, lake or other surface cavity.

1. Rain water :

⇒ Rainwater is considered to be the purest form of natural water as impurities and salts present in water on earth are left behind during vaporization by the sun.

⇒ But when the rain droplets fall, they dissolve gases like CO_2, oxides of sulphur (SO_x) and nitrogen (NO_x) which make the rain water slightly acidic.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

2. River water :

⇒ A river is a naturally flowing watercourse, usually freshwater, flowing towards a sea, lake or another river.

⇒ Rivers are nourished by precipitation, by surface runoff, through springs or from melting of glaciers.

⇒ It contains high percentage of dissolving minerals like NaCl, KCl, $NaNO_3$, $CaCO_3$, $NaHCO_3$ etc.

B. Lake water :

⇒ Lake is a relatively large body of slow moving ore standing water that occupies an inland basin of appreciable size.

⇒ Lake water contains lesser amounts of dissolved minerals but considerable amount of suspended and oreganic matters.

A. Sea water :

⇒ Sea water is the water from sea ore ocean and is the most impure form of natural water.

⇒ It contains about 3.5 % of dissolved minerals out of which about 2.5 % is only NaCl. Sea water also contains a large no. of dissolved gases like N_2, O_2, CO_2 and noble gases and biomatericals like carbohydrates, proteins, amino acids etc.

B. Underground Water :

⇒ Groundwater is the water that occures below the surface of Earth, where it occupies all ore part of the void spaces in soils ore geologic streata.

⇒ It is naturally replenished by rain and snow melt that seeps down into the cracks and crevices beneath and land's surface.

Underground water is of two types.

1. Spring water :

⇒ A spring is a natural outflow of water from an underground supply to the ground surface.

⇒ It is a clearer form of natural water.

⇒ It contains high percentage of minerals like Mg, Ca, Na and K & thus its hardness is very high.

2. Well water :

⇒ A well is a hole drilled, dug ore driven into the earth to obtain groundwater.

⇒ It is a clearer form of natural water.

⇒ It contains many dissolved minerals and some oreganic matter.

Types of Water :

Water is of two types :

(1) Soft water and (2) Hared water.

1. Soft water :

Water which forms lathere with soap solution is called soft water.

Ex:- Rain water, demineralized water, distilled water etc.

2. Hard water :

Water which does not form lathere with soap solution is called hard water. Instead, it forms a curedy white precipitate.

Ex:- Sea water, river water, Pond water etc.

* Hardness of water :-

It is the characteristic of water which prevents the lathering of soap due to the presence of bicarbonate, sulphate and chloride of Magnesium and Calcium in it. When soap reacts with hard water, following reaction takes place.

$$2\,C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

Sodium stearate (Soap) + (Impurity in hard water) → Magnesium stearate (Curedy white ppt.)

* Types of Hardness :-

Hardness of water is of two types:

A. Temporary or Carbonate hardness.

B. Permanent or Non-carbonate hardness.

A. Temporary hardness :

The temporary hardness of water arises due to the presence of bicarbonates of Ca and Mg, [i.e. $Ca(HCO_3)_2$, $Mg(HCO_3)_2$].

It is named temporary hardness because the soluble bicarbonates decompose into insoluble Carbonates simply on heating. Thus, water becomes soft. It is also called Carbonate hardness.

B. Permanent hardness :

The permanent hardness of water arises due to the presence of chlorides and sulphates of Ca, Mg, [i.e. $CaCl_2$, $MgCl_2$, $CaSO_4$ & $MgSO_4$]

It is named Permanent hardness because such a hardness cannot be removed by simply boiling the water.

* Units of hardness :-

(1) PPM - Parts per million Note: 1 ppm = 1 mg/L.

(2) mg/L - Milligrams per Litre

* Softening of Water or removal of hardness :-

Water softening is the process of removing the dissolved Ca and Mg salts that cause hardness in water.

