UNIT V: WATER TECHNOLOGY

Hardness of water-determination of hardness by complexometric method-boiler troubles (priming and foaming, scale formation, boiler corrosion, caustic embrittlement)-internal treatments-softening of hard water (zeolite process and related sums, ion exchange process)-treatment of industrial waste water, portable water ad its specifications -steps involved in purification of water-chlorination, break point chlorination- reverse osmosis and electro dialysis.

---

s

⊙ **Define hard and soft water?**

Hard Water: Water which does not produce lather with soap solution, but produces white precipitate is called hard water. This is due to the presence of dissolved Ca and Mg salts.

Soft Water: Water which produces lather readily with soap solution is called soft water. This is due to the absence of Ca and Mg salts.

⊙ **Define hardness of water. What is the cause of hardness of water? Explain types of hardness.**

Hardness in water is that characteristic which "*Prevents the lathering of soap*". This property is known as hardness. Hardness of water is due to presence of soluble salts of calcium, magnesium and other heavier metals in water.

$2C_{17}H_{35}COONa$ + $CaCl_2$ → $(C_{17}H_{35}COO)_2Ca\downarrow$ + $2NaCl$

(Sodium stearate) (hardness) (calcium stearate insoluble)

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

(Magnesium Stearate insoluble)

Types of hardness:

Hardness of water can be classified as temporary hardness and permanent hardness.

1.Temporary (or) carbonate hardness : It is due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals. Temporary hardness can be removed by boiling. So, it is known as temporary hardness. This hardness is also called as carbonate or alkaline hardness.

The salts responsible for temporary hardness are $Ca(HCO_3)_2$, $Mg(HCO_3)_2$.

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

(Caicium bicarbonate) (calcium carbonate insoluble)

$Mg(HCO_3)_2 \rightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$

Magnesium bicarbonate magnesium hydroxide

2. Permanent (or) non carbonate hardness: It is due to the presence of chlorides, sulphates and nitrates of calcium, magnesium, and other heavy metals. Permanent hardness cannot be removed by simple boiling. They need special methods like lime soda process and zeolite process. This hardness is also called as Non-carbonate or non alkaline hardness.

The salts responsible for permanent hardness are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$ $Ca(NO_3)_2$, $Mg(NO_3)_2$ etc

The sum of temporary and permanent hardness is referred as total hardness of water.

i.e. Total hardness= Temporary Hardness + Permanent Hardness.

⊙ **What are the disadvantages of hard water?**

1) Hard water cannot be used for drinking purpose.
2) It cannot be used for cooking purposes.
3) It cannot be used for bathing and washing purposes as it does not give lather with soap.
4) Hard water cannot be used in laboratories as it gives unwanted chemical reactions.
5) Hard water cannot be used in boilers for steam generation.

6) It cannot be used in sugar and paper industries.
7) Hard water cannot be used in textile and leather industries.

⊙ **How do you express the hardness of water? [or] What are the units of hardness of water. Give the relationship between different units.**

The hardness is expressed in terms of calcium carbonate ($CaCO_3$)equivalents. Because,
i) It is the most insoluble and easily precipitatable salt.
ii) Its molecular weight is 100 and equivalent weight is 50. As these are whole numbers, it is very easy to use them in calculations.

$$\text{Hardness in terms of weight of } CaCO_3 = \frac{\text{Amount of Hardness causing salt X 100}}{\text{Molecular weight of the Hardness causing salt}}$$

Units of hardness:

Parts per million (ppm): It is the parts of calcium carbonate equivalent hardness per 10^6 parts of water.

Milligrams per litre (Mg/L):It is the number of milligrams of $CaCO_3$ eq. hardness present per litre of water.

Clarke's degree (^{0}CL): It is the number of grains (1/7000Lb) of $CaCO_3$ eq hardness per gallon (10Lb) of water.

Degree French (^{0}Fr): It is the parts $CaCO_3$ eq. hardness per 10^5 parts of water.

Milliequivalents per litre: It is the number of milli equivalent of hardness present per litre

Relationship between various units of Hardness:

1ppm = 1mg/L = 0.07 ^{0}Cl = 0.1 ^{0}F

⊙ Explain the EDTA method for the determination of hardness of water.

Estimation of Hardness by EDTA method:

Water hardness is generally caused by the presence of Ca^{+2} and Mg^{+2} ions present in water.The analysis is done by complexometric titration using standard EDTA as titrant and EBT as an indicator.

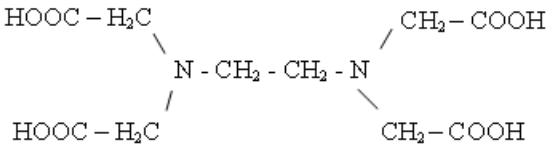
Chemical equations:

1. Metal ions + indicator → [Metal- indicator] complex
   (Blue) (Less stable and wine red color)
2. EDTA + [Metal- indicator] → [Metal- EDTA] complex + indicator
   (Wine red) (Blue)

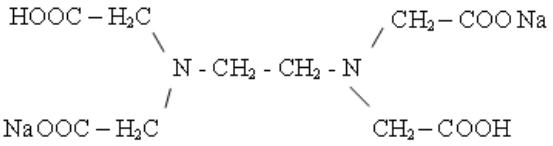
Here metal ions refer to Ca^{2+}, Mg^{2+}, Zn^{2+} or any other heavy metal ion.

EDTA stands for Ethylene Diamine Tetra Acetic acid. As it is insoluble in water, we use its disodium salt.

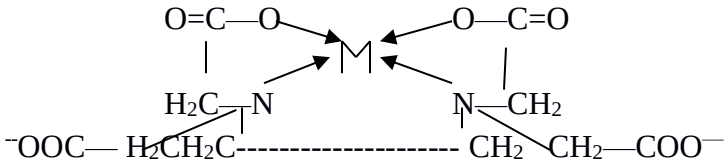
Structure of EDTA:



Disodium salt of EDTA is



Which forms complex ions with Ca^{+2} and Mg^{+2}



M is metal (Ca^{+2}/Mg^{+2})

Principle : By nature, Eriochrome Black T indicator is blue in colour. When EBT indicator is added to water sample, it forms a wine red coloured unstable Ca-Mg-EBT complex. This reaction is carried out under a basic P^H of 8- 10 using ammonia buffer.

