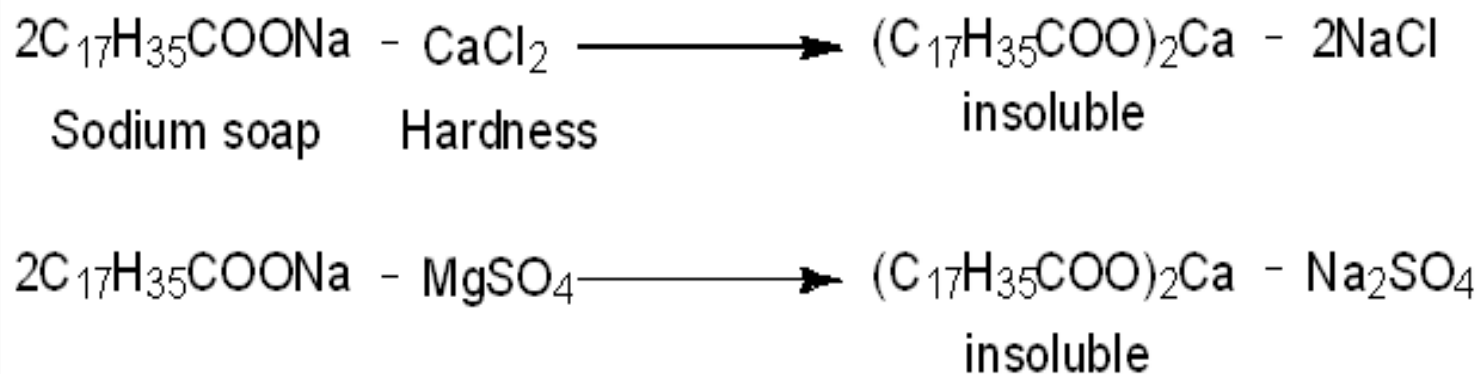


WATER TREATMENT

Hardness of Water

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



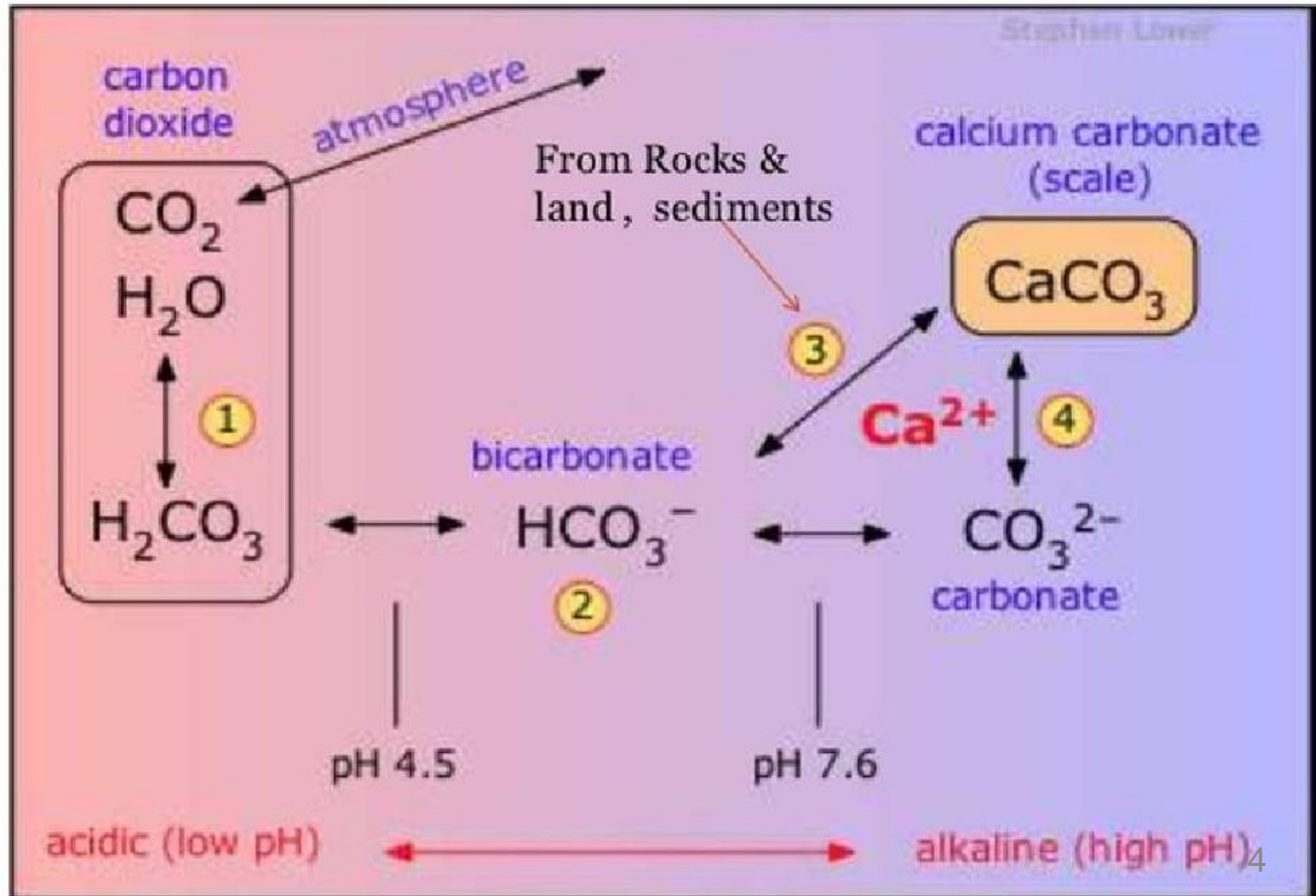
Hard water: Water does not produce lather with soap solution readily, but forms a white curd, is called hard water

Soft water: water which lathers easily on shaking with soap solution, is called Soft water

Hardness of Water

“The Property of water to form an insoluble curdy precipitate with soap instead of lather. In other words it is the soap destroying property of bicarbonates, sulphates chlorides and nitrates of Calcium and Magnesium”

ORIGIN OF HARDNESS - MECHANISM



Types of Hardness of Water

Temporary or Carbonate or Alkaline Hardness is due to the presence of dissolved bicarbonates of calcium, magnesium, and other Heavy metals and the carbonate of iron.

Permanent or Non-Carbonate or Non-Alkaline Hardness is due to the presence of chlorides, sulphates and nitrates of Calcium, Magnesium, Iron and Other heavy metals

Disadvantages of Hardness

Disadvantages are in the form of economic loss of a community and a country at large such as:

- More consumption of soap & detergent
- More consumption of fuel due to scaling formation in the boilers in industries
- Discoloration of food
- Short life of clothes due to deposition of salts in fabrics
- Disturbance of dying process
- Decreased life of cisterns and pipes
- High price of products

Disadvantages

- Consumes More soap and detergent-Financial loss.
- When water boiled, Carbonates precipitates, deposited in boiler, require more energy for heating: Industrial loss and boiler inefficiency, may explode
- Shorten the life of cloth fabrics
- Shorten life span of pipes (deposition and scaling of salts)

UNITS OF HARDNESS

Parts per million (ppm) is the parts of calcium carbonate equivalent hardness per 10^6 part of water i.e., 1ppm=1 part of CaCO_3 eq hardness in 10^6 parts of water.

Miligrams per liter is the number of milligrams of CaCO_3 equivalent hardness present per liter of water.

Clark degree ($^{\circ}\text{Clark}$) is number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water.

French degree ($^{\circ}\text{FH}$ or $^{\circ}\text{f}$) is the part of CaCO_3 equivalent hardness per 10^5 parts of water.

Relation between various units of hardness

1 ppm	= 1 mg/l	= 0.1 $^{\circ}$ Fr	= 0.07 $^{\circ}$ Cl
1 mg/l	= 1 ppm	= 0.1 $^{\circ}$ Fr	= 0.07 $^{\circ}$ Cl

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 .

The equivalents of CaCO_3 :

$$= \frac{\left[\begin{array}{c} \text{Mass of hardness} \\ \text{producing-substance} \end{array} \right] \times \left[\begin{array}{c} \text{Chemical equivalent} \\ \text{of } \text{CaCO}_3 \end{array} \right]}{\text{Chemical equivalent of hardness-producing substance}}$$

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

H.P.S; A (5gm) Soap \longrightarrow Ppt (x) = hardness ??
H.P.S; B (5gm) Soap \longrightarrow Ppt (y) = hardness ??

Reason for converting the amount/wt. of H.P.S. in terms of CaCO_3 equivalent hardness.

How to measure/calculate the hardness?

By bringing them on one scale and for that :

- We compare the hardness produced by A & B or any other H.P.S. with the hardness produced by a standard substance . Here, we take CaCO_3 as a standard as it produces maximum hardness or considered as 100% hardness producing substance.

- The ppt or hardness produced can be compared only by converting them in terms of CaCO_3 equivalents, using a conversion formula which is based on the reaction between the individual H.P.S. With some amount of soap, then the ppt formed can be compared by ppt formed by CaCO_3 soap.
- After going through these reactions it was found that (experimental fact) H.P.S. & CaCO_3 react with their chemical equivalent (for the purpose of calculation of hardness in water treatment, chemical equivalent are arbitrarily fixed as g equivalents/ eq. wt.)

Chem. Equivalents (g equivalents) of H.P.S. = Given amount of soap = Chem equivalent (g equivalents) of CaCO_3

Hence,

$$x \text{ g of H.P.S. (in terms of } \text{CaCO}_3) = \frac{\text{Chem equiv. of } \text{CaCO}_3}{\text{Chem equiv. of H.P.S.}} \times x$$

$$\frac{\text{Equiv. wt of } \text{CaCO}_3}{\text{Equiv. wt. Of H.P.S.}} \times x = \text{Hardness produced by } x \text{ gm of H.P.S. in terms of } \text{CaCO}_3$$

Chem Equiv. of H.P.S.

$$\text{Multiplication Factor} = \frac{\text{equiv. wt. Of } \text{CaCO}_3 \times 2}{\text{equiv. wt. Of H.P.S.} \times 2}$$

Calculation of Equivalent of calcium carbonate

Dissolved salt/ion	Molar Mass	Chemical Equivalent	Multiplication factor for converting into eq. of CaCO ₃
Ca(HCO ₃) ₂	162	81	100/162
Mg(HCO ₃) ₂	146	73	100/146
CaSO ₄	136	68	100/136
CaCl ₂	11	55.5	100/11
MgSO ₄	120	60	100/120
MgCl ₂	95	47.5	100/95
CaCO ₃	100	50	100/100
CO ₂	44	22	100/44
Ca(NO ₃) ₂	164	82	100/164
Mg(NO ₃) ₂	148	74	100/148
HCO ₃ ⁻	61	61	100/122
OH ⁻	17	17	100/34
CO ₃ ²⁻	60	30	100/60
NaAlO ₂	82	82	100/164
Al ₂ (SO ₄) ₃	342	57	100/114
FeSO ₄ .7H ₂ O	278	139	100/278
H ⁺	1	1	100/2
HCl	36.5	1	100/73

Removal of Hardness

- Boiling
- Addition of lime and soda (Precipitation mechanism)
- Use of Zeolite / Permutit (Ion exchange mechanism)
- By use of Ion exchange resins (Ion exchange mechanism)

