

Hardness of water and types of hardness

Softening of water- principle, reactions, advantages, limitations and Comparison of – Lime-Soda process, Zeolite process, and de-mineralization process.

Numericals based on lime-soda and Zeolite process.

Desalination-using electro dialysis and reverse osmosis processes.

Waste water treatment (introduction and importance) – Brief idea about tertiary treatment methods.

Hardness of water

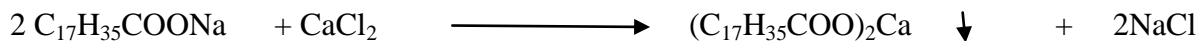
Hardness in water is that characteristic, which prevents the lathering of soap.

or

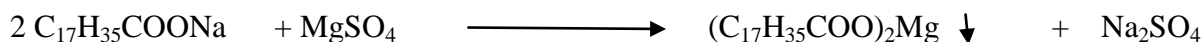
Soap consuming capacity of water is called as hardness of water.

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

A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic acid) does not produce lather, but on the other hand forms a white scum or precipitate. This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium which do not possess any detergent value.



Sodium stearate Hard water Calcium stearate (Insoluble)



Sodium stearate Hard water Magnesium stearate (Insoluble)

(Other metal ions like Fe^{2+} , Mn^{2+} and Al^{3+} also react with the soap in the same fashion, thus contributing to hardness but generally, these are present in natural waters only in traces.

Further acids such as carbonic acid can also cause free fatty acid to separate from soap solution and thus contribute to hardness. However, in practice, the hardness of a water sample is usually taken as a measure of its Ca^{2+} & Mg^{2+} content.)

Defⁿ:-Hard water

When water sample is treated with soap solution, it does not produce lather readily but forms white ppt of Ca stearate and Mg stearate. Such water sample is called as hard water. Such water contains dissolved calcium and magnesium salts in it. In hard water, cleaning quality of soap is depressed and a lot of soap is wasted during washing. Due to presence of dissolved hardness producing salts,boiling point of water is elevated. Consequently, more fuel & time are required for cooking in hard water.

Defⁿ:-Soft water

When water sample is treated with soap solution, it produces lather readily without formation of white ppt of Ca stearate and Mg stearate. Such water sample is called as soft water. Such water does not contain dissolved calcium and magnesium salts in it. In soft water, cleaning quality of soap is not depressed and so soap is not wasted during washing and bathing. Less fuel and time are required for cooking in soft water.

Types of hardness**1. Carbonate or temporary or alkaline hardness:**

Alkaline hardness is defined as the hardness due to the presence of bicarbonates, carbonates and hydroxides of Ca & Mg.

i.e $\text{Ca}(\text{HCO}_3)_2$ calcium bicarbonate

CaCO_3 calcium carbonate

$\text{Ca}(\text{OH})_2$ Calcium hydroxide

$\text{Mg}(\text{HCO}_3)_2$ Magnesium bicarbonate

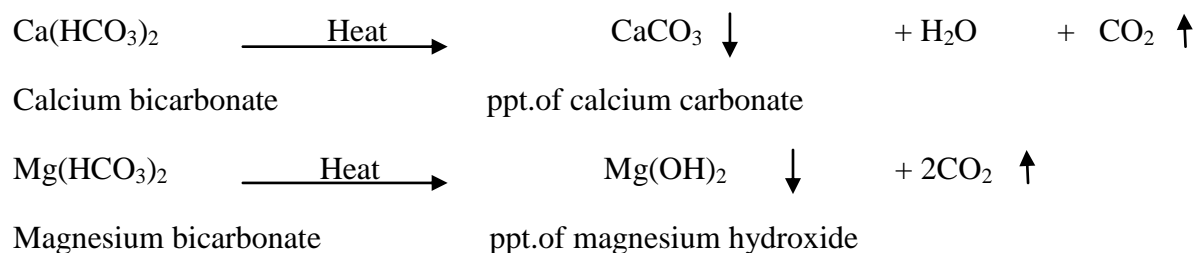
MgCO_3 Magnesium carbonate

$\text{Mg}(\text{OH})_2$ Magnesium hydroxide

Generally, temporary hardness of water sample is due to only bicarbonates of Ca & Mg in water.

In a raw water, the alkaline hardness is almost always the hardness associated with the bicarbonates. However, a treated water or boiler water may also contain hardness due to small quantities of CaCO_3 and $\text{Mg}(\text{OH})_2$ in solution.

Temporary hardness of water sample is removed by only boiling and then filtration. During boiling of hard water, bicarbonates of Ca and Mg are decomposed to form ppts of carbonates or hydroxides.



These ppts are removed by filtration.

1.Non carbonate or permanent or non alkaline hardness

Non alkaline hardness is defined as the hardness due to the presence of chlorides, sulphates and nitrates of Ca and Mg.

i.e CaCl_2 Calcium chloride,

MgCl_2 Magnesium chloride,

CaSO_4 Calcium sulphate,

MgSO_4 Magnesium sulphate,

$\text{Ca(NO}_3\text{)}_2$ Calcium nitrate,

$\text{Mg(NO}_3\text{)}_2$ Magnesium nitrate.

Permanent hardness of water sample can not removed by boiling and then by filtration but it can be removed by special methods like lime soda process, zeolite process and ion exchange process.

Total hardness = Temporary hardness + Permanent hardness.

Hardness of water can be determined accurately on titration with standard EDTA disodium solution using Eriochrome black T indicator at PH 9-10.

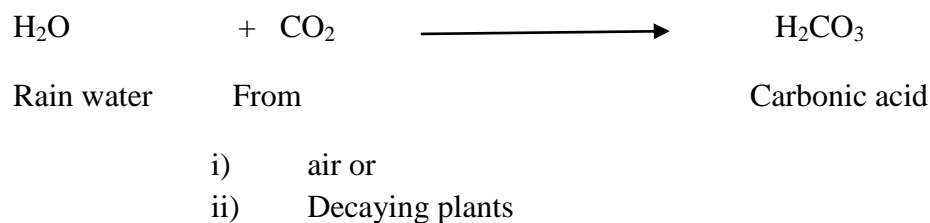
Depending upon the range of hardness, different waters are commonly known by following names.