Ca^{2+} / Mg^{2+} in water + EBT → [Ca / Mg –EBT] unstable wine red complex

When EDTA is titrated against the complex, EDTA replaces all the EBT and forms a stable Ca / Mg –EDTA complex. The liberated EBT indicates the end point as blue.

[Ca / Mg –EBT] + EDTA → [Ca / Mg –EDTA] + EBT

(Wine red/unstable) (Stable) (Steel blue)

So, the end point is the colour change from wine red to blue.

Procedure: Determination of Total Hardness of water: Pipette out 50ml of the water sample into a conical flask. Add 1ml of ammonia- ammonium chloride buffer solution and 2 or 3 drops of Eriochrome black-T indicator. Now the solution is wine red in color. Titrate this solution with standard EDTA solution from a burette until the color changes from wine red to blue. Repeat the titration until the concurrent value is obtained.

Calculations : 1000ml of 1M EDTA = 100 g of $CaCO_3$

$$\text{X ml of Y M EDTA} = \frac{X \times Y \times 100}{1000} \text{ g of } CaCO_3$$

$$= X \times Y \times 100 \text{ mg of } CaCO_3$$

where, X = Volume of EDTA

Y = Molarity of EDTA

$$= \text{——————} \text{ mg of } CaCO_3$$

i.e. Hardness of 50ml of water sample = Z mg of $CaCO_3$

Hardness of 1000ml of water sample = $\frac{1000 \times Z}{50}$ mg of $CaCO_3$

Boiler Feed Water (Water for Steam Generation):

⊙ What are the requirements of boiler feed water?

The setup used to produce steam in industries is known as '*Boiler*'. Water is fed to the boiler and heated to produce steam. The water fed into the boiler is known as "*Boiler feed water*".

A boiler feed water should corresponds with the following compositions

1. Its hardness should be below 0.2 PPM
2. Its caustic alkalinity (due to OH^{--}) should lie in between 0.15 & 0.45 PPM
3. Its soda alkalinity (Due to Na_2CO_3) should be 0.45 –1.0 ppm.

⊙ Discuss briefly the boiler troubles and their treatment?

Excess of impurities if present in boiler feed water generally cause the following problems.

1. Priming and Foaming. 2. Scale and Sludge formation. 3. Caustic embrittlement.
4.Boiler corrosion.

S.No	Requirements for boiler water	If not, it will cause
1	Free from hardness causing salts	Sludge and scale
2	Free from oil and greases	Foaming
3	Free from dissolved salts, suspended impurities	Caustic embrittlement
4	Free from dissolved gases, suspended salts	Boiler corrosion

---

BOILER TROUBLES:

⊙ What is priming and foaming? What are disadvantages of priming and foaming? How they can be prevented?

1. Priming and Foaming:

Due to rapid boiling, the steam may carry some water droplets along with it. This is called *wet steam* The process of wet steam production is called *Priming*. It can reduce the heat of the steam and cause corrosion in the pipelines.

Priming is due to:

i) Improper design of boiler.
ii) High water level.
iii) High velocity of steam.
iv) Uneven boiling.

Priming can be controlled by

i) Proper boiler design.
ii) Maintaining proper water level in the boiler.
iii) Avoid rapid change in steam rate.
iv) Proper boiling.
v) Fitting mechanical steam purifiers.
vi) Efficient softening and filtration of the boiler feed water.

Foaming: If oils and greases are present, they produce bubbles on the water surface. This will increase the wet steam production. This is known as "*Foaming*".

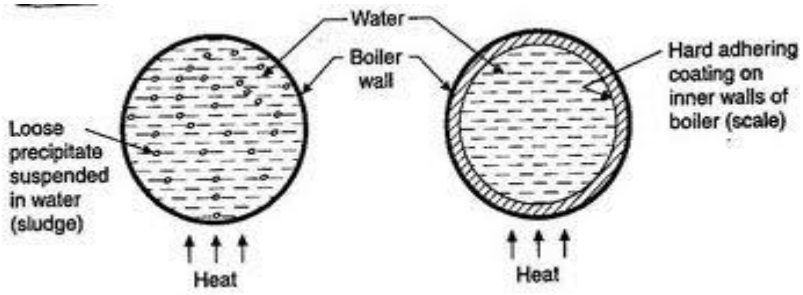
Foaming is prevented by adding

i) Anti foaming agents (e.g.) synthetic poly amides , castor oil.
ii) Coagulants (e.g.) Aluminium hydroxide

Foaming and priming are collectively known as "***Carry over***".

⊙ Explain scale formation and sludge formation in boilers. What are their disadvantages? How are they removed?

2. Scale and Sludge formation in boilers:



In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When their concentration reach saturation point they are thrown out of water in the form of precipitates on the inner walls of boiler.

If the precipitation takes place in the form of loose and slimy precipitate it is called **Sludge.**

On the other hand if the precipitated matter forms a hard adhering coating on the inner walls called **Scale**.

Sludge:

1) Sludge is a soft, loose, slimy precipitate formed within the boiler.
2) Sludge can easily be scrapped off with a wire brush.
3) Sludges are formed at colder portions of the boiler.
4) Sludges are formed by substances which have greater solubilities in hot water than in cold water.
5) Examples of sludges are $MgCO_3$, $MgCl_2$, $CaCl_2$.

Disadvantages of sludge formation:

1) Sludges are poor conductor of heat, so they tend to waste a portion of heat generated.
2) If sludges are formed along scales, then former gets entrapped in the latter.
3) Excessive sludge formation disturbs the working of boiler.

Prevention of sludge formation : 1) By using well softened water
2) By frequently 'blow down operation'.

Scales:

Scales are hard deposits which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer and chisel. Scales are the main source of troubles. Formation of scales may be due to,

1. Decomposition of calcium bicarbonate:

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

$CaCO_3$ is soft is the main cause of scale formation in low pressure boilers but in high pressure boilers $CaCO_3$ is soluble.

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

2. Hydrolysis of Magnesium salts: Dissolved magnesium undergo hydrolysis forming magnesium hydroxide precipitate. which forms a soft type of scale.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2HCl$$

3. Deposition of calcium sulphate: The solubility of calcium sulphate in water decreases with rise of temperature.Therefore $CaSO_4$ is soluble in cold water but almost completely insoluble in super heated water consequently $CaSO_4$ gets precipitated as hard scale on heated portions of the boiler. This is the main cause of scales in high pressure boilers.