Removal of Hardness

A. FOR TEMPORARY HARDNESS:

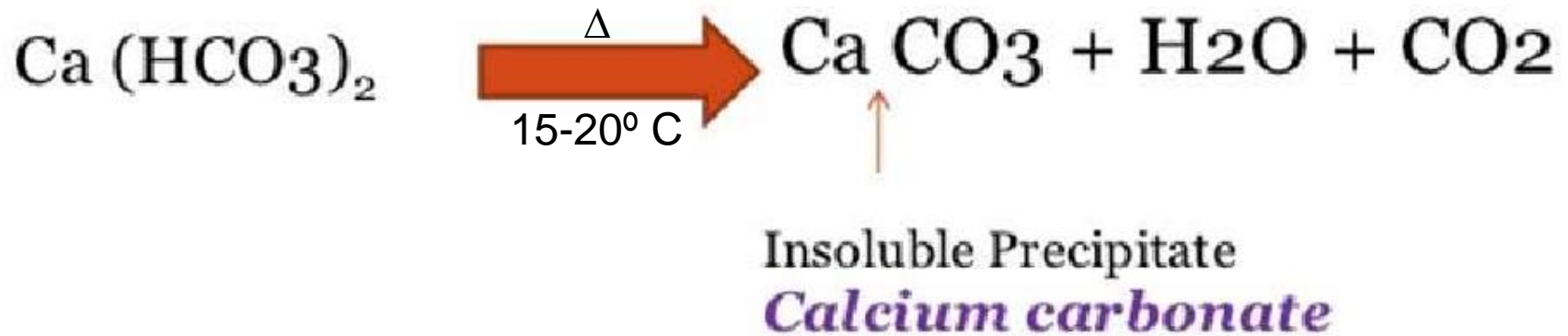
1. Boiling
2. Addition of Lime

B. FOR PERMANENT HARDNESS:

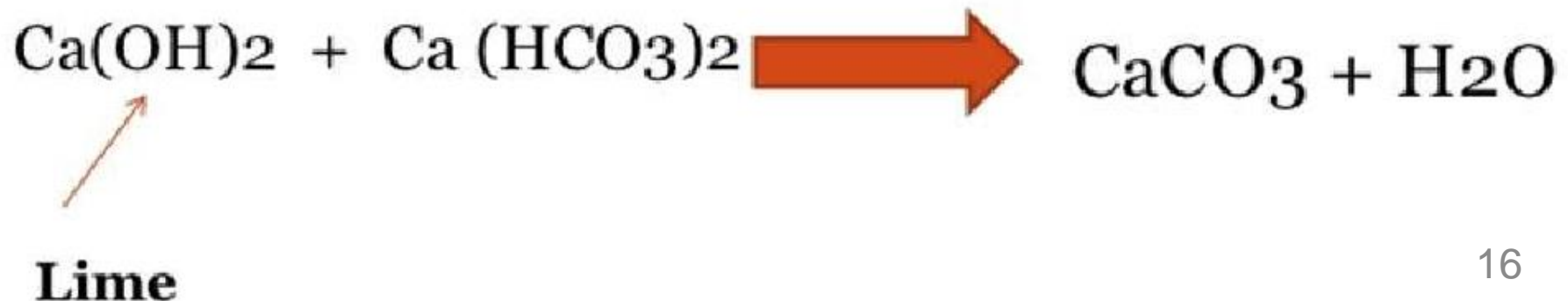
1. Addition of Lime
2. Addition of Sodium Carbonate
3. Base Exchange method / Permutit Process

METHODS TO REMOVE HARDNESS

1. Boiling : (Expensive , no large scale use)



2. ○ Addition of Lime



3. ADDITION OF SODIUM CARBONATE (SODA ASH)

- Removes both **temporary and permanent hardness**



4. Base Exchange Process (large scale)

1. Sodium Permutit is used ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O H}_2\text{O}$)
2. Exchange Na ions for Ca and Mg ions
3. Ca and Mg Permutit is formed .
4. Removes 100% hardness
5. Some raw water is added to protect against corrosive action of 100% soft water

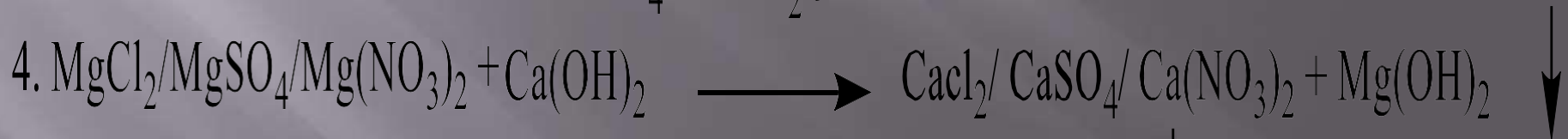
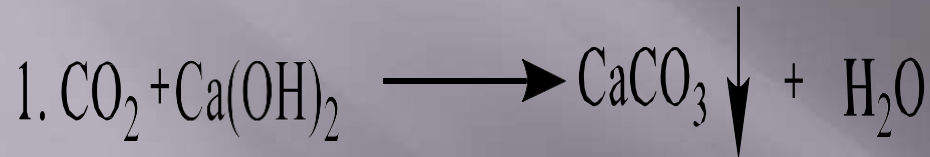
Table 2. Calculation of lime-soda requirement.

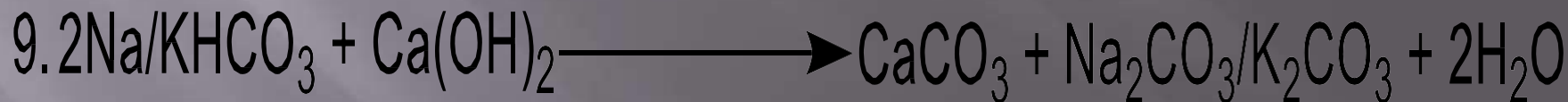
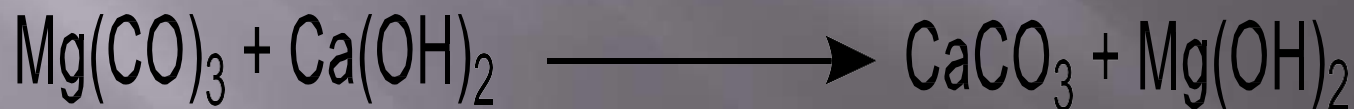
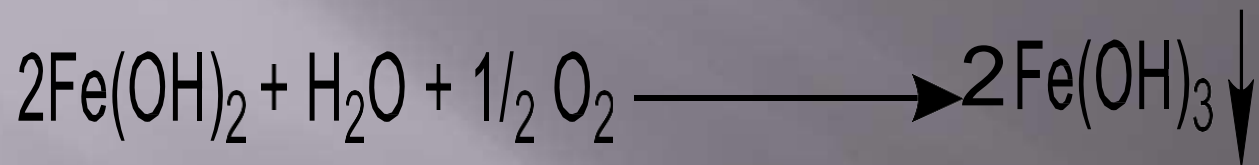
Constituent	Reaction	Need
Ca^{2+} (Perm. Ca)	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	S
Mg^{2+} (Perm. Mg)	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$	
	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
HCO_3^- (e.g., NaHCO_3)	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_3^{2-}$	L - S
$\text{Ca}(\text{HCO}_3)_2$ (Temp. Ca)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	L
$\text{Mg}(\text{HCO}_3)_2$ (Temp. Mg)	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
CO_2	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
H^+ (free acids, HCl, H_2SO_4 , etc.)	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
Coagulants : FeSO_4	$\text{Fe}^{2+} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Fe}(\text{OH})_2 + \text{Ca}^{2+}$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Fe}(\text{OH})_3$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
$\text{Al}_2(\text{SO}_4)_3$	$2\text{Al}^{3+} + 3\text{Ca}(\text{OH})_2 \longrightarrow 2\text{Al}(\text{OH})_3 + 3\text{Ca}^{2+}$ $3\text{Ca}^{2+} + 2\text{Na}_2\text{CO}_3 \longrightarrow 3\text{CaCO}_3 + 6\text{Na}^+$	L + S
NaAlO_2	$\text{NaAlO}_2 + \text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$ 2NaOH is eq to $\text{Ca}(\text{OH})_2$	- L

Softening Reaction of L-S Method

[A] Reaction of lime with hardness producing substance (H.P.S):

Lime = Ca(OH)_2





1. As 100 parts by mass of CaCO_3 are equivalent to 74 parts of Lime (Ca(OH)_2) :

Therefore, Lime requirement for softening:

$74/100 [\text{Temp. Ca}^{2+} + 2 \text{ Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2]$.

All in terms of CaCO_3 eq.

2. As 100 parts by mass of CaCO_3 are equivalent to 106 parts of Soda (Na_2CO_3) :

Therefore, Soda requirement for softening:

$106/100 [\text{Perm. (Ca}^{2+} + \text{Mg}^{2+}) + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^-]$.

All in terms of CaCO_3 eq.

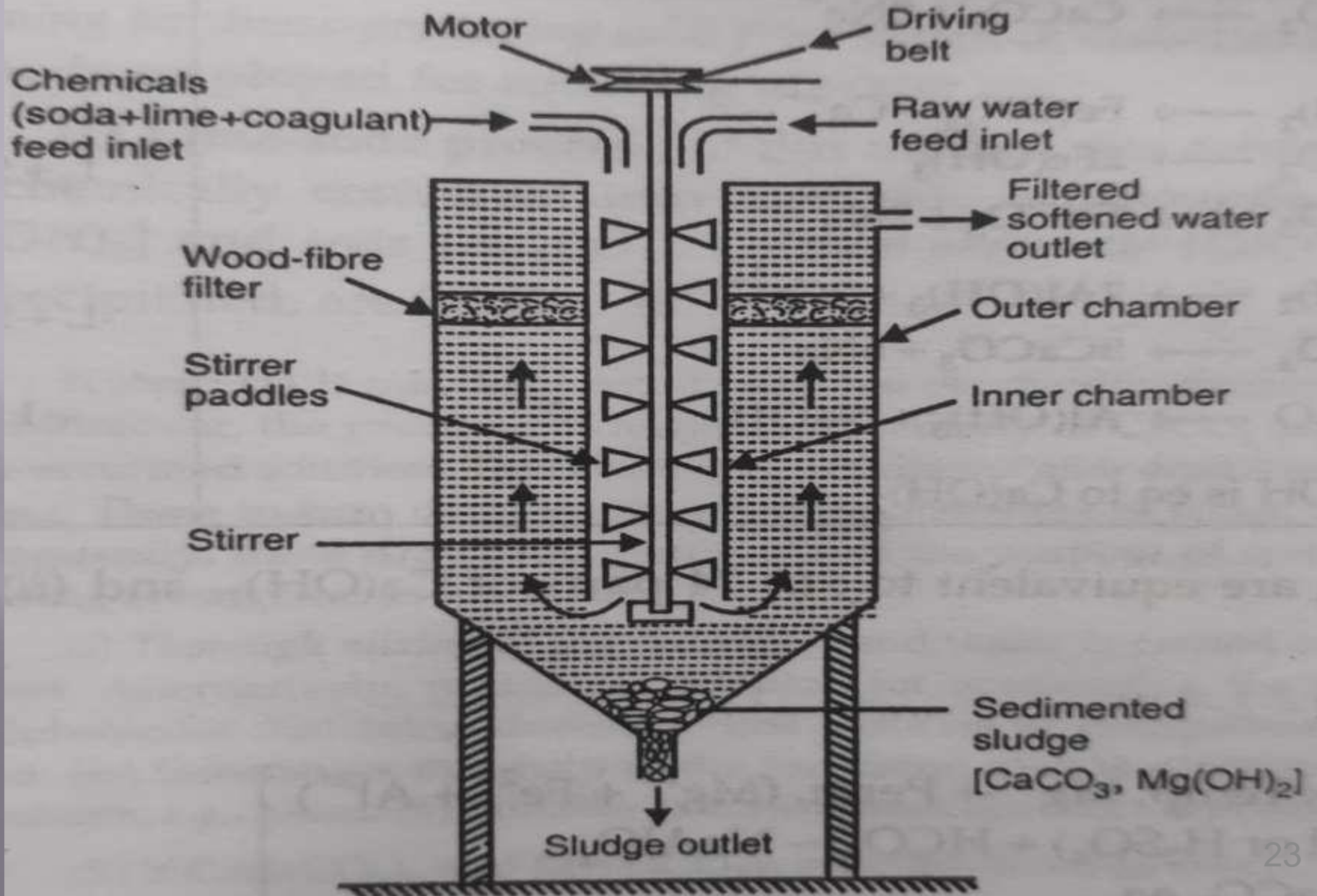
There are two types of Lime-Soda processes.

1. Cold lime-soda process
2. Hot lime-soda process

1. Cold lime-soda process:

In this method, calculated quantity of chemicals (Lime and soda) are mixed with water at room temperature. At room temperature, the ppt formed are finely divided, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (like Alum, Aluminum sulphate, Sodium aluminate, etc.)