1. Removal of Temporary hardness :

When temporary hard water is boiled, the soluble bicarbonates present in water decompose to give insoluble carbonates which settle down easily. Then the soft water is filtered off.

$$\underset{\substack{\text{from Hard water}\\(\text{Soluble})}}{Ca(HCO_3)_2} \xrightarrow{\text{Boil}} \underset{(\text{insoluble})}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

$$\underset{\substack{\text{from Hard water}\\(\text{Soluble})}}{Mg(HCO_3)_2} \xrightarrow{\text{Boil}} \underset{(\text{insoluble})}{MgCO_3\downarrow} + H_2O + CO_2\uparrow$$

2. Removal of Permanent hardness :-

A. Lime Soda Process :

In this process hard water is treated with a calculated quantity of lime and soda. Lime and soda convert the soluble hardness causing chemicals present in hard water into insoluble substances called sludges. The precipitate or sludge formed is then removed by filtration to get soft water.

$$\underset{(\text{Soluble})}{CaCl_2} + \underset{\text{Soda}}{Na_2CO_3} \longrightarrow \underset{(\text{insoluble})}{CaCO_3\downarrow} + 2NaCl$$

$$\underset{(\text{Soluble})}{MgCl_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{(\text{insoluble})}{Mg(OH)_2\downarrow} + CaCl_2$$

Lime-soda process is of two types:

(a) Cold Lime soda process & (b) Hot Lime soda process.

(a) Cold Lime Soda Process :-

Principle : When hard water is treated with calculated amount of lime [$Ca(OH)_2$] and soda [Na_2CO_3] at room temperature 25°c, the soluble Ca and Mg present in hard water are chemically converted into ppt. of Calcium carbonate ($CaCO_3$) and Magnesium hydroxide [$Mg(OH)_2$]. These ppt.s are removed by filtration. Thus, soft water is obtained.

$CaCl_2$ + Na_2CO_3 ⟶ $CaCO_3\downarrow$ + 2NaCl

Hared water — Soda — ppt.

$MgCl_2$ + $Ca(OH)_2$ ⟶ $Mg(OH)_2\downarrow$ + $CaCl_2$

Hared water — Lime — ppt.

Process :

The apparatus consists of a conical shaped steel tank, Raw water, lime, soda and coagulants are added from the top inner vertical circular chamber which is fitted with rotating shaft carrying many paddles. The dissolved salts of Ca and Mg combine with lime soda and coagulants and form an insoluble precipitate as sludge. Softened water rises upwards and the heavy sludge settles down. Then the softened water passes through wood fibre filter and the filtered soft water is collected through the outlet. The sludge settling down at the bottom is removed. The residual hardness left in this process is about 50-60 ppm.