Disadvantages of Scale formation:

1) Wastage of fuel: Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, over heating is done and this causes increases in fuel consumption.

2) Lowering of boiler safety: The over- heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube.
3) Decrease in efficiency: Sometimes scales deposit in the valves and condensers of the boiler and choke them partially. This results in decrease in efficiency of the boiler.
4) Danger of explosion: due to uneven expansion thick scales crack , then the water comes suddenly in contact with over-heated iron plates , results in formation of a large amount of steam suddenly . So sudden high pressure is developed,Which may cause explosion of the boiler.

Prevention of scales formation:

External treatment: Includes efficient softening of water i.e; removing hardness producing constituents of water.

Internal treatment /sequestration : In this process an ion is prohibited to exhibit its original character by " complexing" or converting it into other more soluble salt by adding appropriate reagent (or) scales are removed by blow down operation. Important internal treatment methods are,

a)Colloidal conditioning: In low pressure boilers scale formation can be avoided by adding organic substances like kerosene tannin, agar-agar etc. which get coated on scales thereby yielding non-sticky and loose deposits which can easily be removed by blow down operation.

b) Phosphate conditioning: In high pressure boilers scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming non- adherent and easily removable soft sludge of calcium and magnesium phosphate.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO4)_2 \downarrow + 6NaCl$$

c) Carbonate conditioning: In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

d) Treatment with sodium aluminate ($NaAlO_2$) : Sodium aluminate gets hydrolysed yielding NaOH and a gelatinous ppt of aluminium hydroxide.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3\text{(gelatinous ppt)}$$

The sodium hydroxide so formed precipitates some of the magnesium as $Mg(OH)_2$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2NaCl$$

The flocculent precipitate of $Mg(OH)_2$ and $Al(OH)_3$ produced inside the boiler entraps finely suspended and colloidal impurities including oil drops and silica. Then the loose ppt can be removed by pre-determined blow-down operation.

d) Calgon conditioning:

Calgon is the trade name of sodium hexa meta phosphate- $Na_2[Na_4(PO_3)_6]$.With calcium ions it forms a soluble complex and prevents scale and sludge formation. It is used for high and low pressure boilers.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \rightarrow Na_2[Ca_2(PO_3)_6] + 2\,Na_2SO_4$$

⊙ **Differentiate between sludge and scale in boiler**.

s.no	Sludge	Scale
1.	Sludge is a loose deposit or slimy matter	Scale is hard coating

2	Sludge is less adherent on boiler metal and can be removed easily by brushes, detergents.	Scale is strongly adhered to boiler metal and difficult to remove
3	Sludge is formed at the cooler parts & where flow rate is slow.	Scale is form at the hotter parts.
4	Sludge may lead to chocking	Scale may lead to bulging of metal tube.
5	Sludge formation is due to an increase in concentration of salts in boiler water, ($MgSO_4$, $MgCl_2$)	Scales are formed due to $CaSO_4$, $CaCO_3$,$Mg(OH)_2$, $Ca(HCO_3)_2$ etc.
6	Due to poor conductance, they decrease the boiler efficiency to lesser extent and causing chocking in the pipelines.	Due to poor conductance, they decrease the boiler efficiency to maximum extent, cause reduced fuel economy , improper boiling, boiler explosion etc.,
7	It can be prevented by periodical replacement of concentrated hard water by fresh water. This process is known as "blow down" method.	It can be prevented by special methods like i) external treatment of ion exchange , ii) Internal carbonate, phosphate, Calgon conditioning iii) Mechanical hard scrubbing methods.

⊙ **Write a note on Caustic embrittlement?**

3. Caustic embrittlement:

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler. During softening 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 CO_2 and this makes the boiler water caustic.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

This caustic water flows into the minute hair – cracks present in the inner side of the boiler by capillary action .On evaporation of water the dissolved caustic soda concentration increases progressively . This caustic soda attacks the surroundings 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.

+			--
Iron at rivets, Bends joints etc	concentrated NaOH solution	dilute NaOH solution	Iron at plane surfaces

The iron surrounded by the dilute NaOH becomes cathodic side while the iron in contact with rather concentrated NaOH becomes anodic part which is consequently dissolved (or) corroded.

Prevention of Caustic Embrittlement:

1) By using sodium phosphate as softening reagent instead of Na_2CO_3 .
2) By adding tannin or lignin to boiler water which blocks the hair cracks in boilers thereby preventing infiltration of caustic soda solution in use.

3) By adding sodium sulphate to boiler water: Na_2SO_4 also blocks hair cracks. 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 at pressures up to 10,20 and above 30 atmospheres.

$$\frac{[Na_2SO_4 \text{ concentration}]}{[NaOH \text{ concentration}]}$$

⊙ **Give a brief note on Boiler corrosion?**

4. Boiler corrosion: It is the decay of boiler materials (boiler tubes, drums economizers super heaters and condensers) by a chemical or electrochemical attack.

It may be due to three major reasons:

1) Dissolved Oxygen.
2) Dissolved CO_2.
3) Acids from Dissolved salts like $MgCl_2$.

1) Dissolved oxygen: Water usually contains 8ml of dissolved oxygen per litre at room temperature . Dissolved oxygen in water in presence of prevailing high temperature attacks boiler.

$$2\,Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \downarrow$$
ferrous hydroxide

$$4\,Fe(OH)_2 + O_2 \rightarrow 2\,[Fe_2O_3.2H_2O] \downarrow$$
rust

Removal of dissolved oxygen :

a) Chemical method:

by adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide.

Adding Sodium Sulphite: $2\,Na_2SO_3 + O_2 \rightarrow 2\,Na_2SO_4$

Adding Hydrazine: $N_2H_4 + O_2 \rightarrow N_2 + 2\,H_2O$

Adding sodium sulphide: $Na_2S + 2O_2 \rightarrow Na_2SO_4$

2) Dissolved Carbondioxide: Salts like Calcium bicarbonate on heating produces CO_2 . CO_2 dissolves in water to form carbonic acid which corrodes the boiler metal.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Prevention from CO_2 :

1. Chemical method: By adding calculated amount of ammonium hydroxide

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

2. Mechanical deaeration method (similar to oxygen method)

3) Acids from dissolved salts: Dissolved salts like $MgCl_2$ cause acid formation.

$$MgCl_2 + 2\,H_2O \rightarrow Mg(OH)_2 + 2\,HCl \text{ (Corrosive acid)}$$

The liberated acid reacts with iron (of boiler) in chain –like reactions producing HCl again and again

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$
$$4\,Fe(OH)_2 + O_2 \rightarrow 2\,[Fe_2O_3.2H_2O]$$
rust

Consequently even a small amount of $MgCl_2$ can cause corrosion to a large extent.