Sr.No	Range of hardness in ppm	Nature of water
1	0-25 ppm CaCO_3 equivalent	Very soft water.
2	25-50 ppm CaCO_3 equivalent	Soft water
3	50-100 ppm CaCO_3 equivalent	Moderately soft
4	100-150 ppm CaCO_3 equivalent	Slightly hard
5	150-200 ppm CaCO_3 equivalent	Moderately hard

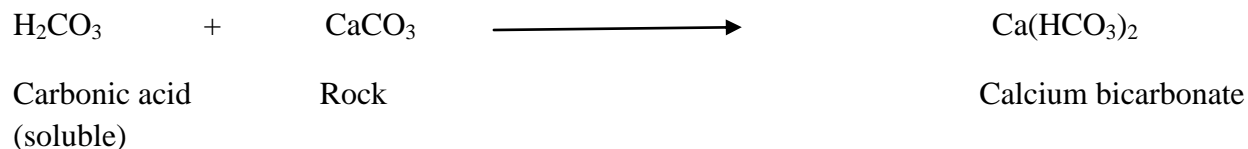
6	200-250 ppm CaCO ₃ equivalent	Hard water
7	Above 250 ppm CaCO ₃ equivalent	Very hard.

Causes of hardness of water

1) Action of dissolved CO₂



Rain water combines with CO₂ & forms carbonic acid then such acidic rain water flow over rocks containing calcium & magnesium carbonates forms soluble salts.



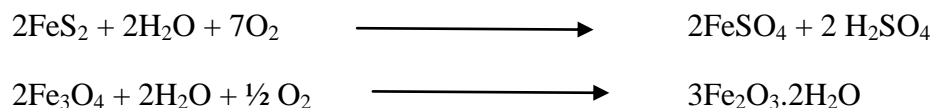
2) On the surface layer, there are also chlorides & sulphates of Ca & Mg & these salts are soluble in water. Thus water gets associated with Ca & Mg salts & becomes hard.

3) Dissolution of minerals-

When rain water flows or deposits on ground or percolates deep down upon non porous hard rock, it comes in contact with various salts in the earth crust. Water soluble salts of heavy metals gives the hardness character to water

4) Action of O₂

Oxygen gas is slightly soluble in water & it can convert some **insoluble minerals to soluble**.



Sources of water

The natural sources of water are

- a) Rain water-It is the purest form of naturally occurring water as it is obtained by a sort of natural distillation.(evaporation and then condensation of water vapours).
- b) Surface water-This is due to run off of water over earth's surface.

Lakes	Streams and rivers	Sea water	Ground water
It is more constant in its chemical composition. The quality of lake water is so good that hardly any treatment is needed for its industrial and domestic use.	This water is less pure than rain water. It contains matter such as clay. It also contains dissolved inorganic salts such as chlorides, sulphates etc. Streams -In hilly areas due to water run off streams are formed. When water from large no.of springs & streams combine together, a river is formed.	It is the most impure form of water. It contains NaCl, MgCl ₂ , KCl etc. All the impurities from river water are carried into sea & thus impurities in sea go on accumulating. Thus sea water becomes more and more salty.	Water from below the earth's crust is called ground water. It is clear in appearance but contains more salts. The rain water after reaching the ground is percolated in soil. During percolation the no. of mineral salts are dissolved in it. So some mineral water (spring water) possesses many times medicinal value as it may contain colloidal sulphur, hydrogen sulphide etc.

Impurities in water

Suspended Impurities	Dissolved Impurities		Colloidal Impurities	Biological Impurities
It includes clay, mud, industrial waste etc.	Gases O ₂ , CO ₂ , H ₂ S, SO ₂ are soluble in natural water.	Mineral salts It includes carbonates, bicarbonates, sulphates, chlorides of Ca & Mg	It includes colloidal particles of clay, fine mud, decayed leaves, organic matter.	It include presence of algae, microorganisms like bacteria(fungi)
Size of particle greater than 10 ⁻³ cm. These can be seen by naked eye.			Size of particles is 10 ⁻⁴ to 10 ⁻⁷ cm. These are invisible to naked eye. These are seen under ultra microscope.	
These remain suspended in water. These produce turbidity, colour & odour.	Gases present in water corrodes the metal, causes acidity, and foul rotten egg smell.	These salts make the water hard.	These impurities neither settle down on standing nor can be removed by filter paper. When associated with bacteria, these become the main cause of diseases.	It causes bad odour of water. It is dangerous for human consumption. Due to biological growth it causes corrosion of equipment. These affect the efficiency of heat transfer equipment.
They are removed by sedimentation or by filtration with the help of sand or cloth or wire mesh filter paper.	Dissolved gases can be removed by boiling the water or aeration method.	These are removed by chemical treatments like soda lime process, ion exchange process etc.	These are removed by coagulation followed by sedimentation.	They need first metal mesh filtration & then sterilization to remove.

Disadvantages of hard water

The disadvantages of using hard water are

1) For domestic use :

- A) Washing: Hard water does not form lather easily with soap, but forms precipitates of Ca and Mg stearates. The formation of insoluble, curdy precipitates continues till all calcium and magnesium salts present in water are precipitated. After that, the soap gives lather with water. This results in wastage of soap. The sticky precipitate adheres & stains the fabric cloth, which becomes more prominently visible on ironing. Presence of iron salts may also cause staining on cloth.
- B) Bathing: hard water does not form lather freely with soap & leaves a sticky deposition on the body. Thus cleaning quality of soap is suppressed & lot of it is wasted .Moreover, due to adsorption of particles of sticky precipitates of Ca and Mg soaps, the skin becomes dry and dark in colour.
- C) Cooking: If salt concentration is more boiling point increases. Hence if hard is used more time is required for cooking & fuel requirement is high. Also if hard water is used for making tea or coffee, it imparts unpleasant taste and muddy looking extract. Moreover, the dissolved salts particularly, bicarbonates of Ca and Mg are deposited as insoluble carbonates on the inner walls of water heating vessels. This results in overheating of utensils and their life is also shortened.
- D) Drinking : Very hard water or very soft water is not recommended for drinking purposes. It has bad effects on our digestive system, & also the possibility of formation of calcium oxalate crystals in the kidney or bladder leading to the formation of kidney stones.