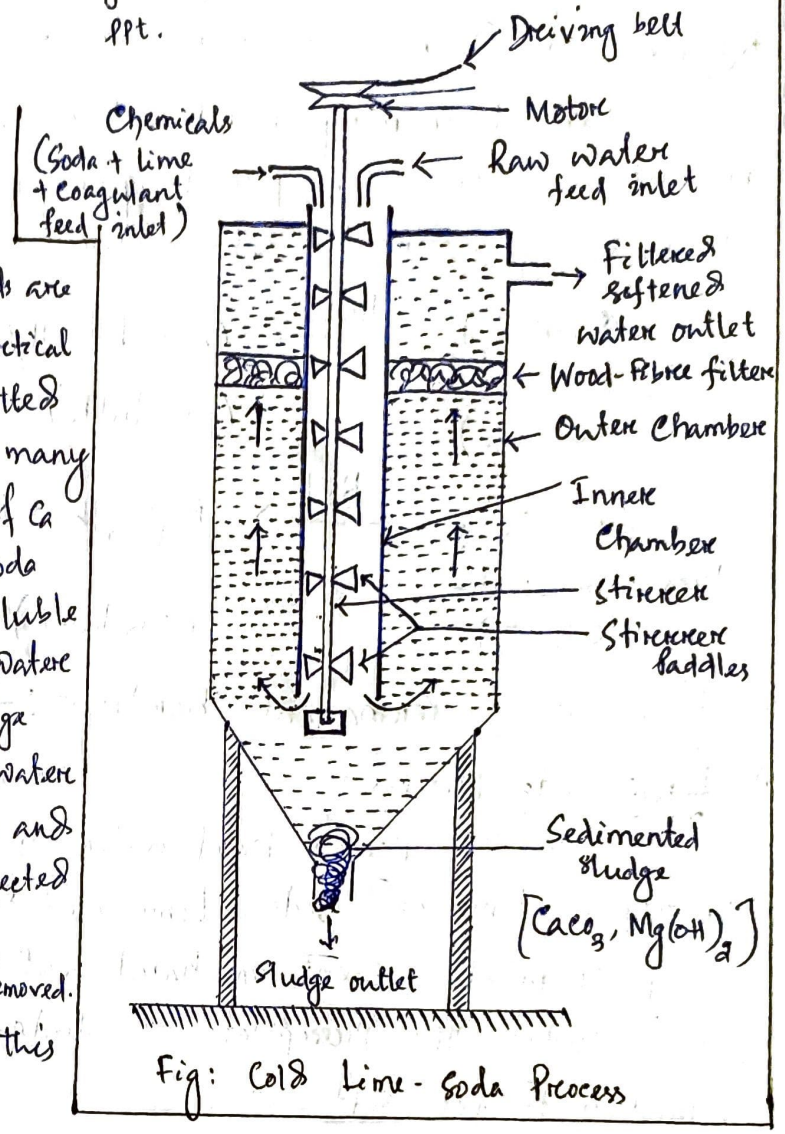


Fig: Cold Lime-Soda Process

Disadvantages :

⇒ It is a slow process because reactions during water softening take place in very dilute solutions and room temp.

⇒ It requires coagulant for settling particles of ppt. formed during reaction of water softening.

⇒ Softening capacity of this process is less.

⇒ Soft water obtained by this process consists of dissolved gases.

(b) Hot Lime Soda Process :-

Principle : This process involves treatment of hared water with lime and soda at a temp. of 80-150°c.

Process : In the hot lime soda process, the reactions takes place at higher temperature near about boiling point of water. The chemical mixing process is same as the cold lime soda process, but steam is applied in mixture tank. As a result, precipitation becomes almost complete very quickly.