Prevention:

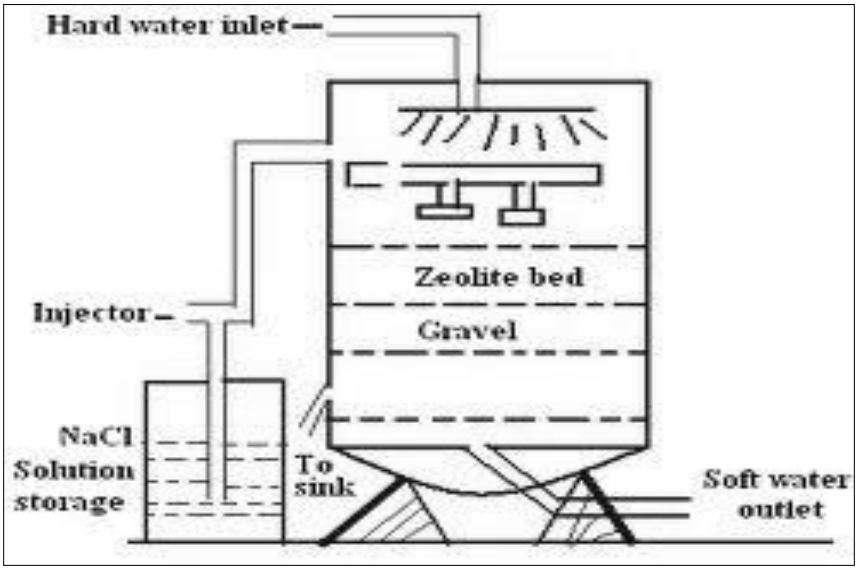
i) This will be prevented by alkali neutralization.

Neutralisation:	$HCl + NaOH \rightarrow NaCl + H_2O$

ZEOLITE PROCESS:

⊙ **Describe Zeolite process with a neat diagram. What is the chemical composition of Zeolite? How are they classified? Explain the mechanism of the treatment of hard water by Zeolites**.

Zeolite or permutit process : Chemical structure of sodium zeolite may be represented as: $Na_2O.Al_2O_3.xSiO_2.YH_2O$ or (Na_2Ze) where (x=2 to 10) ; (Y= 2 to6). Zeolite is hydrated sodium alumina silicate. It is capable of exchanging reversibly its sodium ions for hardness-producing ions in water.



Zeolites are also known as permutits.
Zeolites are of two types:
(i) Natural zeolites.
(ii) Synthetic zeolites.

(i)Natural zeolites are non- porous.
For example, natrolite,
$Na_2O.Al_2O_3.4SiO_2.2H_2O$.
(ii)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 passed 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.

Chemical Reactions taking place during the softening process are

Na_2Ze	+	$Ca(HCO_3)_2$	→	CaZe	+	$2\ NaHCO_3$
Na_2Ze	+	$Mg(HCO_3)_2$	→	MgZe	+	$2\ NaHCO_3$
Na_2Ze	+	$CaCl_2$	→	CaZe	+	2 NaCl
Na_2Ze	+	$CaSO_4$	→	CaZe	+	Na_2SO_4
Na_2Ze	+	$MgCl_2$	→	MgZe	+	2 NaCl
Na_2Ze	+	$MgSO_4$	→	MgZe	+	Na_2SO_4
(Zeolite)		(Hardenes causing species)		(Exhausted zeolite)		

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 regenerated by treating the bed with a concentrated (10%) brine solution. (NaCl).

Chemical Reactions taking place during the regeneration process are

$CaZe$ (Exhausted zeolite) + $2NaCl$ (Brine) → Na_2Ze (Regenerated zeolite) + $CaCl_2$ (Washings)

$MgZe$ (Exhausted zeolite) + $2NaCl$ (Brine) → Na_2Ze (Regenerated zeolite) + $MgCl_2$ (Washings)

Limitations of zeolite process:

1. Hard water should not contain Mineral acids.
2. Hard water should not contain turbidity and suspendended matter.
3. Hard water should not contain coloured ions such as Mn 2+ and Fe 2+.

Advantages of zeolite process:

1. zeolite process produces water of about 10 ppm residual hardness.
2. It is quite clean.
3. It requires less time for softening.
4. The plant occupies less space as it is compact.
5. It requires less skill for maintenance as well as operation.
6. The process involves no coagulation, no filtration and no precipitates.
7. It can operate under pressure and can be designed for fully automatic operation.

Disadvantages of zeolite process:

1. The treated-water contains more sodium salts than in the lime-soda process.
2. The method only replaces Ca 2+ and Mg 2+ ions, but leaves all the acidic ions in the soft water.
3. Water having high turbidity cannot be treated efficiently by this method.
4. The method cannot be used for treating acidic water, because the zeolite undergoes disintegration
5. The raw water to be softened must be free from suspended matter; otherwise the pores of zeolite material are blocked and the bed looses its exchange capacity.

⊙ **Describe the demineralisation of water by ion – exchange method.**

Ion exchange method:

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-exchange properties.

In this method the hard water is first passed through an acidic resin (RH) to remove the cations [Ca 2+ ,Mg 2+] and then it is passed through a basic resin [R'(OH)] to remove the anions. Thus both types of ions are totally removed.

Ion exchange resins are two types

1. Cation exchange resin.
2. Anion exchange resin.

Acidic resin or Cation exchange resin is represented by RH .

Basic resin or anoin exchange resin is represented by R'(OH)

Softening Process:

The hard water is first passed through cation exchange column, when all the cations like Ca 2+ ,Mg 2+ are removed from it and the equivalent amount of H + ions are released from the column to water. After passing

through cation exchange column, the hard water is passed through anion exchange column, when all the anions like SO 4 2- , Cl - present in the water are removed and equivalent amount of OH - ions are released from the column to H + and OH - ions released from cation exchange and anion exchange columns respectively combine to from 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 demineralized water. It is also free from acidity or alkalinity. Thus it is as pure as distilled water.