2)For Industrial Use

- A) Textile industry: Soap is wasted in washing yarn, fabric, etc. good amount of lather is not formed & it forms undesirable precipitates of Ca and Mg stearates, which adhere to the fabrics. These fabrics, when dyed later on, do not produce exact shades of colour and uniform dyeing is not possible, because hard water decreases the solubility of acidic dyes. Basic dyes even precipitate out in such hard water. Organic matter imparts foul smell. Fe, Mn, colour or turbidity, causes uneven dyeing and leaves stains & spots on the fabric.
- B) Sugar Industry: cause difficulty in the crystallization of sugar. If hard water is used in sugar refining it results in the formation of deliquescent sugar, which may undergo decomposition during storage.

C) Dye Industry

Hard water is also harmful to use in dye industry. Dye is a colouring matter used for colouration of textile cloth, wool, silk, synthetic fibers and plastics etc. The dissolved salts of Ca, Mg and Fe may react with dyes to form undesirable precipitates due to which impure shades of dyes are produced on the fibers. If iron is also present in water, it produces spots or yellow stains on the cloths. Hence water used for this industry should be free from Ca, Mg and Fe impurities.

D) Paper Industry

During the manufacture of paper, the material like rosin size (a mixture of 70% rosin soap + 30% rosin acid) is added to the paper pulp to make the surface smooth and glossy. If hard water is used for paper manufacturing then Ca^{++} , Mg^{++} ions from hard water is used to react with the material. Hence, the paper will not have the desired smoothness and glossiness. Moreover, due to the presence of Fe^{++} and Mn^{++} impurities in water, the whiteness of paper may be affected.

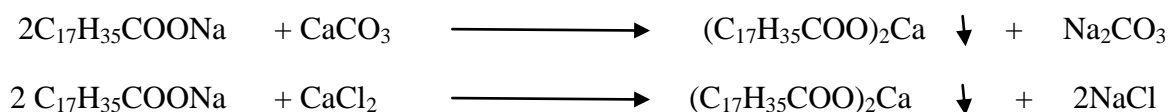
For steam generation in Boilers

Degree of hardness

A number of salts can cause hardness and the type of hardness producing substance and its concentration can vary from sample to sample. To compare the hardness of different samples of water it would be easier if the hardness by different salts can be expressed in terms of a single salt. The hardness of water is conveniently expressed in terms of equivalent amount of CaCO_3 . Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water. The reason for choosing CaCO_3 as the standard for reporting hardness of water is

- i) The ease in calculations as its molecular weight is exactly 100.
- ii) Moreover, it is the most insoluble salt that can be precipitated in water treatment.

Suppose the given water is hard due to the presence of CaCl_2 . The soap consuming capacity of this hard water and a standard hard water containing CaCO_3 can be calculated by using following equation;



1 mole of (100 parts by weight or 2 equivalents) would react with same amount of soap as 1 mole of CaCl_2 (or 111 parts by weight or 2 equivalents). Therefore, the weight of CaCl_2 is multiplied by a factor 100/111 to give the weight in terms of CaCO_3 .

100 g of CaCO_3 = 111 g of CaCl_2 = 136 g of CaSO_4 = 162 g of $\text{Ca}(\text{HCO}_3)_2$ = 95 g of MgCl_2 = 120 g of MgSO_4

Thus 111 parts by weight of CaCl_2 would react with the same amount of soap as 100 parts by weight of CaCO_3 .

Thus, in order to convert the amount of CaCl_2 present (Let a milligrams per liter) as its CaCO_3 equivalent, the amount of CaCl_2 should be multiplied by a factor of 100/111.

1 gram mole of CaCl_2 = 1 gram mole of CaCO_3

111 g of CaCl_2 = 100 g of CaCO_3

1 gram of CaCl_2 = 100 / 111 g of CaCO_3

a mg / l of CaCl_2 = a x 100 / 111 mg/l of CaCO_3

Equivalents of CaCO_3 = mass of hardness producing substance in mg/l x multiplication factor in mg/l or ppm

Units of hardness: The following are the most common units of hardness

1. Parts per million (ppm) : is parts by weight of CaCO_3 equivalent hardness present per million (10^6) parts by weight of water.

Or $1\text{ ppm} = 1$ part of CaCO_3 equivalents hardness in (10^6) parts by weight of water.

2. Milligrams per liter (mg/liter) : It is the number of milligrams of CaCO_3 equivalent hardness present in one litre of water.

$1\text{ mg/litre} = 1$ mg of CaCO_3 equivalent hardness/litre of water.

Relationship between ppm and mg/litre

Since, weight of 1 litre of water $= 1\text{ kg} = 1000\text{ g} = 1000 \times 1000\text{ mg} = 10^6\text{ mg}$

$1\text{ mg/litre} = 1\text{ mg of CaCO}_3\text{ equivalent hardness} / 10^6\text{ mg of water} = 1\text{ part by wt. of CaCO}_3\text{ equivalent} / 10^6\text{ parts by weight of water} = 1\text{ ppm.}$

Thus mathematically both the units are equal

Hence, $1\text{ mg/l} = 1\text{ ppm.}$

3. Degree Clarke ($^\circ\text{Cl}$) or Grains per imperial gallon (gpg): It is the number of parts by weight of CaCO_3 equivalent hardness present in 70,000 parts by weight of water. Or it is number of grains of CaCO_3 equivalent hardness present per gallon of water.

In English system hardness is expressed in terms of grains ($1\text{ grain} = 1/700\text{ lb}$) per gallon (10 lbs) i.e $1^\circ\text{Cl} = 1\text{ gpg} = 1\text{ part of CaCO}_3\text{ per } 70,000\text{ parts of water.}$

$1\text{ ppm} = 1\text{ mg/litre} = 0.07^\circ\text{Cl}$

4. Degree French ($^\circ\text{Fr}$) : It is the number of parts by weight of CaCO_3 equivalent hardness present in 10^5 parts by weight of water.

Thus, $1^\circ\text{Fr} = 1\text{ part by weight of CaCO}_3\text{ equivalent hardness} / 10^5\text{ parts by weight of water.}$

Relationship between all the four units of hardness:

As $1\text{ ppm} = 1\text{ part per } 10^6\text{ parts of water}$ $1^\circ\text{Fr} = 1\text{ part per } 10^5\text{ parts of water.}$ $1^\circ\text{Cl} = 1\text{ part per } 70,000\text{ parts of water.}$

$1\text{ ppm} = 1\text{ mg/litre} = 0.07^\circ\text{Cl} = 0.1^\circ\text{Fr} \text{ \& } 1^\circ\text{Cl} = 1.43^\circ\text{Fr} = 14.3\text{ ppm} = 14.3\text{ mg/litre.}$

Units	ppm	mg/l	$^\circ\text{Fr}$	$^\circ\text{Cl}$
ppm	1	1	0.1	0.07
mg/l	1	1	0.1	0.07
$^\circ\text{Fr}$	10	10	1	0.7
$^\circ\text{Cl}$	1/0.07	1/0.07	1/0.7	1

Softening of Water

The process of removal of hardness producing salts like carbonates, bicarbonates of calcium and magnesium salts (temporary hardness) and chlorides, sulphates and nitrates of calcium and magnesium (permanent hardness) from raw water is known as softening of hard water.