Cold Lime Soda Plant



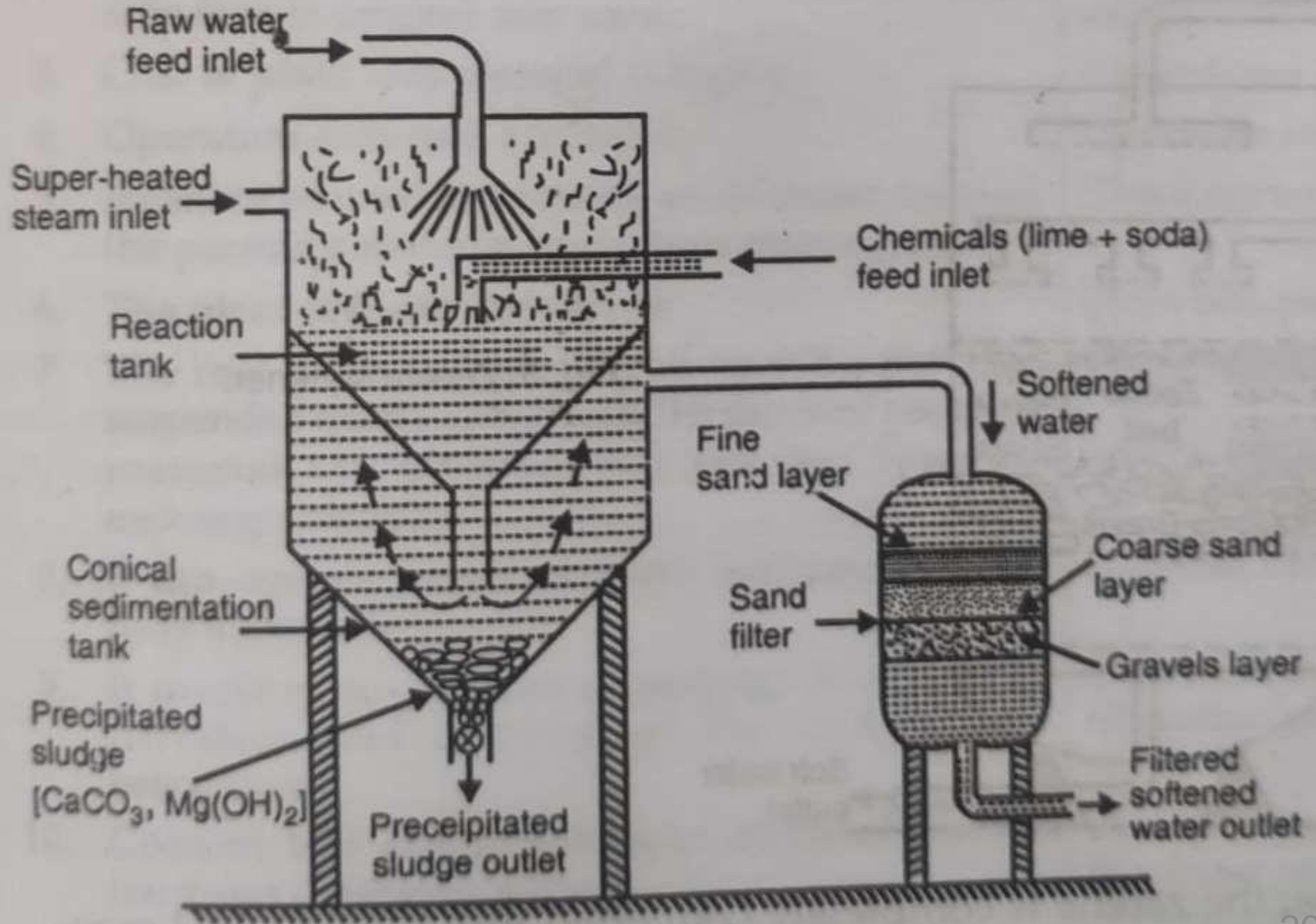
(ii) **Hot lime soda process:**

It involves in treating water with softening chemicals at a temperature of 80-150 °C . Since hot process is operated at temperature close to boiling point of the solution so,

- The reaction proceeds faster.
- The softening capacity of hot process is increased in many folds.
- The precipitate and sludge formed settle down rapidly and hence no coagulants are needed.

- Much of dissolved gases (such as CO_2 , O_2 , H_2S *etc.*) and air driven out of the water.
- Viscosity of softened water is lower, so filtration of water becomes easier. This increases the filtering capacity of filters.
- Hot lime soda process produces water of comparatively lower hardness (15- 30 ppm).

Hot Lime Soda Plant



2. Zeolite and Permutit process

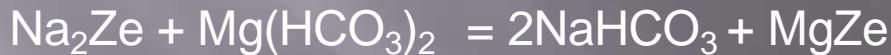
- General formula = $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$,
Where $x = 2-10$ and $y = 2-6$.
- Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly its sodium ions for Ca^{+2} and Mg^{+2} .
- Common zeolite is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ is known as Natrolite.
- Green sand *etc.* are used for water softening.

- Sodium Aluminate, Aluminium Sulphate and Sodium Silicates are heated together at very high temperature providing Artificial Zeolite as Permutit. These are glassy and porous and have greater softening capacity than green sand/ Natural Zeolites.
- They are prepared by heating together china clay, feldspar and soda ash.
- There are innumerable alternative means of preparation of Permutit/Artificial Zeolites in literature.

Methods of softening:

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

Reactions taking place are :



Regeneration of Zeolite:

- The process is also commercially successful since the Ca/Mg zeolites formed by passing hard water through the bed can be easily regenerated into Na_2Ze by passing brine solution through the bed of inactivated zeolite.



- The washing containing CaCl_2 or MgCl_2 are wasted. The water softened by this process can be used for laundry purposes.

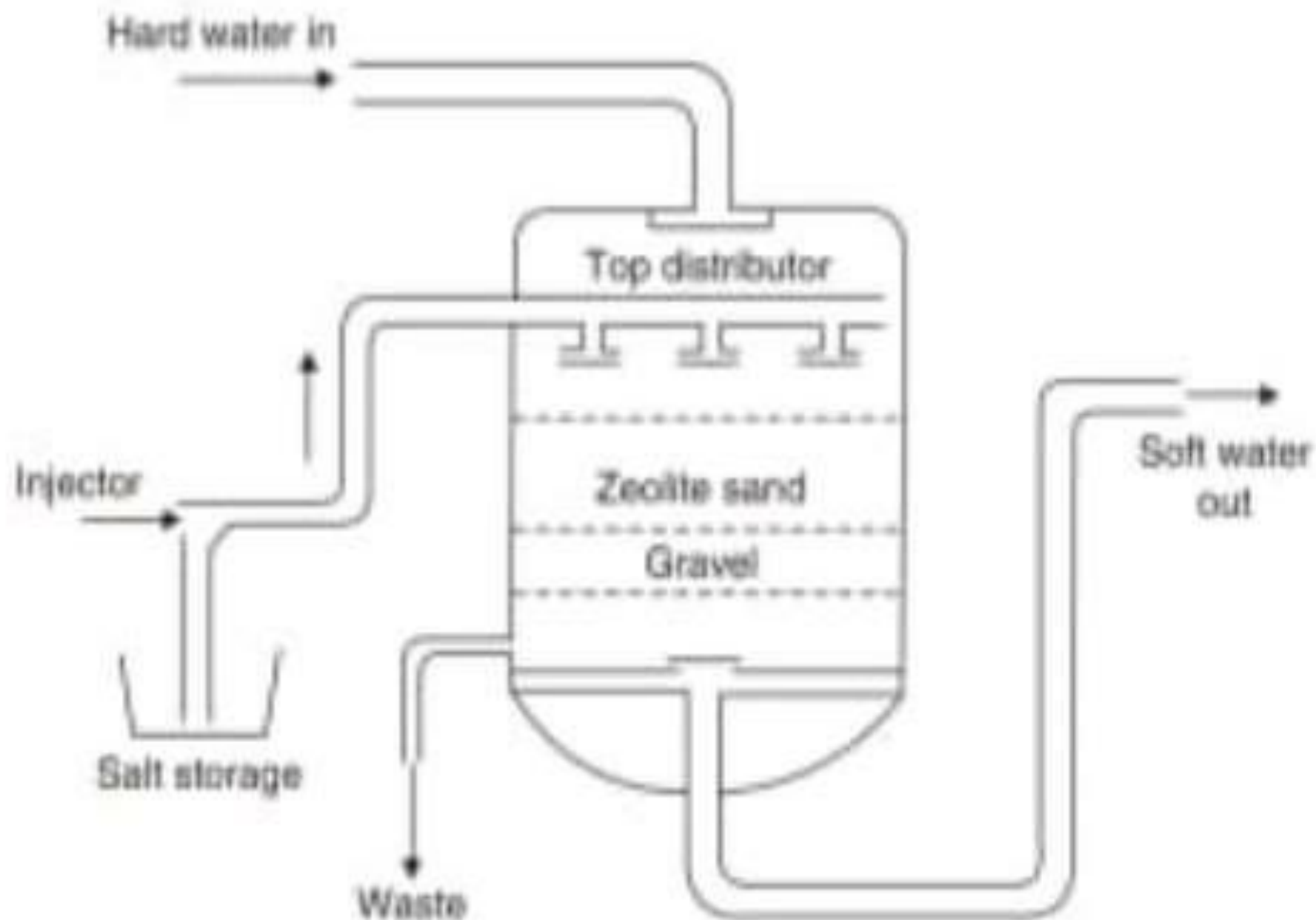
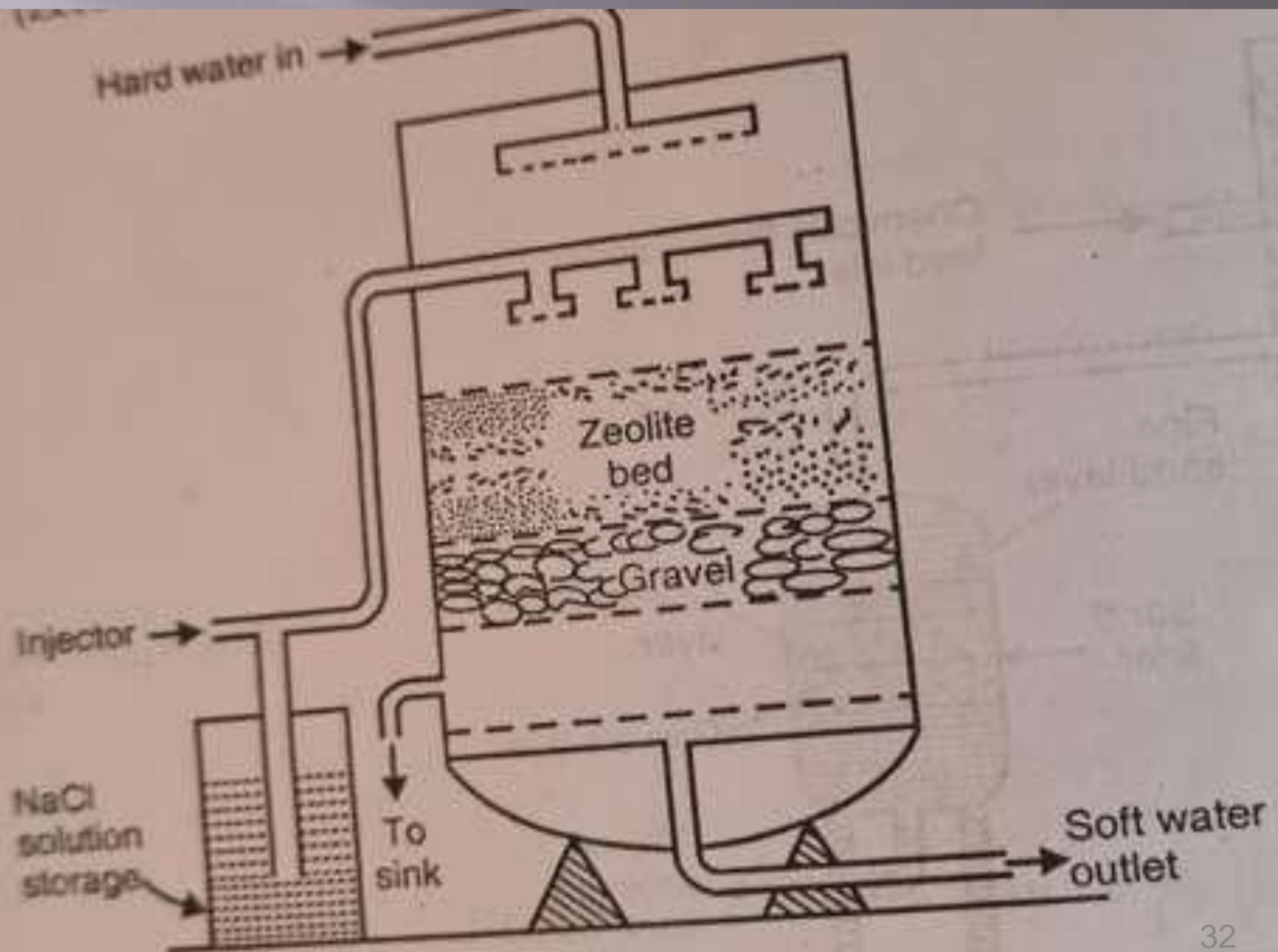


Fig. 17.3 Softening of hard water by permutit process.



Limitations of Zeolite process:

1. 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.
2. If water contains large quantities of coloured ions such as Mn^{+2} and Fe^{+2} , they must be removed first, because these ions produce Mn and Fe zeolites, which cannot be easily regenerated.
3. Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralised with soda, before admitting the water to the zeolite softening plant.

Advantages of Zeolite process:

1. It removes the hardness almost completely and water of about 10 ppm hardness is produced.
2. The equipment used is compact, occupying a small space.
3. No impurities are precipitated, so there is no danger of sludge formation in the treated-water at a later stage.
4. The process automatically adjust itself for variation in the hardness of incoming water
5. It is quite clean
6. It requires less time for softening and less skill for maintenance as well as operation.