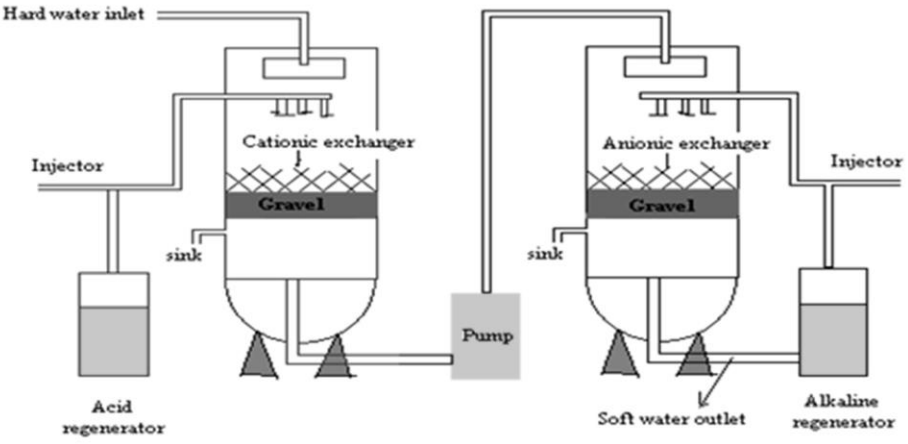


Fig.4.10. Demineralization process

Chemical reactions at cation exchange resin

$2RH + Ca(HCO_3)_2 \rightarrow R_2Ca + 2H_2CO_3$

$2RH + Mg(HCO_3)_2 \rightarrow R_2Mg + 2H_2CO_3$

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

$2RH + CaSO_4 \rightarrow R_2Ca + H_2SO_4$

$2RH + MgCl_2 \rightarrow R_2Mg + 2HCl$

$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$

Chemical reactions at anion exchange resin

$R^1OH + HCl \rightarrow R^1Cl + H_2O$

$2R^1OH + H_2SO_4 \rightarrow R^1_2SO_4 + 2H_2O$

$R^1OH + H_2CO_3 \rightarrow R^1HCO_3 + H_2O$

Regeneration of Acid Resin and Basic Resin :

After a long use, the capacities of cation and anion exchangers to exchange H + and OH - ions respectively are lost, then they are said to be exhausted.

The exhausted acidic resin can be regenerated by the addition of Hydrochloric acid.

The exhausted basic resin can be regenerated by the addition of NaOH.

Then the regenerated ion exchange resins are used again.

Regeneration of cation exchange resin

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

Regeneration of anion exchange resin

$R^1_2SO_4 + 2NaOH \rightarrow 2R^1OH + Na_2SO_4$

Advantages:

1. This process produces water of about 1 to 2 ppm residual hardness.
2. In this method, both types of hardness are removed.
3. The quality of water obtained is equivalent to distilled water.
4. The process can be used to soften highly acidic or, alkaline waters.
5. There is no wastage of water.

Disadvantages:

1. Capital cost is high since chemical and equipment both are costly.
2. If water contains turbidity then the efficiency of the process is reduced.

Potable Water (or) Drinking Water (or) Municipal Water

⊙ **What are the specifications of potable water? Discuss the various steps involved in the treatment of water for domestic purpose?**

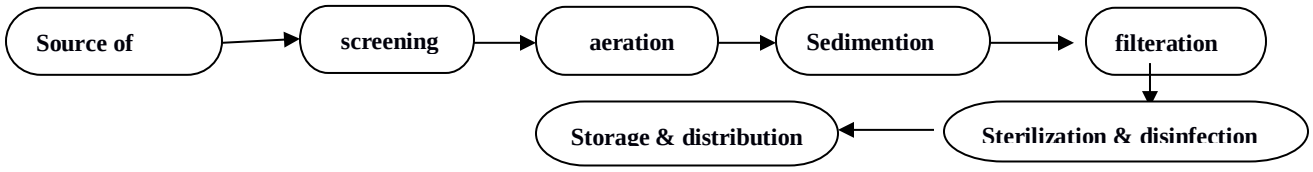
Municipalities have to supply potable water, i.e., water which is safe to drink, and fit for human consumption.

Requirements of drinking (potable) water :

1) Free from colour, odour, bacteria, dissolved gases
2) Should have pleasant taste
3) Turbidity should be below 10 ppm
4) Chloride content should be below 250 ppm.
5) Flouride content should be below 1.5 ppm.
6) Hardness salt content should be below 500 ppm.
7) P^H should be in the range of 6.5 – 8.0

To get these properties, the water is treated properly.

Purification of water for domestic use:



I) Removal of suspended impurities:

Sources:Natural water from rivers , canals etc., does not confirm to all the required specifications of drinking water. For removing various types of impurities , the following treatment processes are employed:

1) Screening : The water is passed through screens having large number of holes in it, to remove floating impurities like wood pieces, leaves etc.

2) Aeration: The water is subjected to aeration which helps in exchange of gases between water and air. ssssIncreases the oxygen content of water

3) Sedimentation: is a process of allowing water to stand undisturbed in big tanks about 5 m deep when most of the suspended particles settle down at the bottom , due to the force of gravity. The clear supernatant water is drawn from tank with the help of pumps.