Methods of Softening of Water

Lime soda process

Zeolite Process (or Permutit Process)

Ion Exchange Process (or demineralization or Deionization process)

Lime soda process

Principle

In this process when hard water is treated with calculated amount of lime Ca(OH)_2 and soda ash Na_2CO_3 , the soluble calcium and magnesium salts responsible for hardness present in hard water are chemically converted into precipitate of calcium carbonate CaCO_3 and magnesium hydroxide Mg(OH)_2 . These precipitates are removed by filtration, thus soft water is obtained.

This is cheap and convenient process. Residual hardness remains 15-60 ppm CaCO_3 equivalent. Generally 5 to 10% excess of the calculated quantities of the chemicals are added in water (to ensure complete precipitation and to adjust the PH of water about 8.0).

Lime soda process are of 2 types

Cold lime soda process and

Hot lime soda process

Reactions of Lime Soda Process

Reactions of Lime

Lime	Soda	Hardness	Multiplication factor	1) With temporary hardness
L		T	100/162	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$
2L		T	100/146	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$
2L		T	100/84	$\text{MgCO}_3 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{Mg}(\text{OH})_2$
L		T	100/100	CaCO_3
L		T	100/116	FeCO_3
L		T	100/177.8	$\text{Fe}(\text{HCO}_3)_2$

If the impurities are given as CaCO_3 or MgCO_3 these should be considered due to $\text{Ca}(\text{HCO}_3)_2$ or $\text{Mg}(\text{HCO}_3)_2$ resp and they are only expressed in terms of CaCO_3 and MgCO_3 .

Lime	Soda	Hardness	Multiplication factor	2) With Dissolved Gases
L			100/44	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
L			100/34	$\text{H}_2\text{S} + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaS} + 2\text{H}_2\text{O}$

Lime	Soda	Hardness	Multiplication factor	3) With Free Acids
L +	S		100/ 36.5 x 2	$2\text{HCl} + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCl}_2 + 2\text{H}_2\text{O}$
L +	S		100/98	$\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
L +	S		100/63x2	$2\text{HNO}_3 + \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}(\text{NO}_3)_2 + \text{Mg}(\text{OH})_2$
L +	S		100/1x2	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}^{++} + 2\text{H}_2\text{O}$

Lime	Soda	Hardness	Multiplication factor	4) With Coagulants
L+	S		100/342/3 =3x100/342	$\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \longrightarrow 2\text{Al}(\text{OH})_3 + 3\text{CaSO}_4$
L+	S		100/278	$\text{FeSO}_4 + \text{Ca}(\text{OH})_2 \longrightarrow \text{Fe}(\text{OH})_2 + \text{CaSO}_4$
-L	-S		100/82x 2	NaAlO ₂ does not react with lime but it reacts with water. $\text{NaAlO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{Al}(\text{OH})_3$ NaOH is equivalent to $\text{Ca}(\text{OH})_2$ & Na_2CO_3

Lime	Soda	Hardness	Multiplication factor	5) With bicarbonate ion or Sodium bicarbonate or Potassium bicarbonate
L	-S		100/ 84 x 2	$2\text{NaHCO}_3 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$
L	-S		100/ 100 x 2	$2\text{KHCO}_3 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 + \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$
L	-S		100/ 61 x 2	HCO_3^-

Lime	Soda	Hardness	Multiplication factor	6) With Permanent Hardness (Except due to Calcium) i.e with permanent magnesium hardness
L+	S	P	100/95	$\text{MgCl}_2 + \text{Ca(OH)}_2 \longrightarrow \text{Mg(OH)}_2 + \text{CaCl}_2$
L+	S	P	100/120	$\text{MgSO}_4 + 2\text{Ca(OH)}_2 \longrightarrow \text{Mg(OH)}_2 + \text{CaSO}_4$
L+	S	P	100/148	$\text{Mg(NO}_3)_2 + \text{Ca(OH)}_2 \longrightarrow \text{Mg(OH)}_2 + \text{Ca(NO}_3)_2$
L+	S	P	100/24	Mg^{++}
L+	S	P	100/54.9	Mn^{++}
L+	S	P	100/55.8	Fe^{++}
L+	S	P	100/27	Al^{+++}
L+	S	P	100/63.54	Cu^{++}
L+	S	P	100/65.38	Zn^{++}

Lime reaction with such permanent hardness causing salts produces calcium permanent hardness.

Lime	Soda	Hardness	Multiplication factor	7) Ignore or Impurities which are not considered during the calculation of lime requirement
Ignore	Ignore			NaCl
Ignore	Ignore			KCl
Ignore	Ignore			Na_2SO_4
Ignore	Ignore			SiO_2
Ignore	Ignore			Fe_2O_3
Ignore	Ignore			K_2SO_4
Ignore	Ignore			SO_4^{--}
Ignore	Ignore			Cl^-
Ignore	Ignore			Turbidity

Lime	Soda	Hardness	Multiplication factor	1) With OH^-
L+	S		100/2 x 17	OH^- This is supplied by lime and therefore shown as requirement for lime. Due to the excess of lime the Ca^{++} ions will require soda.