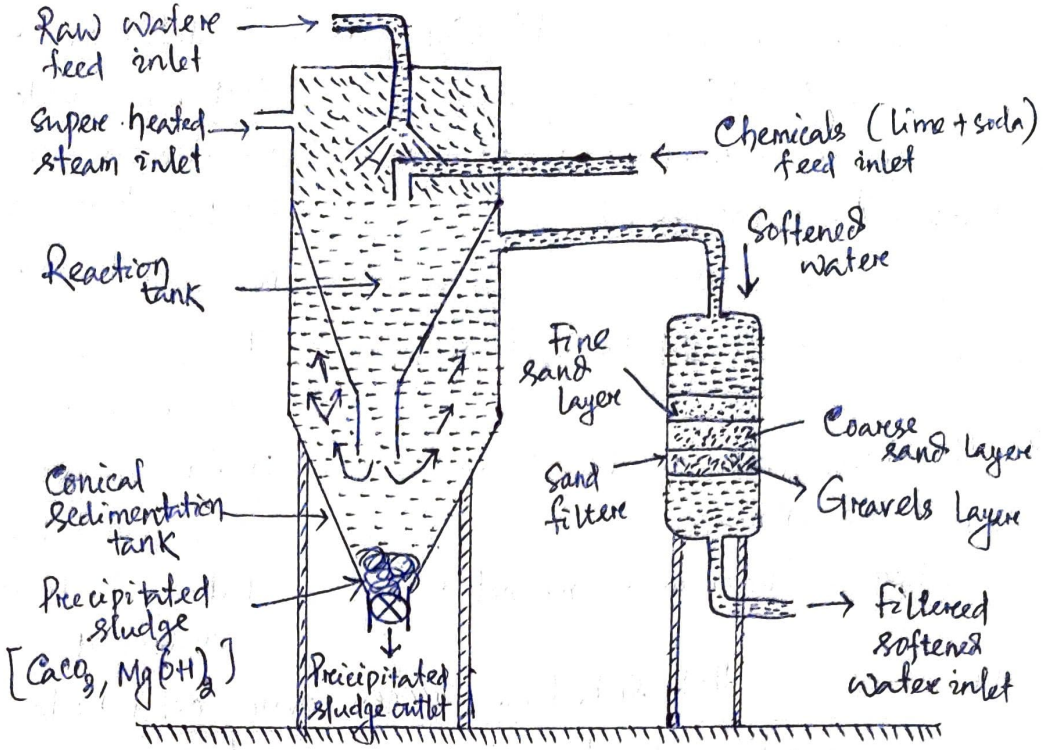


Fig: Hot lime soda process

Apparatus: The apparatus consists of three main parts.

(a) Reaction tank - in which hard watere, lime and soda are mixed thoroughly.

(b) Conical sedimentation vessel - in which sludges settle down.

(c) Sand filtere - where sludge is completely removed.

Advantages:

1. It is much economical.
2. The reaction is completed within a short period.
3. The reaction proceeds fastere. Hence the softening capacity is increased.
4. No coagulant is required, as the sludge settles down easily.
5. Dissolved gases like CO_2, air etc. are removed.
6. Under hot condition, viscosity of watere is lowered. Thus filtration becomes easiere.
7. Pathogenic bacterias are destroyed.
8. The residual hardness left in this process is much lowere (15-30 ppm) as compared to that in the cold lime-soda process (50-60 ppm).

Disadvantages:

⇒ For efficient and economical softening careful operation and skilled supervision is required.

⇒ Disposal of large amounts of sludge creates problem.

⇒ This can remove hardness only upto 15 ppm, which is not suitable for high pressure boilers.

* Difference between cold lime-soda and hot lime-soda process :-

Cold lime-soda process	Hot lime-soda process
1. The process is conducted at room temperature (at 25°c).	The process is conducted at high temperature (80-150°c).
2. Coagulant like alum is needed in it.	No coagulant is required in it.
3. It takes about 24 hours to complete.	The process is completed within 15 minutes.
4. Hardness left in the water is about 60 ppm.	Hardness left in this process is 30 ppm to the maximum.
5. Pathogenic bacterias are not destroyed.	Pathogenic bateria if any are destroyed.

* Advantages of hot soda lime process over cold soda lime process :-

(i) The precipitation reaction becomes almost complete.
(ii) The reaction takes place faster.
(iii) The sludge settles rapidly.
(iv) No coagulant is needed.
(v) Dissolved gases are removed.
(vi) Residual hardness is low as compared to the cold lime-soda process.

* Ion-Exchange Process [Deionization or De-mineralization Process]:

In this method, the ions responsible for hardness are exchanged with other ions which don't make water hard.

Organic ion-exchangers (Ion-exchange resins) :-

These are organic polymers having:
(i) high molecular weight.
(ii) Open and permeable molecular structure.
(iii) acidic ($-COOH$, $-SO_3H$) or basic groups ($-OH$, $-NH_2$) attached with them.

Ion-exchange resins are of two types:

(a) Cation-exchange resin ($R-H^+$):

If the active ion in ion-exchanger is a cation, generally acidic functional groups, the resin is called cation-exchange resin.
Ex:- ($Resin-H^+$) sulphonated Polystyrene resin etc.

(b) Anion-exchange resin ($R-OH^-$):

If the active ion in ion-exchanger is an anion, generally basic functional groups, the resin is called anion-exchange resin.
Ex:- HO^- resin, NH_2^--resin etc.