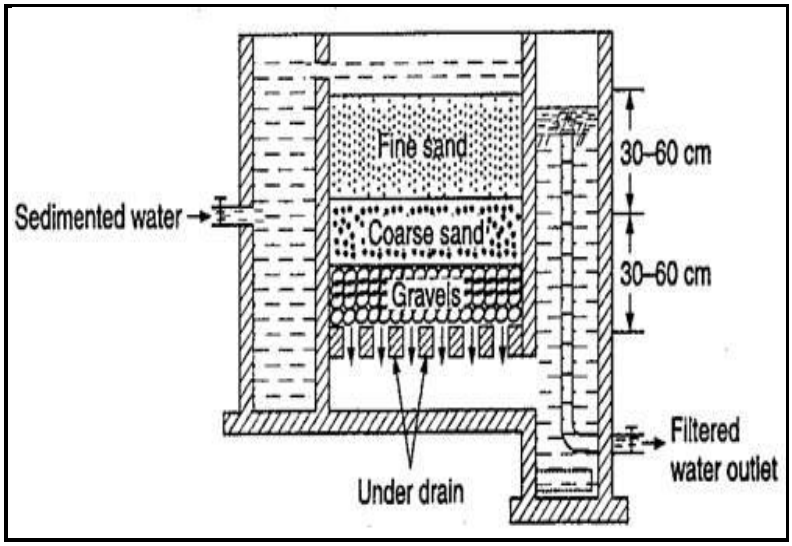
4) Sedimentaion with coagulation: It is the process of removing fine suspended and colloidal impurities by the addition of required amount of chemicals(coagulants) to water before sedimentation Coagulants when added to water , forms an insoluble gelatinous flocculants precipitate, which descent through water adsorbs very fine suspended impurities forming bigger flocs, which settles down easily. Coagulants like alums, and sodium aluminate and salts of iron are added.

$Al_2(SO_4)_3$ + $Ca(HCO_3)_2$ ----------> $2Al(OH)_3 \downarrow$ + $3CaSO_4$ + $6CO_2$

(coagulant) Colloidal particle flocculant ppt

5)Filteration: Filteration helps in removal of the colloidal and suspended impurities and most of the bacteria's microorganisms etc., by passing water through a bed of fine sand and other proper-sized granular materials. Filteration is carried out by using sand filter.

Operation of sand filter: A sand filter consists of a thick top layer of fine sand placed over coarse sand layer and gravels. It is provided with an inlet for water and an underdrain channel at the bottom for exit of filtered water. Sedimented water entering the sand filter is uniformly distributed over the entire fine sand bed. During filteration the sand pores get clogged, due to retention of impurities in the pores. When the rate of filteration is slow , the working of filter is stopped and about 2-3 cm of the top fine sand layer is scrapped off and replaced with clean sand and the filter is put back into use again.



II. Removal of micro-organisms By sterilization and disinfection:

Sterilisation or disinfection:

The process of destroying or killing the disease producing bacteria ,micro-organisms etc; from the water and making it safe for use is called disinfection. The chemicals or substances which are added to water for killing the bacteria etc are known as disinfectants.

The disinfection of water can be carried out by following methods

1. By boiling: By boiling Water for 10-15 minutes, all the disease-producing bacteria's are killed and water becomes safe for use. But it affects the taste and not for higher volume water.

2. By Chlorination:

a) By adding Bleaching powder ($CaOCl_2$): Bleaching powder ($CaOCl_2$) reacts with water and forms hypochlorous acid which kills bacteria. $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

$Cl_2 + H_2O \rightarrow HCl + HOCl$ (Hypochlorous acid which kills bacteria)

b) By using Chloramines: when chlorine and ammonia are mixed in the ratio 2 : 1 a compound chloramine is formed. It decomposes slowly to release chlorine which kills bacteria.

$Cl_2 + NH_3 \rightarrow ClNH_2$ (Chloramine) + HCl

$ClNH_2$ (Chloramine) $+ H_2O \rightarrow$ HOCl (Hypochlorous acid) $+ NH_3$

c) By liquid chlorine: Chlorine (either in gas or in concentrated solution form) produces hypochlorous acid, which is a powerful germicide.

$Cl_2 + H_2O \rightarrow$ HOCl + HCl

(hypochlorous acid)

Bacteria + HOCl $\rightarrow$ Bacteria are killed.

Factors affecting efficiency of chlorine:

1.Time of contact: number of micro-organisms destroyed by chlorine per unit time is proportional to the number of micro-organisms remaining alive.

2.Temperature of water: The death rate of micro organisms by chlorine increases with rise in water temperature.

3.P^H vaule of water: it is more effective at lower pH values (between 5 - 6.5)

Advantages of chlorine: It is effective and economical it requires very little space for storage. It is stable and does not deteriorate on keeping, it can be used at low as well as high temperatures, it does not introduces salt impurities in the treated water.

Disadvantages: Excess of chlorine, produces a characteristic unpleasant taste and odour, its excess produces an irritation on mucus membrane. The quantity of free chlorine in treated- water should not exceed 0.1 to 0.2 ppm , It is more effective below 6.5pH and less effective at higher pH values.

⊙ **Write a short notes on Break - point chlorination?**

Breakpoint chlorination:

The point at which the added chlorine completely removes bacteria, NH_3, Organic and inorganic impurities is known as "Breakpoint chlorination".

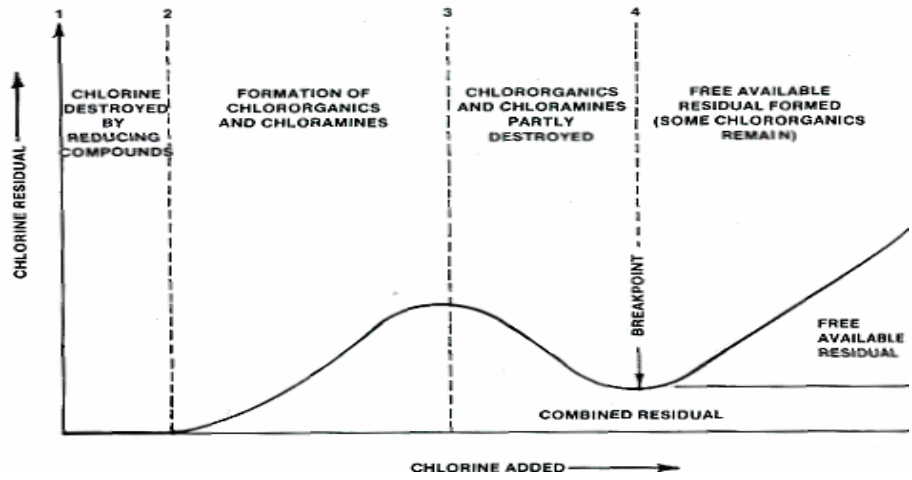
The water contains:

a) Bacteria

b) Ammonia

c) Organic impurity (sewage)

d) Inorganic salt impurities (Effluents, H_2S , Fe salts)



Advantages of break-point chlorination:

(i) it oxidizes completely organic compounds, ammonia and other reducing substances.

(ii)It removes colour in water

(iii)it destroys 100% disease – producing substances

(iv) it removes both odour and taste from the water.