Disadvantages of zeolite process:

1. The treated-water contains more sodium salts than in lime-soda process.
2. The method only replaces Ca^{+2} and Mg^{+2} 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.

3. 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.

Permutit method

1. Water of 10-15 ppm residual hardness is obtained.
2. Treated-water contains larger amount of sodium salts than in original raw water
3. Cost of plants and material is higher
4. Operation expenses are lower.
5. It cannot be used for treating acidic water, because the permutit material undergoes disintegration.
6. The plant occupies less space.

Lime-soda method

- Water of, generally, 15-50 ppm hardness is obtained.
- Treated-water contains lesser amount of sodium salts.
- Capital cost is lower.
- Operation expenses are lower.
- There is no such limitations.
- The plant occupies less space.

Permutit method

7. The raw water to be softened must be free from suspended matter; otherwise the pores of permutit material are blocked and the bed loses its exchange capacity.

8. It can operate under pressure and can be made fully automatic.

9. It involves no problem of settling, coagulation, filtration and removal of the sludges and precipitates

10. Control test comprises only in checking the hardness of treated-water.

11. Treated-water contains more dissolved solids.

Lime-soda method

There is no such limitations.

It cannot operate under pressure.

It involves difficulty in settling, coagulation, filtration and removal of the sludges and precipitates

In order to meet the changing hardness of incoming water, frequent control and adjustment of reagents is needed.

Treated-water contains lesser dissolved solids.

De-ionization or De-mineralization process

- A. Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro-porous structure, and the “functional group” attached to the chains are responsible for the ion-changing properties.
- B. Resins containing acidic functional groups (COOH , SO_3H , etc.) are capable of exchanging their H^+ ions with other cations. Which comes in their contacts.
- C. Those containing basic functional groups ($-\text{NH}_2$ as hydrochloride) are capable of exchanging their anions with other anions, which comes in their contact.

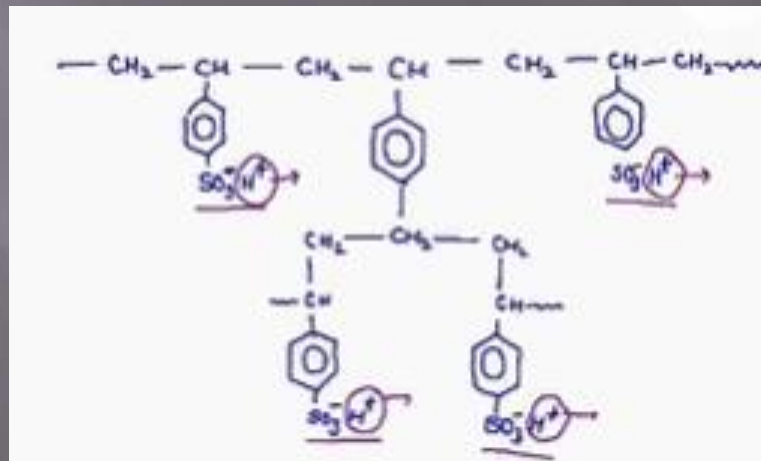
De-ionization or De-mineralization process

The ion exchange may be classified as :

- I. Cation exchange resins
- II. Anion exchange resins

1. Cation exchange resins (RH^+)

These are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water i.e., Ca^{+2} and Mg^{+2} .

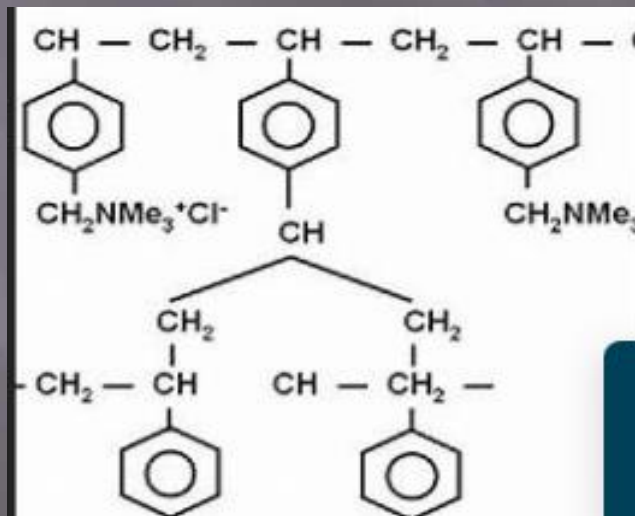


De-ionization or De-mineralization process

2. Anion exchange resins (R^1OH^-)

These are styrene-divinyl benzene or amine-formaldehyde copolymers which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as integral part of the resin matrix.

The resins on treatment with NaOH solution is capable of exchanging the OH^- with different anions of water i.e., Cl^- , SO_4^{2-} etc.



De-ionization or De-mineralization process

The hard water is passed through cation exchange resin similar to the permutit process whereby the cation like Ca^{+2} , Mg^{+2} are removed from the hard water and exchanged with H^{+} as follows:



After the hard water is again passed through anion exchange column, which exchanges all the anions like Cl^{-} , SO_4^{2-} etc. present in the water with OH^{-}



These H^+ and OH^- ions combine to form water molecule. Thus the water coming out finally from the two exchangers is ion free and called deionized or demineralized water.

De-ionization or De-mineralization process

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 :



De-ionization or De-mineralization process

The column is washed with deionised water and washing (which contains Ca^{+2} , Mg^{+2} 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. Na^+ regeneration can be represented as :



The column is washed with deionised water and washing (which contains Na^+ and Cl^- ions) is passed to sink or drain.

The regenerated ion exchange resins are then used again.

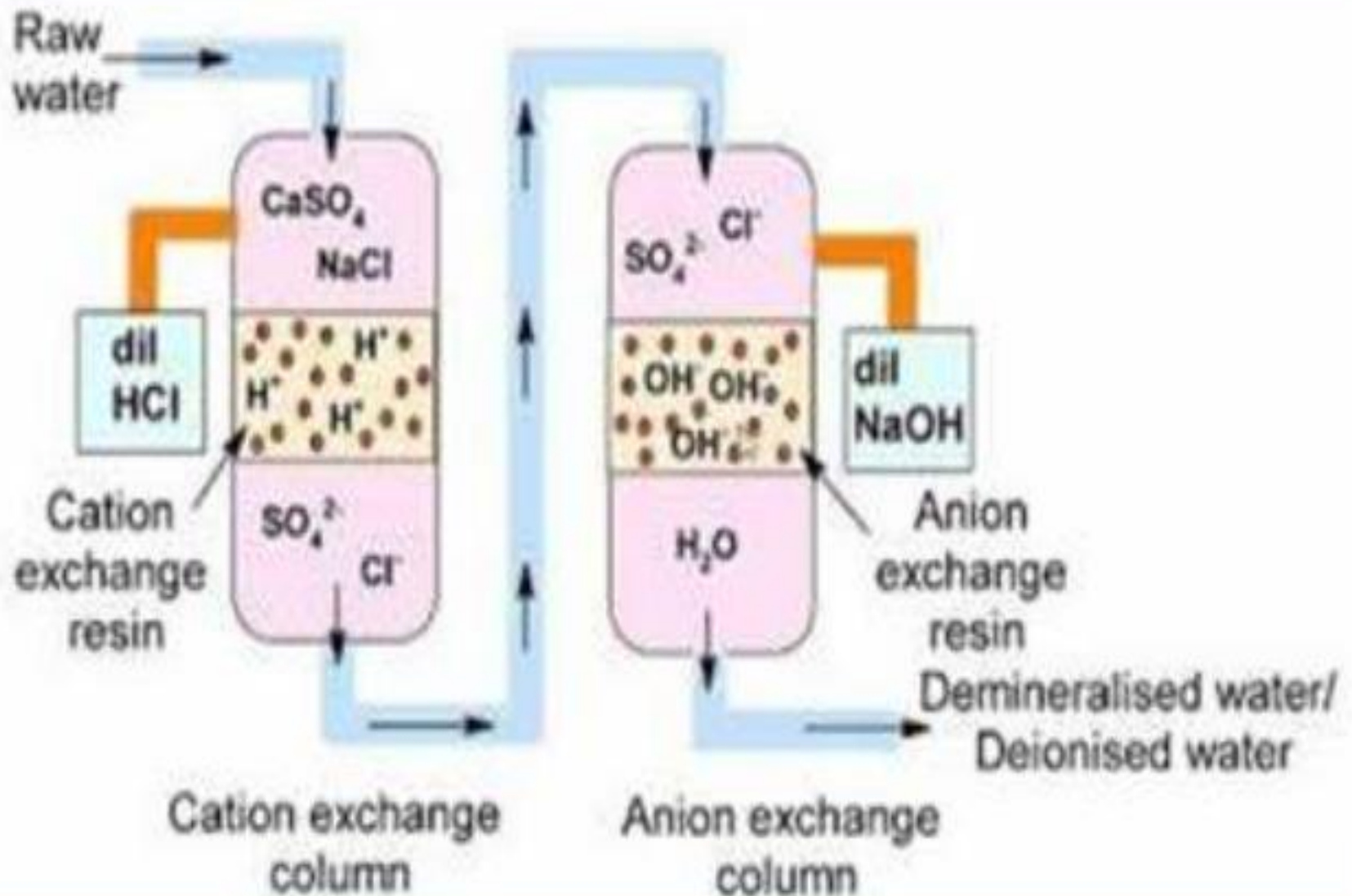
De-ionization or De-mineralization process

Advantages:

- 1) The process can be used to soften highly acidic or alkaline waters.
- 2) Use of water of very low hardness (say 2 ppm). So it is very good for treating water for use in high-pressure.

Disadvantages:

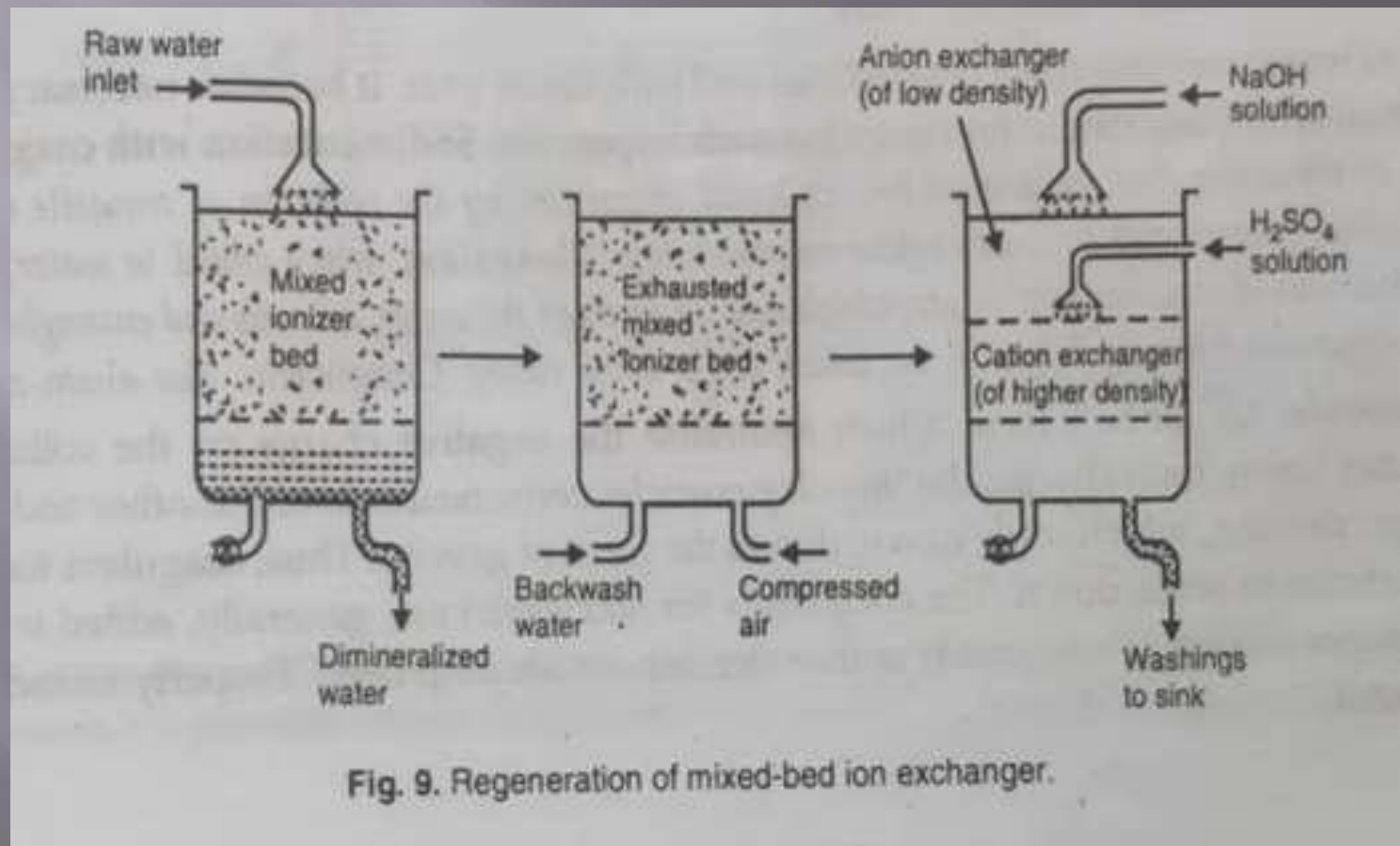
- 1) The equipment is costly and more expensive chemicals are needed.
- 2) Contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm.
- 3) It has to be removed first by coagulation and filtration.