Process: The hard water is passed through a column of cation exchange resin called zeo-carb. All the cations present in hard water get exchanged with H^+ ions of the resin.

$$CaCl_2 + 2H^+\text{-resin} \longrightarrow Ca(\text{resin})_2 + 2H^+ + 2Cl^-$$

$$MgSO_4 + 2H^+\text{-resin} \longrightarrow Mg(\text{resin})_2 + 2H^+ + SO_4^{2-}$$

(In hard water) (Cation exchange resin)

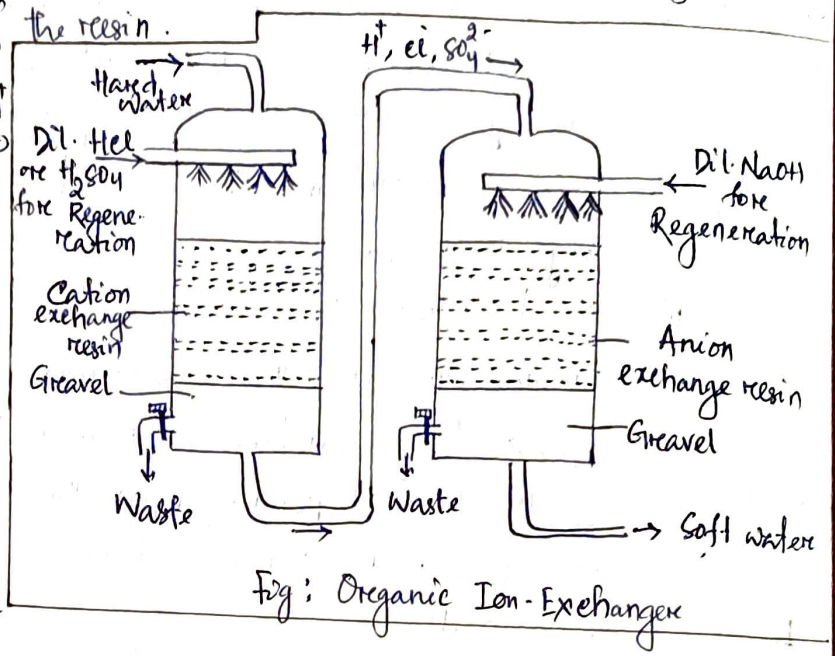


Fig: Organic Ion-Exchanger

Then the hard water is passed through the column of anion exchange resin. All the anions present in water get exchanged with OH^- ions of the resin.

$$Cl^- + OH^-\text{-resin} \longrightarrow Cl^-\text{-resin} + OH^-$$

(In water) (Anion exchange resin) (Exhausted resin)

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

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

Thus, the water coming out from the exchanger is free from cations as well as anion. Such water is known as deionised or demineralized water.

Regeneration of resins:

When all the H^+ and OH^- ions of the resins are exchanged by the cations and anions present in hard water, then the resins are said to be exhausted and regeneration can be done.

The cation-exchange resin can be regenerated by the treatment with dilute acids like dil. HCl or dil. H_2SO_4.

$$Ca(\text{resin})_2 + 2HCl \longrightarrow CaCl_2 + 2H^+\text{-resin}$$

(Exhausted resin) (regenerated resin)

Similarly, the anion-exchange resin can be regenerated by the treatment with dilute alkali, dil NaOH solution.

$$Cl^-\text{-resin} + NaOH \longrightarrow HO^-\text{-resin} + NaCl.$$

(exhausted resin) (Regenerated resin)

The regenerated resins may be used again.

* **Advantages of Ion-exchange process:-**

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

(ii) It produces water of very low hardness (upto 2 ppm). So it is good for treating water for use in high pressure boilers.

* **Dis-advantages of Ion-Exchange Process:-**

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

→ If water contains turbidity, then output of the process is reduced.