(v) it prevents growth of any weeds in

water.

De-chlorination: Over chlorination after break point gives bad odour and taste in water. These objectionable qualities can be removed by filtering the over-chlorinated water through a bed of carbon (or) treating with sulphur dioxide

$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

DESALINATION OF BRACKISH WATER:-

⊙ **What is desalination?**

Definition: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.

Brackish water = Water containing dissolved salts with a peculiar salty taste. Ex: Sea water

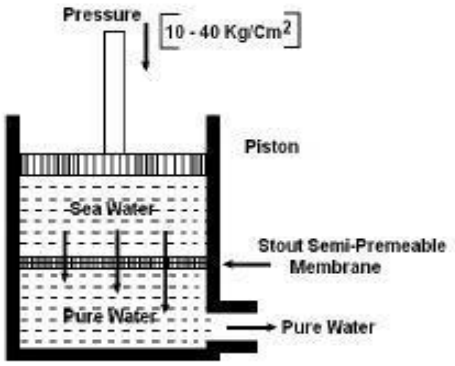
Desalination = Removal of common salt-NaCl from water.

Commonly used methods for desalination of brackish water are:-1) Reverse Osmosis 2)Electrodialysis.

⊙ **Explain the reverse osmosis process for desalination of brackish water?**

Reverse Osmosis Method:

Osmosis:When a semi-permeable membrane separates two solutions of different concentrations, solvent molecules move from dilute side to concentrated side until the two concentrations become equal. This process is called osmosis. The pressure gradient produced due to osmosis is called osmotic pressure.



Reverse Osmosis:

When a pressure greater than the osmotic pressure is applied on the concentrated side, solvent molecules move from concentrated side to the dilute side across the membrane. This is called reverse osmosis. This principle is used in Reverse Osmosis plants to soften hard water.

Method:

In this method hard water and soft water are taken in two different chambers separated by a semi permeable membrane. When a pressure greater than the osmotic pressure is applied on the hard water side, the water molecules move from hard water side to soft water side leaving the impurities on the membrane due to reverse osmosis.Thus hard water is converted to soft water by Super filtration or hyper filtration.The semi permeable membrane is made of polysulphone or cellulose acetate or polyamide.

Advantages:

1. It is used for converting sea water into drinking water.
2. In this method ionic, non-ionic, colloidal, and organic particles are removed from water.
3. The semi permeable membrane can be replaced and reused.
4. There is no wastage of water.
5. It is a simple and reliable process.
6. Capital and operating expenses are low
7. The life of semi-permeable membrane is about 2 years and it can be easily replaced within few minutes.

⊙ **Explain Electrodialysis process for desalination of brackish water?**

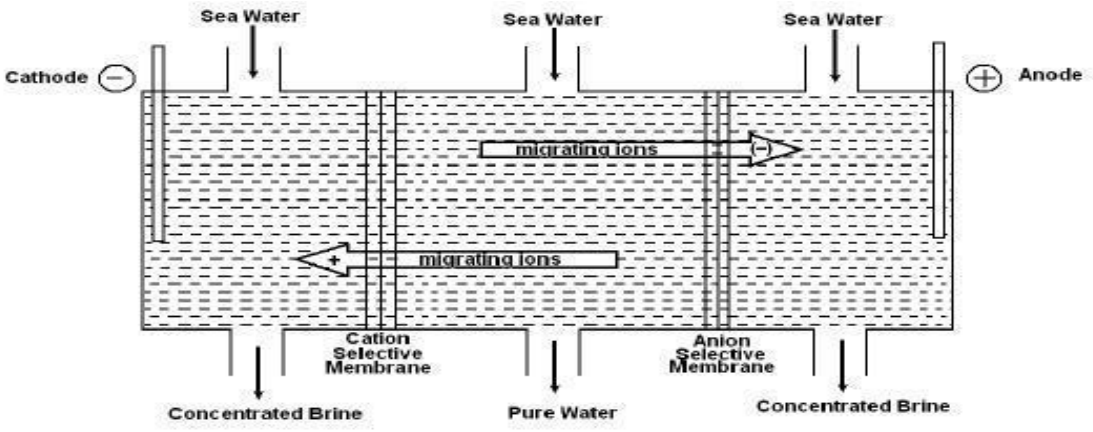
Electrodialysis:-The process of removing ionic pollutants from water using membranes and electric field is known as Electro dialysis.

Construction and working:-

- An Electro dialysis cell consists of a large number of paired sets of plastic membranes.
- The membranes are ion selective. E.g. Cation selective membrane will allow only cation to pass through it, as this membrane consists of negatively charged fixed groups which repel anions and do not allow going it.
- The anion selective membrane will allow only anions to pass through it, as this membrane consists of positively charged fixed groups which repel cation and do not allow to go it.
- When an electric field is applied ,perpendicular to the direction of flow of water the anion move towards positively charged electrode throw the anion selective membrane in neighboring compartment but after the there is cation selective membrane & the movement stopped.
- Similarly cation move in the direction of negatively charged electrode & go in neighboring compartment .they cannot move further because next is anion selective membrane.
- The result will be alternate compartments to them with negligible concentration of ionic substances. Thus we get alternate stems of pure water from the electrodialysis cell.

Applications:-

1. Removal of ionic pollutants (Toxic, salts, ionic dyes, etc.) from treated industrial waste.
2. Removal of salt from tree water, to get pure water.
3. Removal of limited quantity of salts from sea water to get drinking (mineral) water.



Advantages:

1. It is most compact unit.
2. The cost of installation of the plant and its operation is economical.
3. If electricity is available, it is a best process.