Reactions of Soda

Lime	Soda	Hardness	Multiplication factor	1) With permanent calcium hardness
	S	P	100/111	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{NaCl}$
	S	P	100/136	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$
	S	P	100/164	$\text{Ca}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{NaNO}_3$
	S	P	100/40	Ca^{++}

Lime	Soda	Hardness	Multiplication factor	2) With carbonate ion
	S		100/60	CO_3^{--}

Lime	Soda	Hardness	Multiplication factor	3) With Free Acids
L +	S		100/36.5 x 2	$2\text{HCl} + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaCl} + 2\text{H}_2\text{O} + \text{CO}_2$
L +	S		100/98	$\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$
L +	S		100/63x2	$2\text{HNO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaNO}_3 + \text{H}_2\text{O} + \text{CO}_2$
L +	S		100/1 x 2	$2\text{H}^+ + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$

Lime	Soda	Hardness	Multiplication factor	4) With Coagulants
L+	S		100/342/3 = 3 x 100/ 342	$\text{Al}_2(\text{SO}_4)_3 + 3\text{Na}_2\text{CO}_3 \longrightarrow \text{Al}_2(\text{CO}_3)_3 + 3\text{Na}_2\text{SO}_4$
L+	S		100/278	$\text{FeSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{FeCO}_3 + \text{Na}_2\text{SO}_4$
-L	-S		100/82 x 2	<p>NaAlO_2 does not react with lime but it reacts with water.</p> <p>$\text{NaAlO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{Al}(\text{OH})_3$ NaOH is equivalent to $\text{Ca}(\text{OH})_2$ & Na_2CO_3</p>

Advantages of Lime Soda Process

pH of softened water is nearly 8.5

Economical process

Softened water contains total dissolved solids lesser than raw water.

Water containing colloidal impurities can also be softened

Acidic water can be softened.

Residual hardness in the softened water is small 15-25 ppm (if hot process is employed).

Bacterial impurities reduced.

Disadvantages of Lime Soda Process

This method requires thorough study of water regarding amounts of various salts and gases.

It cannot be used for household purposes as the requisite amount of chemicals is not known.

Precipitate matter is to be handled in this method.

Water for the use of high pressure boiler is not so good.

It is also not fit for many industrial purposes as the water obtained is supersaturated with CaCO_3 .

Even though slight excess of lime and soda are added, residual hardness remains in the treated water. (15-60 ppm CaCO_3 equivalent) or Lime soda process cannot produce water of zero hardness

[Explanation: In lime soda process, slight excess of lime Ca(OH)_2 is used than the calculated amount of lime required for particular raw water sample. Hence soft water produced by cold lime soda process consists little amount of un-reacted lime i.e soft water produced by this process consists of Ca^{++} ions responsible for residual hardness in water. Therefore lime soda process can not produce water of zero hardness.]

Cold Lime Soda Process

In this process, when hard water is treated with calculated amount of lime Ca(OH)_2 and soda ash Na_2CO_3 at room temperature 25°C , the soluble Ca and Mg salts present in hard water are chemically converted into ppt. of calcium carbonate CaCO_3 and magnesium hydroxide Mg(OH)_2 . Coagulant is added to settle down the sludge and precipitate. These precipitates are removed by filtration. Thus soft water is obtained.

Hot Lime Soda Process

In this process, when hard water is treated with calculated amount of lime Ca(OH)_2 and soda ash Na_2CO_3 at $80-150^\circ\text{C}$ (by passing steam), the soluble Ca and Mg salts present in hard water are chemically converted into ppt. of calcium carbonate CaCO_3 and magnesium hydroxide Mg(OH)_2 . [Due to higher temperature, the viscosity of the water decreases and hence the rate of aggregation of particles of precipitates increases i.e big size particles are formed and it settle by gravity force.]. These precipitates are removed by filtration. Thus soft water is obtained.

Lime soda process can be carried out in

- a) Batch process
- b) Cold continuous process
- c) Hot continuous process

a) Batch process/Process by use of Intermittent Type Softener

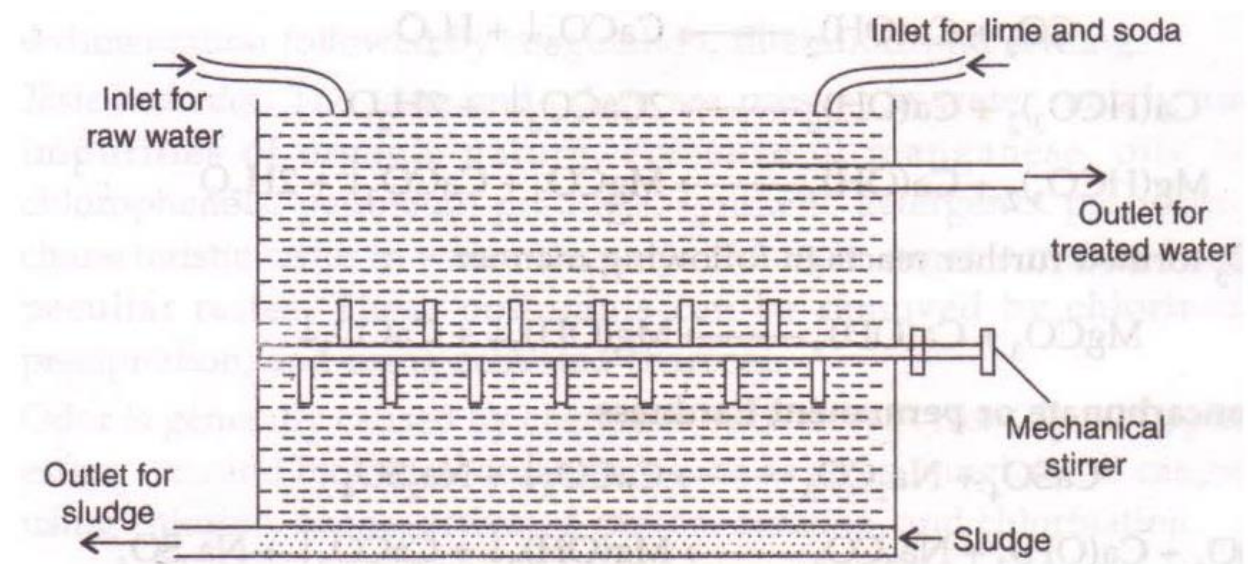


Fig : Intermittent Type Softener

This process is used for large quantity of water required for industries.

There is a big tank with inlets for water and chemicals.

There are outlets for soft water and the sludge (ppt). There is a mechanical stirrer.

Process :- Proper quantities of lime, soda and coagulant (alum or sodium aluminate or FeSO_4) are added to water in the tank and stirred. After completion of reactions, stirring is stopped and the precipitates formed are allowed to settle up to 2 hours. Coagulant helps to settle the precipitates at bottom. Then the supernatant soft water is taken out and sludges are released out from bottom. If needed, the softened water is sent to filtering unit for clarity. Residual hardness when exact quantities of lime and soda added is 50-60 ppm CaCO_3 equivalent.

b) Cold Continuous Lime Soda Process

This method is used when soft water requirement of industry is small.