Demineralized Water

Mixed-bed deionizer :

Consists essentially of a single cylinder containing an intimate mixture of hydrogen exchanger and strongly basis anion exchanger.



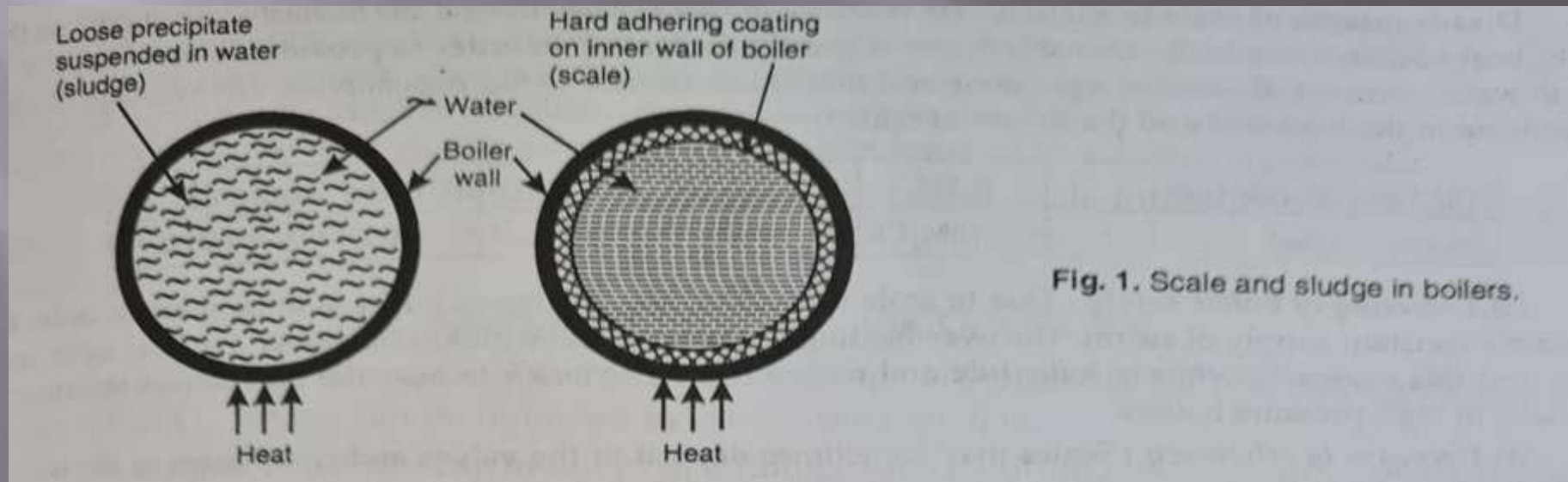
Scale and Sludge formation in Boilers

- In boilers, water evaporates continuously and the concentration of the dissolved salt increase.
- When the concentration reaches to saturation point they are thrown out of water in the form of precipitate on the inner walls of the boiler.
- If the precipitation takes place in the form of loose and slimy precipitate, it is called the sludge.
- If the precipitation takes place in the form of hard and adhering crust/coating, it is called the scale.

(A) Sludge

It is a soft, loose and slimy precipitate formed within boiler.

- It can easily be scrapped off with a wire brush.
- It is formed at a comparatively colder portion of the boiler.
- It collect in the area of the system where the flow rate is slow or at bend.
- Sludges are formed by substances which have greater solubilities in hot water than in cold water such as, MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 etc.



Disadvantages of Sludge formation:

1. Sludges are poor conductor of heat, so they tend to waste a portion of heat generated.
2. If Sludge are formed along with scales, then the former gets entrapped in the latter and both get deposited as scale.
3. Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

Prevention of Sludge formation:

- (1) By using well softened water
- (2) By frequently blow down operation, i.e., drawing off a portion of concentrated water.

(B) Scales

These 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 boiler troubles. Formation of scales may be due to:

(1) Decomposition of calcium bicarbonate



However, Scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, CaCO_3 is soluble.



(2) Deposition of calcium sulphate : The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of CaSO_4 , is 3,200 ppm at 15 °C and it reduces to 55 ppm at 230°C and 27 ppm at 320°C. In other words, CaSO_4 , is soluble in cold water, but almost completely insoluble in super-heated water.

Consequently, CaSO_4 , gets precipitated as hard scale on the heated portions of the boiler. This is the main cause of scales in high-pressure boilers.

Note: Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(3) Hydrolysis of Magnesium salts: Dissolved Magnesium salts undergo hydrolysis (at prevailing high temperature inside the boiler) forming Magnesium hydroxide precipitate, which forms a soft type of scale, e.g..



(4) Presence of Silica: (SiO_2), even present in small quantities, deposits as calcium silicate (CaSiO_2) and/or magnesium silicate (MgSiO_3). These deposits stick very firmly on the inner side the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter

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, excessive or over-heating is done and this causes increase in fuel consumption. The wastage of fuel depends upon the thickness and the nature of scale :

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(2) Lowering of boiler safety: Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.

(3) Decrease in efficiency: Scales may sometimes 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: When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes in formation of a large amount of steam suddenly. So sudden high- pressure is developed, which may even cause explosion of the boiler.

Removal of scales:

- (i) With the help of scraper or piece of wood or wire brush, if they are loosely adhering.
- (ii) By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water), if they are brittle.
- (iii) By dissolving them by adding them chemicals, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes.
- (iv) By frequent blow-down operation, if the scales are loosely adhering.

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 "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. Caustic cracking can be explained by considering the following concentration cell:

Iron at rivets, bends, joints, etc.	⁺	Concentrated NaOH solution		Dilute NaOH solution		⁻	Iron at plane surfaces
---	--------------	----------------------------------	--	----------------------------	--	--------------	------------------------------

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

Caustic embrittlement can be avoided:

- (i) by using sodium phosphate as softening reagent instead of sodium carbonate,
- (ii) by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these is kept as 1:1:2:1 and 3:1 m boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

(iii) by adding sodium sulphate to boiler water Na_2SO_4 , also blocks hair-cracks, thereby preventing infiltration of caustic soda solutions in these. It has been observed that caustic cracking can be prevented, if Na_2SO_4 , is added to boiler water so that the ratio :

$$\frac{[\text{Na}_2\text{SO}_4 \text{ concentration}]}{[\text{NaOH concentration}]}$$

DRINKING WATER OR MUNICIPAL WATER

Municipalities have to supply potable water, e., water which is safe to drink. Drinking or potable water, fit for human consumption, should satisfy the following essential requirements :

- (1) It should be sparkling clear and odorless.
- (2) It should be pleasant in taste.
- (3) It should be perfectly cool.
- (4) Its turbidity should not exceed 10 ppm.
- (5) It should be free from objectionable dissolved gases like hydrogen sulphide.

(6) It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.

(7) Its alkalinity should not be high. Its pH should be about 8.0.

(8) It should be reasonably soft.

(9) Its total dissolved solids should be less than 500 ppm.

(10) It should be free from disease-producing micro-organisms.

Purification of water for domestic use

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

Note: Municipal water treatment does not aim at removing the dissolved salts present. Consequently, municipalities do not generally supply softened water.

(A) Removal of suspended impurities

(1) Screening

The raw water is passed through screens, having large number of holes, when floating matters are retained by them.

(2)Sedimentation

This 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 then drawn from tank with the help of pumps. The retention period in a sedimentation tank ranges from- 2-6 hours.

When water contain fine clay particles and colloidal matter, it becomes necessary to apply sedimentation with coagulation for removing such impurities.

(3) Sedimentation with coagulation

This is the process of removing fine suspended and colloidal impurities by the addition of requisite amount of chemicals (called coagulants) to water before sedimentation.

Coagulant when added to water, forms an insoluble gelatinous, flocculant precipitate, which descent through the water, adsorbs and entangles very fine suspended impurities forming bigger flocs, which settle down easily.

Coagulants like alum or ferrous sulphate provide Al^{+3} or Fe^{+3} , which neutralize the negative charge on the colloidal clay particles.

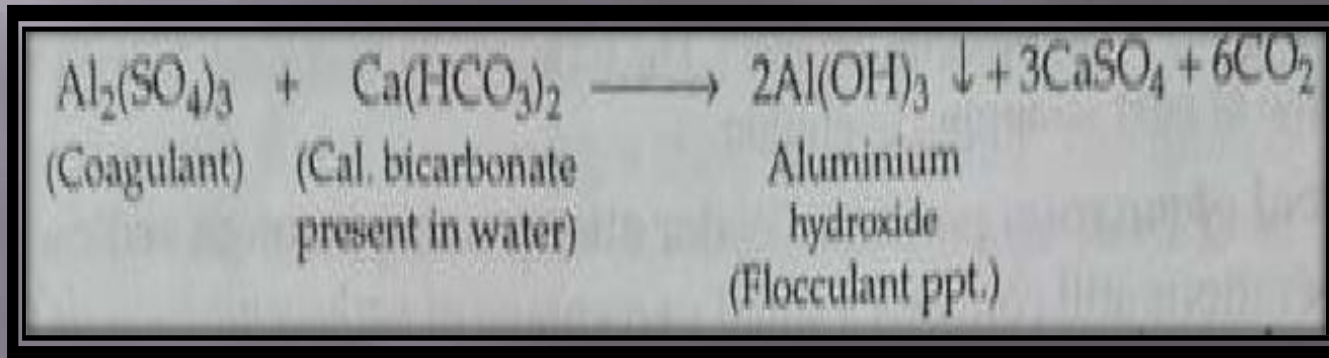
After losing their charge, the tiny clay particles come nearer to one another and combine to form bigger particles, which settle down, due to the force of gravity.

Thus, coagulant forces even colloidal particles to settle down. The coagulants (or flocculants) are, generally added in solution form. For proper mixing of coagulants with water, mixers are employed. Properly mixed water is then sedimented.

Chemical coagulants: The following are the most commonly used coagulants :

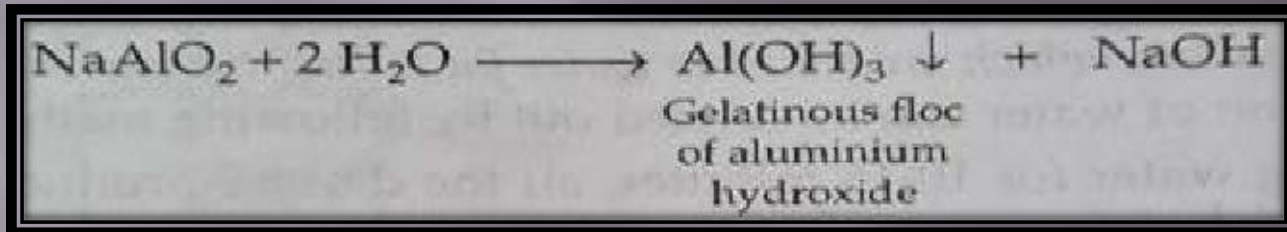
(i) Alum $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$

This is the most widely used in water treatment plants. Alum reacts in water in the presence of alkalinity of water. If natural alkalinity is not present, sufficient lime is also added.



(ii) Sodium aluminate (NaAlO_2)

This is obtained from bauxite refineries in the form of a thick solution. This can very easily be used for treating water having no alkalinity (i.e., pH less than 7). pH range for best results is 5.5-8.0.