Industrial waste water Treatment:

Sources of Industrial Waste Industrial wastewater means used up water from industries. The characteristics of waters depend on the nature of industry. Generally pollution properties are:

Physical pollution - Temperature ,Colour ,Odour ,Taste ,Solids

Chemical pollution - pH, Acidity, Dissolved salts

Organic pollution - Organic Matter

Biological pollution - Biological Activities

Its Origin, Character and Treatment :

Sno.	Industries producing wastes	Origin of major wastes	Major characteristics	Major Treatment and Disposal methods
1.	Tannery	Unhairing, Soaking, Delining, Bating of hides	High total solids,Hardness,Salt, Sulfides,chromium, pH, B.O.D and Precipitated lime	Equalization, Sedimentation, Biological treatment
2.	Textiles	Cooking of fibres, desizing of fabric.	Highly alkaline,coloured, high B.O.D,High Suspended solids and Temperature.	Neutralization,chemical precipitation, Biological Treatment,Aeration and /or trickling filter.
3.	Dairy	Dilution of Milk,Separated milk, buttermilk.	High in Dissolved Organic matter mainly protein, Fat and lactose	Biological Treatment,Aeration,Trickling-Filters and Activated sludge process.
4.	Distilleries	Steeping and Pressing of Grain,residue from Distilleries of alcohol, Condensate from Stillage Evaporation.	High in dissolvedOrganic solids, Containing Nitrogen and Fermented Starches.	Recovery,Concentration By Centrifugation and Evaporation, Trickling filterUse in feeds.
5.	Meat	Stockyards,Slaughtering of Animals, Rendering of Bones and fats,Residues in condensates,Grease and Wash water,Pickling of	High in dissolved and suspended organic matter, blood other Proteins and fats.	Screening,settling and/or floatation,Trickling filter.

		Chickens.		
6.	Beet sugar	Transfer, screening, juicing waters, drainage from lime sludge, Condensates.After evaporation, juice and extracted sugar.	High in dissolved suspended organic matter, containing sugar and protein.	Re- use of wastes, coagulation, Lagooning.
7.	Rice	Soaking,cooking and washing of ice.	High B.O.D,Total and suspended Solids (mainlyStarch)	Lime coagulation digestion.
8.	Cane sugar	Spillage from extraction,clarification evaporation entrainment in coolingand condensed waters.	Variable pHSoluble organic matter with high B.O.D of carbonaceous nature.	Neutralization,Recirculation,chemical treatment,Aerobic oxidation.
9.	Paper and pulp	Cooking,Refining,washing of FibresScreening of paper pulp.	High or low pH, colour,high suspended,Colloidal and dissolved solids inorganic filters.	Settling,Lagooning,Biological treatment,Aeration,Recovery of by products.
10.	Steel	Coking of coal,Washing of blast furnace flue gases and pickling of steel.	Low pH,acids, phenol,ore, coke, limestone,alkali, oils,Fine suspended solids.	Neutralization, recovery and reuse, chemical coagulation.
11.	Metal plating	Stripping of oxides, cleaning and plating of metals.	Acid, metals,Toxic low volume mainly mineral water.	Alkaline chlorination of cyanide, reduction and precipitation of chromium,Lime precipitation of other metals.
12.	Petroleum refineries	Drillingmud,salt, oil and some natural gas, Acid sludge's and miscellaneous oils from refining.	High suspended solids(sand, clay), high dissolved solids,high B.O.D,odour,phenol& sulfur Compounds from refinery.	Selective screening,Drying of reclaimed sand,diversion,recovery,injection of salts, Acidification and burning of alkaline sludge.
13.	Atomic energy plants	Processing ores, laundering of contaminated clothes,Research Lab wastes,Processing of fuel, power plant cooling water.	Radioactive elements can be very acidic and hot.	Concentration and containing or dilution and dispersion.
14.	Fertilizer	Chemical reactions of basic elements,Spills,	Sulfuric, phosphorous and nitric acids,	Neutralization, detaining for Re-use, sedimentation, Air stripping of NH_3,

Equalization:

Equalization is a method of retaining wastes in a basin so that the effluent discharged is fairly uniform in its characteristics (pH, colour ,turbidity ,alkalinity , B.O.D etc). A secondary but significant effect is that of lowering the concentration of effluent contaminants. A retention pond serves to level out the effects of peak loadings on the plant while substantially lowering the B.O.D and suspended solids load to the aeration unit.

Lagooning:

Lagooning in oxidation ponds is a common means of both removing and oxidizing organic matter and waste waters as well. Stabilization or oxidation of waste in ponds is the result of several natural self purification phenomena. The first phase is sedimentation- settleable solids are deposited in an area around the inlets to the ponds, some suspended and colloidal matter is precipitated by the action of soluble salts, decomposition of the resulting sediment by microorganisms changes the sludge into inert residues and soluble organic substances, which intern are required by other micro-organisms and algae for their metabolic processes.

Numerical Problems based on hardness of water:

1) Calculate the temporary and permanent hardness of water sample containing Mg(HCO 3) 2 = 7.3mg/L, Ca(HCO 3) 2 = 16.2mg/L, MgCl 2 = 9.5mg/L, CaSO 4 =13.6mg/L).

2) Calculate the temporary and total hardness of a water sample containing Mg(HCO 3) 2 = 73mg/L, Ca(HCO 3) 2 = 162mg/L, MgCl 2 = 95mg/L, CaSO 4 =136mg/L.

3) A sample of water is found to contain 40.5 mg/L $Ca(HCO_3)$; 46.5mg/L $mg(HCO_3)_2$; 27.6 mg/L $MgSO_4$; 32.1 mg/L $CaSO_4$ and 22.45 mg/L $CaCl_2$ Calculate the total hardness of water?

4) A sample of water has 15mg of MgSO 4 in 500ml.Express the hardness of this sample of water in ppm of CaCO 3

Numerical Problems based on hardness of water by EDTA method:

1) A sample of 100 ml of hard water consumes 25 ml of 0.01M EDTA solution. Calculate the hardness of the sample of water.

2) A sample of 100 ml of water consumed 12.5 ml of 0.01 M EDTA solution. In another titration 100 ml of the same sample, after boiling for half an hour consumed 8.2 ml of the same EDTA solution. Calculate the carbonate and non-carbonate hardness of the sample of water.

3) In EDTA titration 20ml of standard solution of Calcium carbonate containing 2.5mg of CaCO 3 in 100ml of distilled water required 25 ml ofEDTA solution. When 100ml of a sample of hard water was titrated against the same EDTA solution, it required 33.4ml of EDTA solution.
Calculate the hardness of water in mg/litre of CaCO 3

Numerical Problems based on Zeolite softner:

1) A zeolite bed exhausted by softening 4000 liters of a water sample requires 10 liters of 15%NaCl solution for regeneration. Calculate the hardness of water sample.
2) A zeolite bed exhausted by softening 3500 litres of a water sample, requires 10 liters of 10% NaCl solution for regeneration. Calculate the hardness of water sample.

S