Process:- Raw water and proper quantities of chemicals (Lime, Soda, Coagulant) are continuously fed from top of inner vertical bottom pot, which is fitted with stirrer.

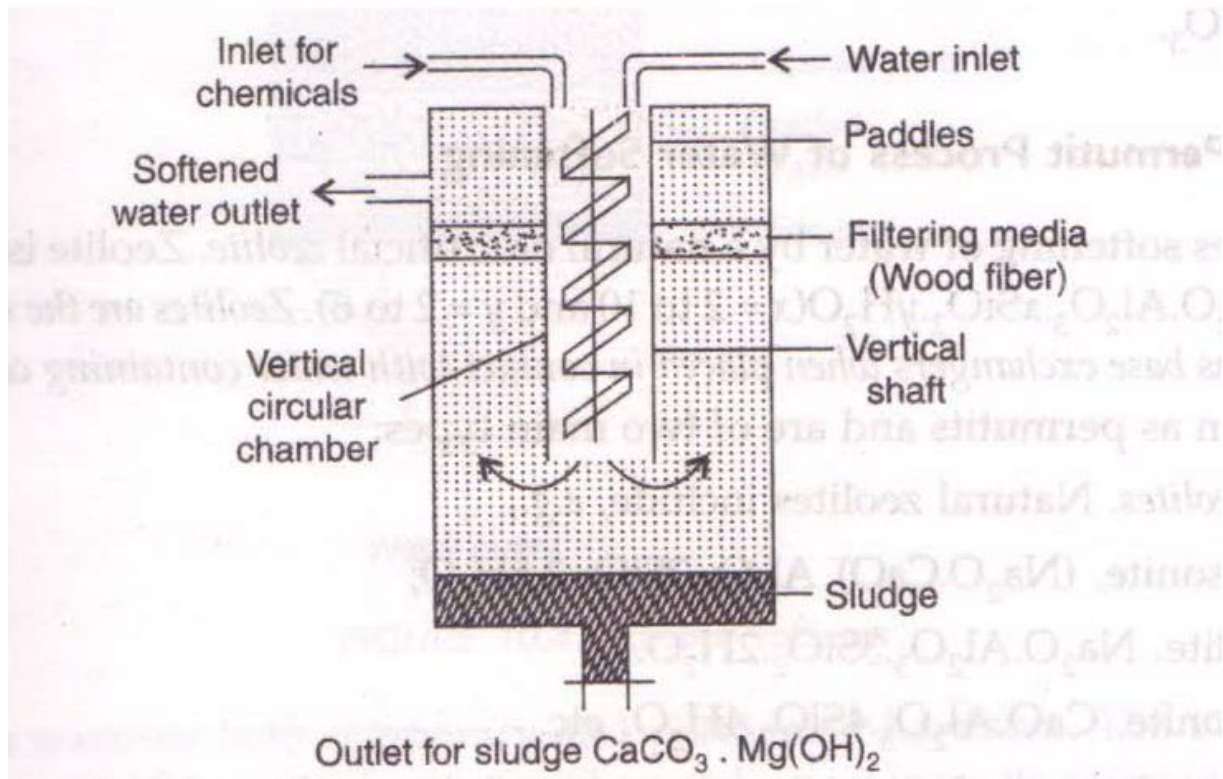


Fig:- Cold Continuous Lime Soda Process softener

Due to vigorous stirring, hardness causing chemicals react with lime and soda to form precipitates. Coagulant functions to settle the precipitates faster at the bottom.

By the time softened water rises up in outer coaxial pot. Then it passes through wood fiber filter and softened water comes out continuously. Residual hardness is 50-60 ppm CaCO_3 equivalent.

c) Hot Continuous Lime Soda Process

This process is used when soft water requirement of industry is small but water of much lower residual hardness is obtained i.e 15-25 ppm CaCO_3 equivalent.

The reaction is carried out in hot condition, therefore

- i) The reaction takes place faster.
- ii) Precipitates settle faster and there is no need of coagulant.

[Explanation: Hot lime soda process takes place at higher temperature i.e at 80-150 $^{\circ}\text{C}$. Due to higher temperature, the viscosity of the water decreases and hence the rate of aggregation of particles of precipitates increases i.e big size particles are formed and it settle by gravity force. Hence during this process, coagulants are not required.]

- iii) The residual hardness of softened water is in 15-25 ppm range.
- iv) Dissolved gases at higher temperature get expelled out.

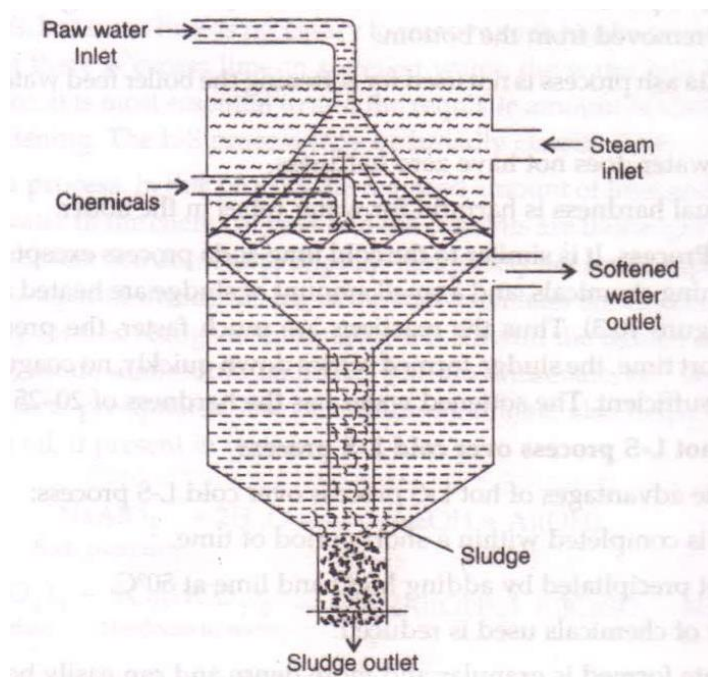


Fig:- Hot Continuous Lime Soda Process softener

Process:- Raw water and chemicals (lime & Soda) enter in the cylindrical pot, which get heated due to steam contact. There is upper funnel like pot having long stem. The precipitates formed from the reaction of hard water and chemicals settle easily and soft water comes out. The softened water may be passed through sand filter for clarity.