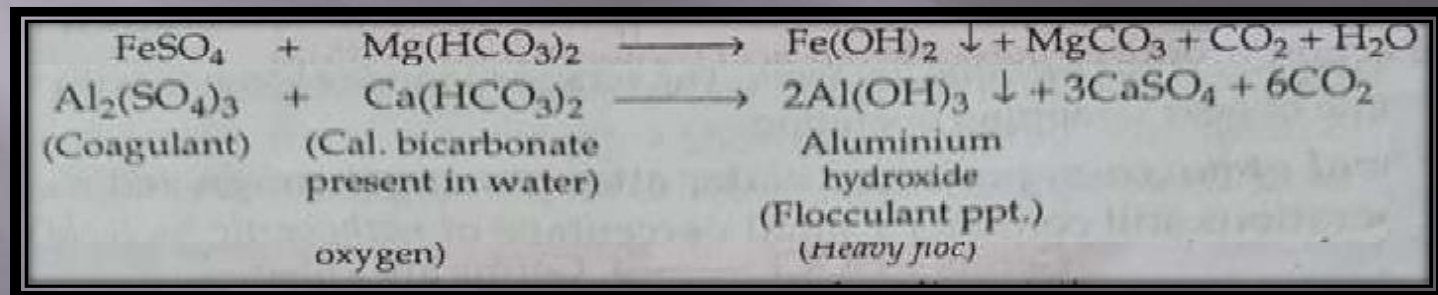


The aluminium hydroxide floc causes sedimentation. The sodium hydroxide thus- produced, precipitates magnesium salts as Mg(OH)_2 .



(iii) Copperas or ferrous sulphate [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$]

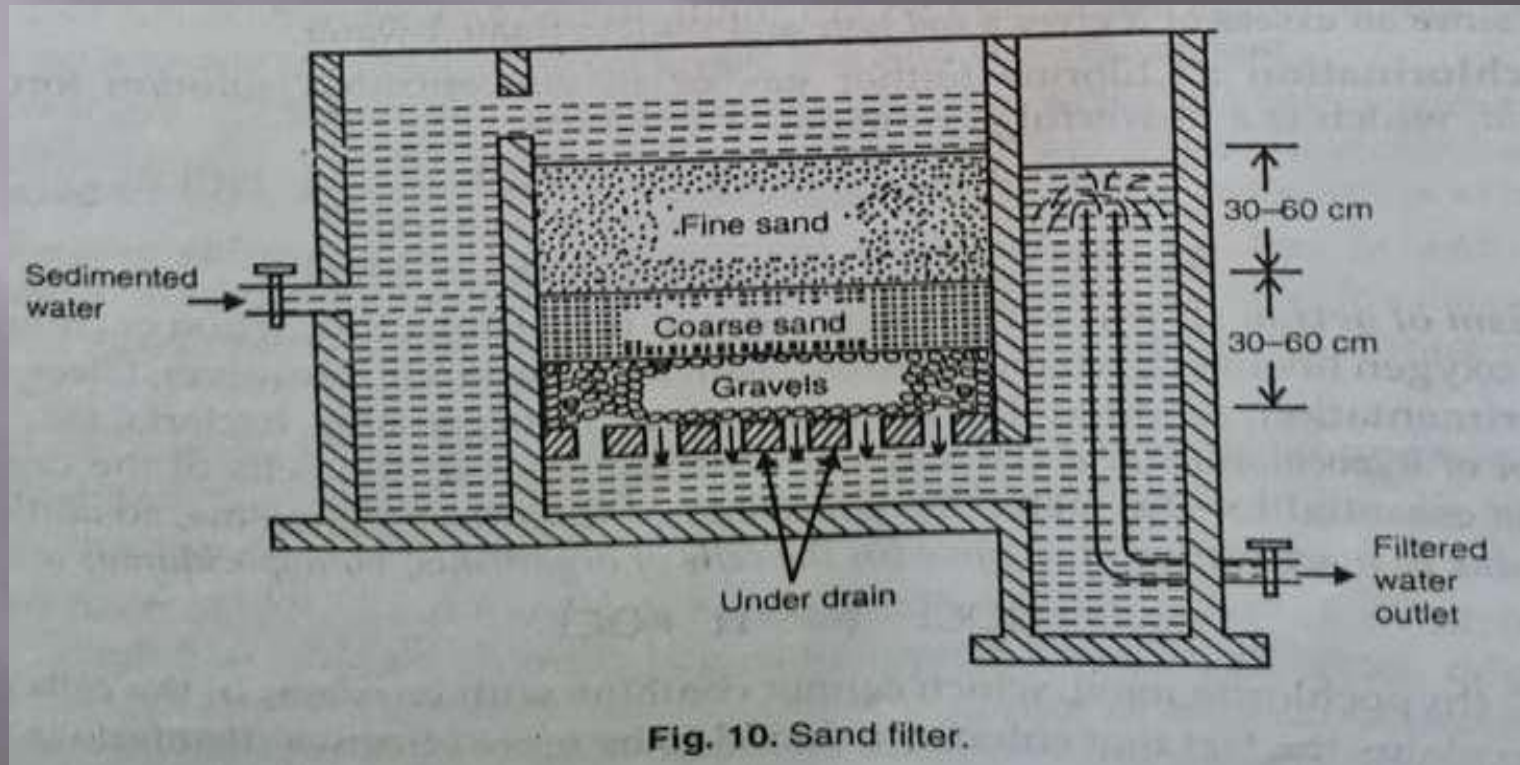
This is also commonly used for coagulation purposes. It gives good results above pH values of 8.5, (i.e., slightly alkaline). Copperas reacts in water in the presence of alkalinity. If alkalinity is not present, sufficient lime is also added.



$\text{Fe}(\text{OH})_3$, is in the form of heavy floc, which causes quick sedimentation.

(4) Filtration

This is the process of removing colloidal matter and most of the bacteria's, micro-organisms, etc.. by passing water through a bed of fine sand and other proper-sized granular materials. Filtration is carried out by using sand filter.

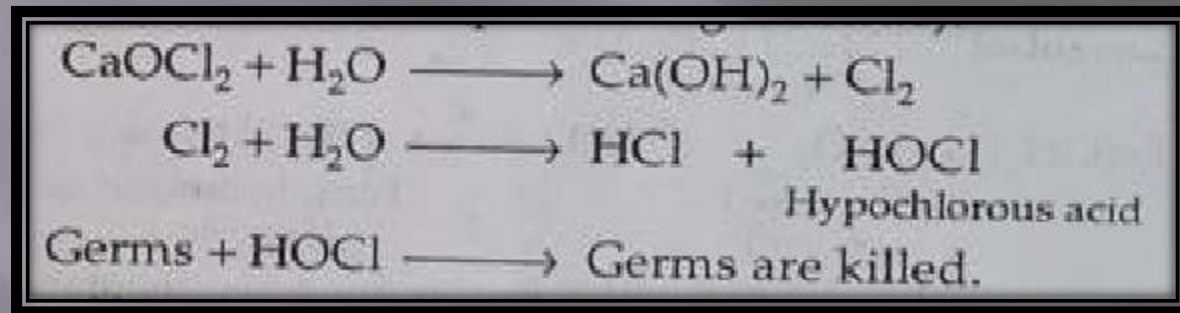


(B) Removal of Micro-organisms: Water after passing through sedimentation, coagulation and filtration operations still contains a small percentage of pathogenic bacteria (disease-producing). Consequently, water used, particularly for drinking or municipal purposes, must be freed from these disease-producing bacteria, micro-organisms, etc. The process of destroying/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:** water for 10-15 minutes, all the disease-producing bacteria are killed and water becomes safe for use.

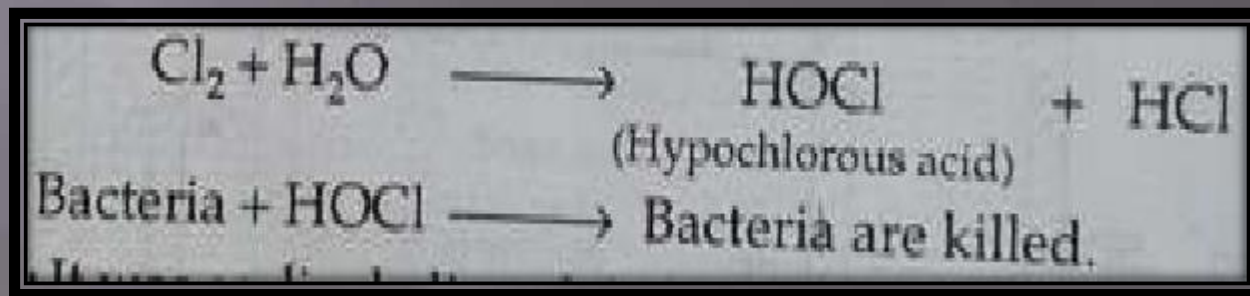
(2) By adding Bleaching powder : In small water-works, about 1 kg of bleaching powder per 1,000 kiloliters of water is mixed and water allowed to stand undisturbed for several hours. The chemical action produces hypochlorous acid (powerful germicide).



The disinfecting action of bleaching powder is due to the chlorine made available by it.

Drawbacks:

- (1) Bleaching powder introduces calcium in water, thereby making it more hard
- (2) Bleaching powder deteriorates, due to its continuous decomposition during storage. So, whenever it is to be added, it has to be analyzed for its effective chlorine content.
- (3) Only calculated quantity of bleaching powder should be used, since an excess of it gives a bad taste and smell to treated-water.
- (3) **By chlorination** : Chlorine (either gas or hypochlorous acid, which is a powerful germicide.



Mechanism of action

- It was earlier believed that the disinfecting action of chlorine was due to the nascent oxygen liberated, which oxidizes harmful bacteria, etc.
- However, Gleen and Stumpf, after long experimentation, reported that the death of micro-organisms, bacteria, etc., results from chemical reaction of hypochlorous acid (HOCl) with the enzymes in the cells of the organisms, etc.



- Since enzyme is essential for the metabolic processes of the micro-organisms, so death of microorganisms results due to inactivation of enzyme (in the cells of organisms) by hypochlorous acid.
- Producing OCl^- (hypochlorite ions), which cannot combine with enzymes in the cells of micro-organisms.
- This explains the fact that chlorine is found to be more effective disinfectant at lower pH values (below 6.5). This is due to the fact that HOCl is about 80 times more destructive to bacterias than OCl^- ions.

- Liquid chlorine is most effective, when applied to filtered water at such a point where adequate mixing is done.
- Chlorine is the most widely used disinfectant throughout the world.
- Apparatus used for this purpose is known as chlorinator (see Fig. 11), which is a high tower, having a number of baffle plates.

- Water and proper quantity of concentrated chlorine solution are introduced at its top. During their passage through the tower, they get thoroughly mixed.
- The treated-water is taken out from the bottom. For filtered-water, about 0.3 to 0.5 ppm of chlorine is sufficient.

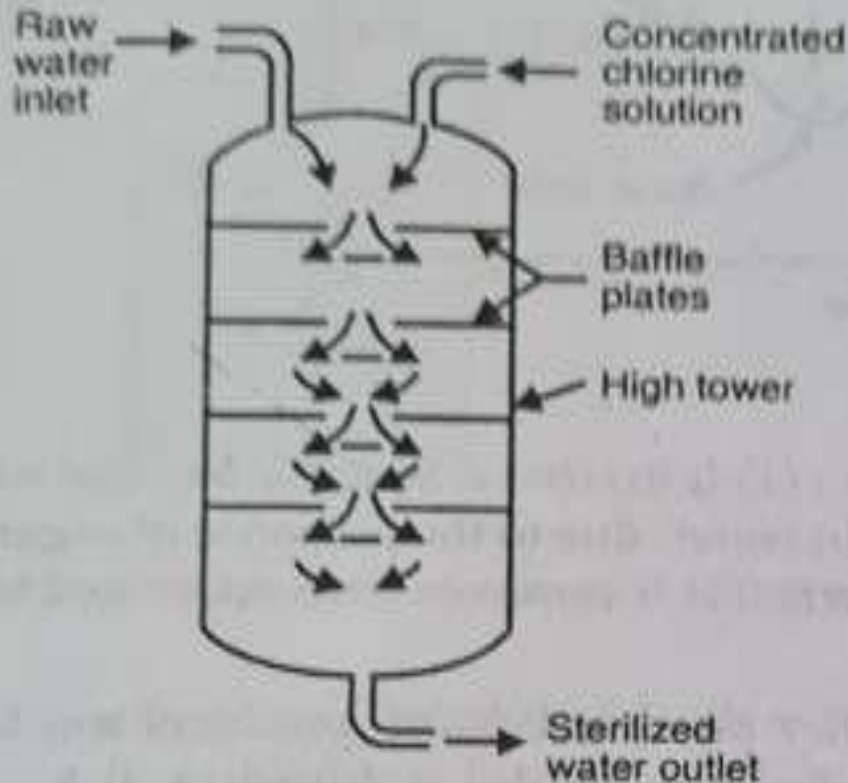


Fig. 11. Chlorinator.

Factors affecting efficiency of chlorine

(i) **Time of contact:** It has been experimentally shown that number of micro-organisms destroyed by chlorine per unit time is proportional to the number of micro-organisms remaining alive. Consequently, the death rate is maximum to start with and it goes on decreasing with time.

ii) **Temperature of water:** The rate of reaction with enzymes increases with temperature. Consequently, death rate of micro-organisms by chlorine increases with rise in water temperature.

(iii) **pH value of water:** It has been found that at lower pH values (between 5-6.5), a small contact period is required to kill same percentage of organisms.