Difference between Cold and Hot Lime Soda Process

Sr No	Cold Lime Soda Process	Hot Lime Soda Process
1	It is slow process. 2-3 hrs required	It is fast process. Nearly 15 min. required
2	It takes place at room temperature	It takes place at about 80-150 ⁰ C
3	Its softening capacity is low.	Its softening capacity is high.
4	Soft water produced by this method, having residual hardness 50-60 ppm	Soft water produced by this method ,having residual hardness 15to 25 ppm
5	Soft water produced by this method consists of dissolved gases.	Soft water produced by this method is free from dissolved gases.
6	Coagulant is added to settle down the sludge and precipitate.	No need of coagulant.

Zeolite Process Or Permutit Process

Permutits or Zeolites are complex mixtures of aluminates and silicates with water of hydration.

Sodium zeolite is hydrated sodium aluminosilicate and possesses the property of exchanging loosely held Na^+ in it with hardness causing metal ions in water.

Chemical formula of sodium zeolite can be written as , $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$

(Where $x = 2-10$ and $y = 2-6$)

Principle:- Loosely held sodium ions of sodium zeolite get easily exchanged with heavy metal ions like Ca^{++} , Mg^{++} etc. in water to make the water soft. Sodium zeolite is converted into calcium and magnesium zeolites. Water becomes free from hardness causing Ca^{++} , Mg^{++} etc but becomes rich in sodium salts.

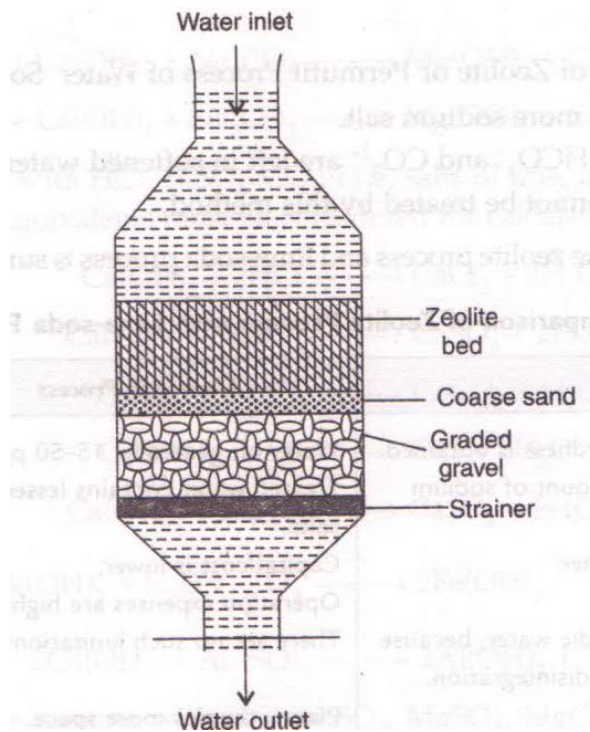
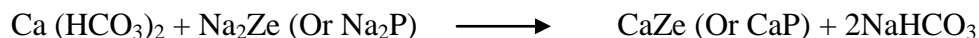
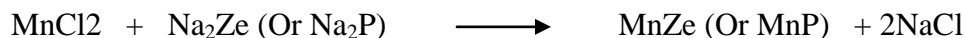
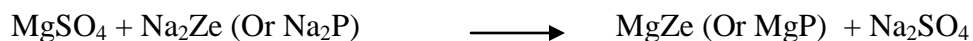


Fig :- Permutit or Zeolite Softener

Process:-

For softening of water zeolite softener is kept in a cylinder and hard water is allowed to percolate through a bed of zeolite at a certain specified rate. The hardness causing (Ca^{++} , Mg^{++} etc) are retained by the zeolite according to reactions given below and outgoing water contains sodium salts.

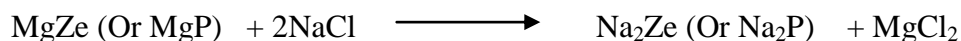
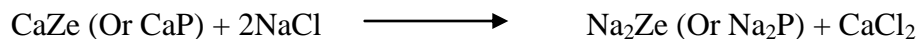




Regeneration

During softening of water, sodium zeolite progressively transforms into calcium and magnesium zeolites. After all the sodium zeolite is transformed, the bed becomes inactive or functionless or exhausted. At this stage, it ceases to soften water and so the supply of hard water is stopped and the exhausted bed of zeolite is made active or regenerated by adding brine solution (10% NaCl solution).

Because of high concentration of Na^+ ions of brine, the adsorbed Ca^{++} , Mg^{++} ions in bed, get detached and the zeolite gets regenerated and thus original sodium zeolite is recovered.



The washing of the bed will contain CaCl_2 and MgCl_2 which are led to drain.

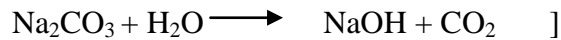
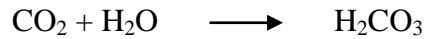
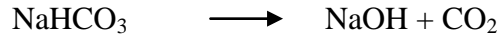
Advantages:-

- 1) This method is self adjusting for different hardness of water.
- 2) Hardness of the softened water is almost zero.
- 3) Equipment occupies small space
- 4) Requires less skill in operation and maintenance and can be worked under pressure.
- 5) Method requires less time and there is no danger of sludge formation.

Limitations and Disadvantages

- 1) Water containing colloidal and suspended impurities, clogs the bed. Therefore such water needs coagulation, filtration before softening.
- 2) Higher acidic and alkaline water if admitted, it destroys zeolite, therefore it has to be neutralized before use.
- 3) Zeolite process only removes cations like Ca^{++} , Mg^{++} but all the anions like CO_3^{--} , HCO_3^- , SO_4^{--} in water are not removed by this process.
- 4) Coloured ions like Mn^{++} , Fe^{2+} etc are captured by bed permanently and regeneration of exhausted bed (MnP or Mnze and FeP or Feze) is not easy. Hence zeolite process is not recommended for water containing high concentration of Fe^{2+} and Mn^{2+} .
- 5) The softened water contains sodium salts instead of hardness causing salts. Hence, the total dissolved salts in the water, softened by zeolite process is high.
- 6) Warm water cannot be used to soften by this process.
- 7) Water softened by zeolite process is unfit for use in high pressure boilers.