Advantages of chlorine

- (i) It is effective and economical.
- (ii) It requires very little space for storage.
- (iii) It is stable and does not deteriorate on keeping.
- (iv) It can be used at low as well as high temperatures.
- (v) It introduces no salt impurities in the treated-water.
- (vi) It is most ideal disinfectant.

Disadvantages

- (1) Excess of chlorine, if added, produces a characteristic unpleasant taste and odour. Moreover, 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.
- (2) It is more effective below 6.5 pH and less effective at higher pH values.

Break-point chlorination (or free-residual chlorination) involves in addition of sufficient amount of chlorine to oxidize:

(a) organic matter,

(b) reducing substances, and

(c) free ammonia in raw water: leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing (pathogenic) bacteria.

When the dosage of applied chlorine to water rich in organic compound or ammonia is gradually increased, the results obtained can be depicted graphically in Fig. 12, in which appearance of following four stages occurs :

(1) The addition of chlorine at the dip or break, is called 'break point chlorination. This indicates the point at which free residual chlorine begins to appear. Usually, all tastes, odours (chlorinous and others) disappear at break-point, resulting in appearance of water, free from bad tastes and odours.

(2) Moreover, because of the highly persistent and powerful disinfection possessed by available free chlorine, any type of pathogenic organisms present in water are destroyed, thereby making disinfection highly efficient.

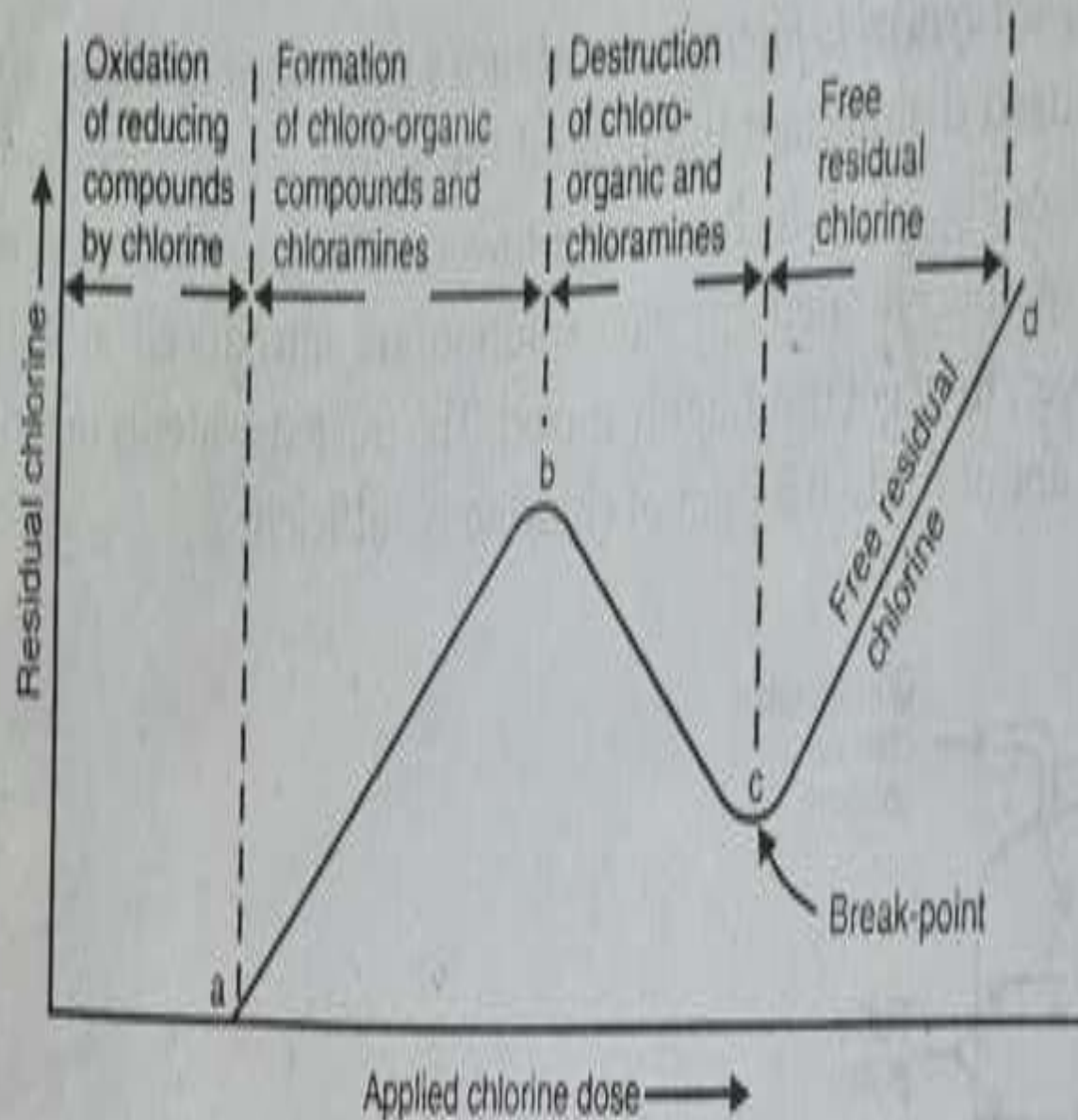


Fig. 12. Break-point chlorination curve.

Advantages of break-point chlorination

- (1) It oxidizes completely organic compounds, ammonia and other reducing compounds.
- (2) It removes colour in water, due to the presence of organic matters.
- (3) It destroys completely (100%) all the disease-producing bacteria.
- (4) It removes both odour and taste from the water.
- (5) It prevents the growth of any weeds in water.

De-chlorination

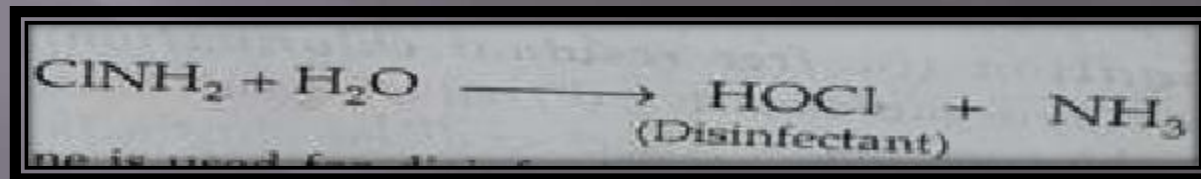
Over-chlorination after the break-point produces unpleasant taste and odour in water. These objectionable qualities may be removed by filtering the over-chlorinated water through a bed of molecular carbon.

Alternatively, a small percentage of activated carbon may be added directly to the water and after allowing a short reaction period, it is then removed by filtration. Objectionable qualities resulting from over-chlorination may also be remedied by the addition of a small percentage of Sulphur dioxide or sodium sulphite or sodium thiosulphate, etc.,

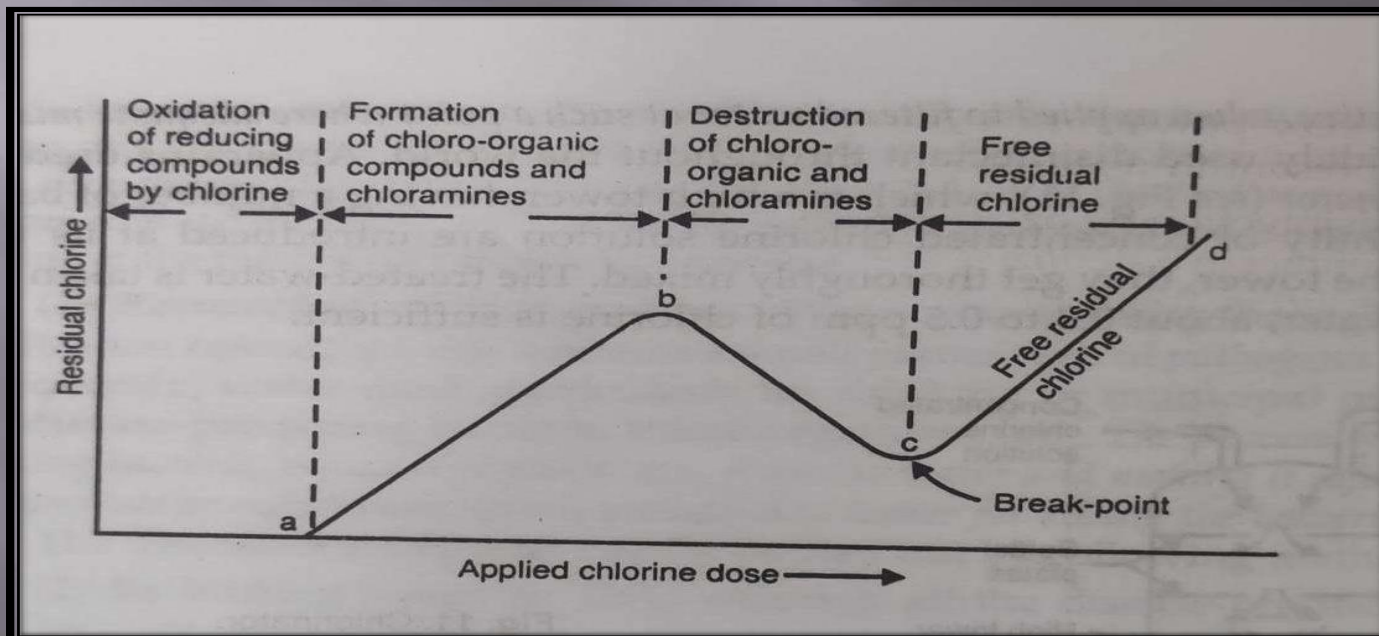
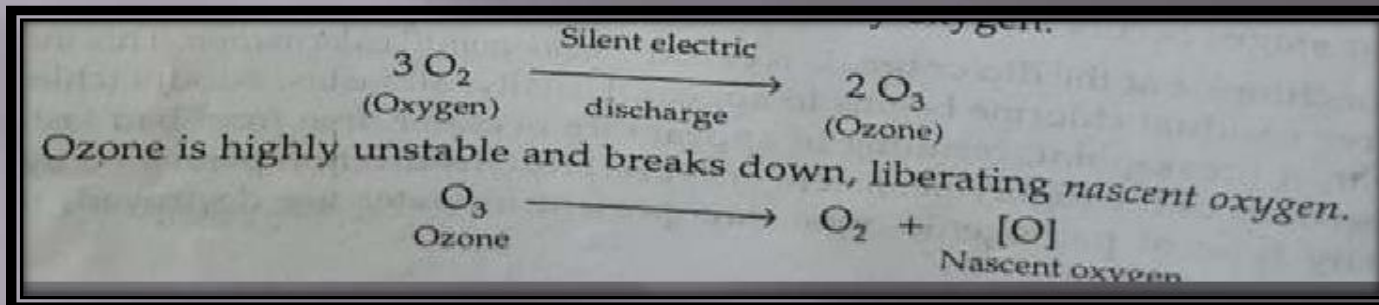
(4) By using chloramine Chloramine (ClNH_2): chlorine and ammonia are mixed in the ratio 2:1 by volume a compound called chloramine is formed.



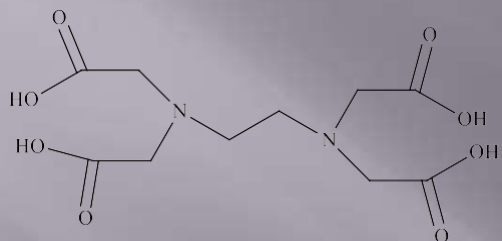
Chloramine is much more lasting than chlorine alone and consequently, it is a better bactericidal than chlorine alone.



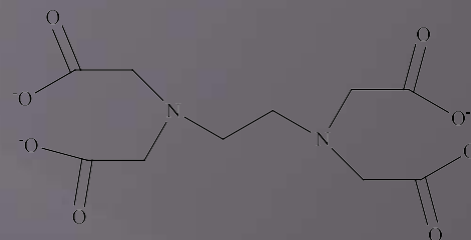
(5) Disinfection by ozone Ozone (g) is an excellent disinfectant, which is produced by passing silent electric discharge through cold and dry oxygen.



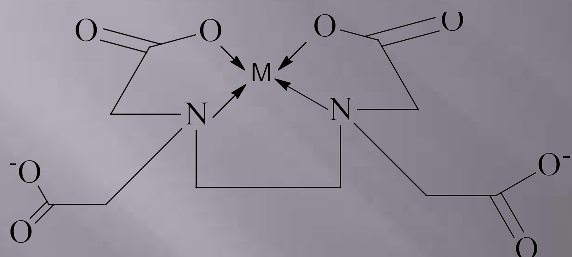
EDTA Method : This is a Complexometric method



Ethylenediamine tetraacetic acid (EDTA)

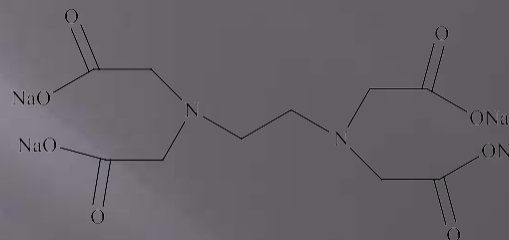


EDTA in the form of its sodium salt yields the anion



or

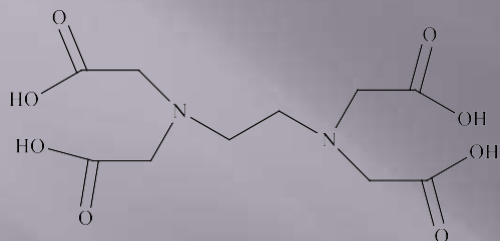
MY^{2-}



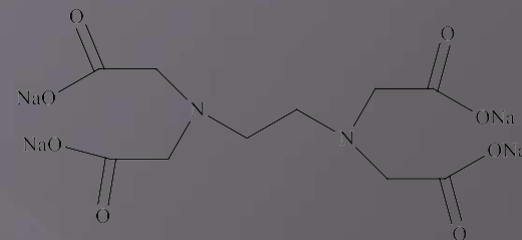
EDTA as its disodium salt

Here M = Ca or Mg
Anionic EDTA forms complex with
Ca⁺² and Mg⁺²

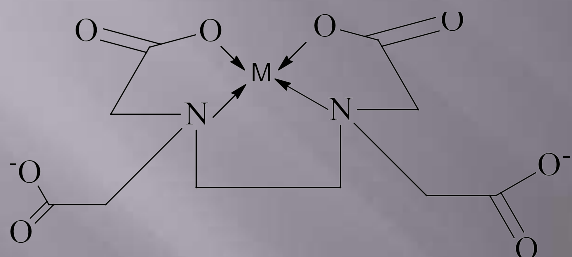
Some important structures



Ethylenediamine tetraacetic acid (EDTA)

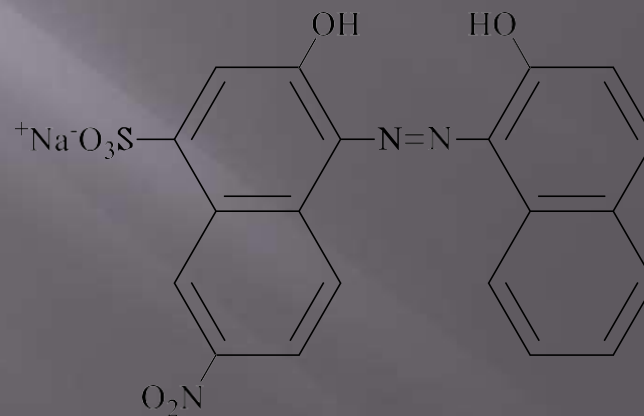


EDTA as its disodium salt ($\text{Na}_2\text{H}_2\text{Y}$) (Titriplex-111)



or

MY^{2-}



Sodium-1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphite ion

Here M = Ca or Mg

Dative bond = 4

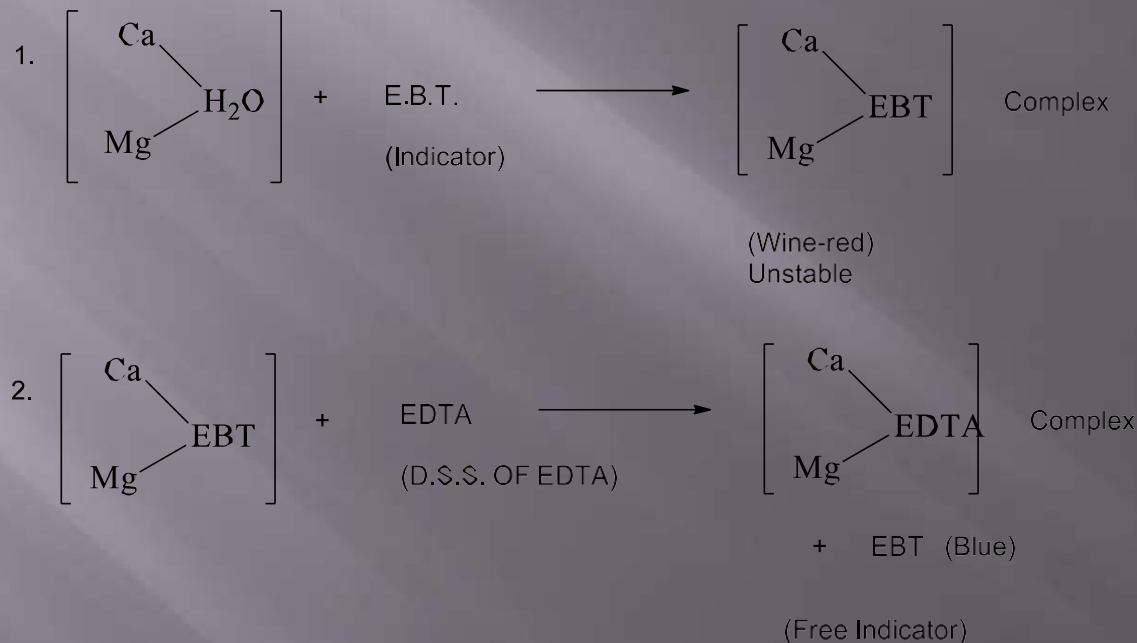
Covalent bond = 2

Hexacoordinated

Structure of Indicator

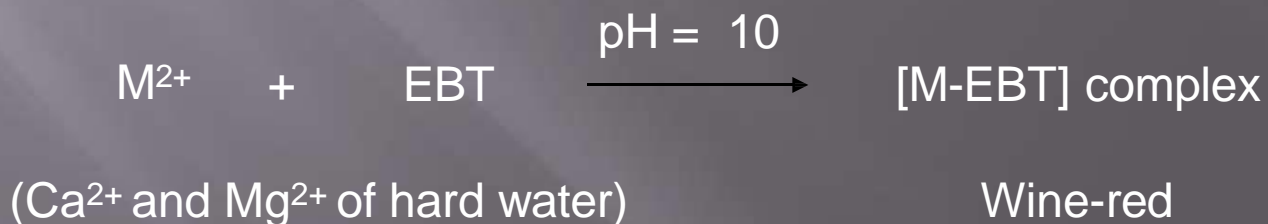
Reaction of M ions (Ca^{+2} / Mg^{+2} with EDTA and EBT during estimation of hardness by EDTA method / Complexometric method

Chemical reaction:

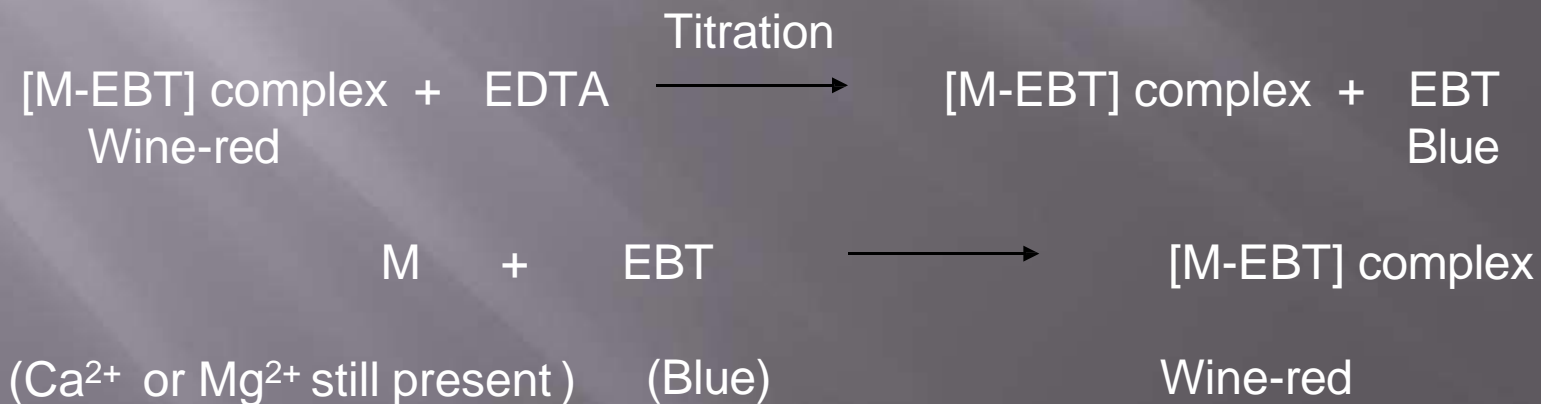


In order to determine the equivalence point (i.e., just completion of metal-EDTA complex formation), indicator eriochrome black-T or EBT (an alcoholic solution of blue dye) is employed,

which form unstable wine-red complex with Cu^{2+} and Mg^{2+} ions. However, this indicator is effective at a pH of about 10. When EBT is added to hard water buffered to a pH of about 10 (by employing $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$ buffer), a wine-red unstable complex is formed. Thus:



So initially a wine-red colored is obtained. During the course of titration against EDTA solution, EDTA combines with M^{2+} (or Ca^{2+} or Mg^{2+}) ions from stable complex, M-EDTA and releasing free EBT, which instantaneously combines with M^{2+} ions still present in the solution thereby wine-red color is retained. Thus:



However, When nearly all M^{2+} (or Ca^{2+} or Mg^{2+}) ions have formed $[M-EDTA]$ complex complex, then next drop of EDTA added displaces the EBT indicator from $[M-EBT]$ complex and the wine-red color changes to blue color (due to EBT). Thus, at equivalence point.



Thus, change of wine-red color to distinct blue marks the end-point of titration. Various steps involved in this method are :

1. Preparation of standard hard water : Dissolve 1.0 of pure,, dry CaCO_3 in minimum quantity of HCl and then evaporate the solution to dryness on a water bath. Dissolve the distilled water to make 1 L solution. Each mL of this solution thus contain 1 mg of CaCO_3 hardness.
2. Preparation of EDTA solution : Dissolve 1.0 of pure EDTA crystals + 0.1 g MgCl_2 in 1L of distilled water.
3. Preparation of indicator : 0.5 g of Eriochrome black-T in 100 ml of alcohol

4. Preparation of buffer solution : Add 67.5 g of NH_4Cl to 570 mL of Concentrated ammonia solution and then dilute with distilled water to 1L.

5. Standardization of EDTA solution : Rinse and fill the burette with EDTA solution with EDTA solution. Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drop indicator. Titrate with EDTA solution, till wine-red color changes to clear blue. Let volume used by V_1 mL.

6. Titration of unknown hard water: Titration 50 mL of water sample just in step (5). Let volume used by V_2 mL.

7. Titration of permanent hardness : Take 250 ml of the water sample in a large beaker, boil it till the volume is reduced to about 50 ml (when all the bicarbonates are decomposed to insoluble CaCO_3 + Mg(OH)_2).

Filter, wash the precipitate with distilled water, collecting filtrate and washings in a 250 ml measuring flask.

Finally make up the volume to 250 ml with distilled water. Then, titrate 50ml of boiled water sample just as in step (5) Let volume used by V_3 ml.

Calculations: 50 ml of standard hard water

$$= V_1 \text{ mL of EDTA}$$

$$50 \times 1 \text{ mg of CaCO}_3 = V_1 \text{ mL of EDTA}$$

$$1 \text{ mL of EDTA} = 50 / V_1 \text{ mg of CaCO}_3 \text{ eq}$$

$$\text{Now 50 ml of given hard water} = V_2 \text{ mL of EDTA}$$

$$= V_2 \times 50 / V_1 \text{ mg of CaCO}_3 \text{ eq}$$
$$1 \text{ L (1,000 mL) of given hard water}$$

$$= 1000 V_2 / V_1 \text{ mg of CaCO}_3 \text{ eq}$$

Total hardness of water

$$= 1,000 V_2 / V_1 \text{ mg/L}$$

$$= 1000 V_2 / V_1 \text{ ppm}$$

Now 50 ml of boiled water = V_3 mL of EDTA

$$= V_3 \times 50 / V_1 \text{ mg of CaCO}_3 \text{ eq}$$

1000 ml (= 1 L) of boiled water = $1000 V_3 / V_1$ mg of CaCO_3 eq

$$\text{Permanent hardness} = 1000 V_3 / V_1 \text{ ppm}$$

and Temporary hardness = [Total-Permanent] hardness

$$= 1000 [V_2 / V_1 - V_3 / V_1] \text{ ppm}$$

$$= 1000 (V_2 - V_3) / V_1 \text{ ppm}$$

Advantages of EDTA method: This method is definitely preferable to the other methods, because of the: greater accuracy, convenience and more rapid procedure