[Explanation :-The soft water obtained by zeolite process consists of sodium salts like NaHCO_3 , Na_2CO_3 etc. If such water is used in boiler for steam generation, NaHCO_3 decomposes producing CO_2 , which causes boiler corrosion by formation of carbonic acid (H_2CO_3) and Na_2CO_3 hydrolyses to NaOH which causes caustic embrittlement in boiler.



8) Water to be softened by zeolite process should be treated first with lime soda process.

[Explanation:- If mineral acids are present in water then it destroy zeolite. Lime soda process removes acidity of hard water.

If hard water containing Mn^{++} , Fe^{2+} ions is used in zeolite process then MnP & FeP formed cannot be regenerated by brine solution. Lime soda process removes Fe^{++} & Mn^{++} ions in hard water by formation of their corresponding ppts. These ppts are removed by filtration.

So water to be softened by zeolite process should be treated by lime soda process.]

Ion Exchange or Deionization or Demineralization Process

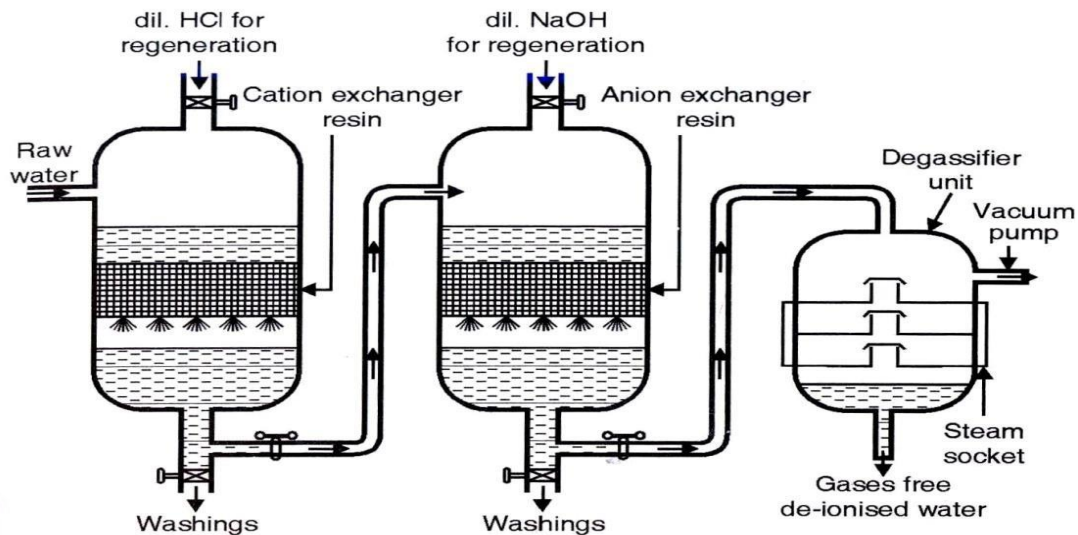
This method uses cation exchanger resin and anion exchanger resin. These resins are the water insoluble, long chain organic polymers having micro-porous structure and they possess functional groups.

Principle:-

The raw water passes through cation exchanger resin, all cations from water, are exchanged with H^+ and when it passes through anion exchanger resin, all anions are adsorbed in exchange of OH^- , to make water free from all ions.

Water of distilled water quality (i.e free from all minerals or ions) is obtained by this process and is the best for all industrial purposes, especially boilers, heat exchangers, pharmaceutical industries.

Process:-

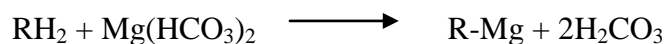
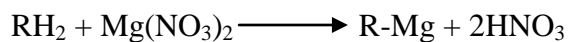
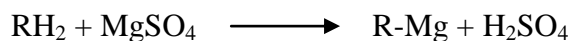
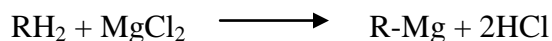
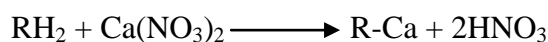
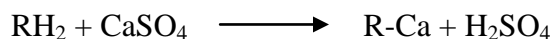
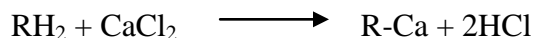


De-ionisation or ions exchange process

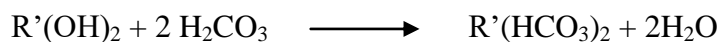
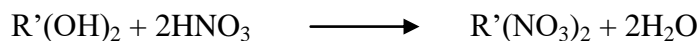
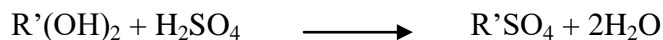
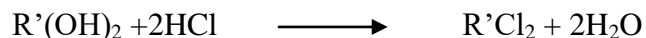
The deionizer unit consists of a column containing cation exchanger resin and another column connected to it, is containing anion exchanger resin. There can be a degasifier unit connected in addition.

Raw water enters first into the cation exchanger resin, where all cations from water are retained with bed and instead of them H^+ ions are released in the water.

Reactions of Cation Exchanger Resin

With temporary hard water**With permanent hard water**

Then the water passes through anion exchanger resin where all anions from water are retained by bed and instead of them OH⁻ ions are released in water.

Reactions of Anion Exchanger Resin**With temporary hard water****With permanent hard water**

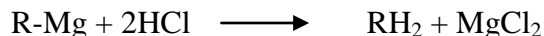
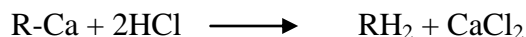
Thus all cations are captured in cation exchanger resin and all anions are captured in anion exchanger resin. The H⁺ ions released in water by cation exchanger react with OH⁻ ions released by anion exchanger to form water. Thus all ions or minerals from water are removed by the two exchangers. Any gas, if at all, is dissolved in water it can be removed by the degasifier unit. A degasifier is a tower whose sides are heated and connected to a vacuum pump. High temperature and low pressure reduces the amount of dissolved gases like carbon dioxide and oxygen in water.

Regeneration of resins

When capacity of resins reduces they are called as exhausted or inactive.

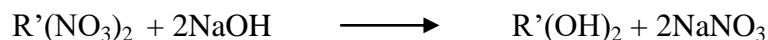
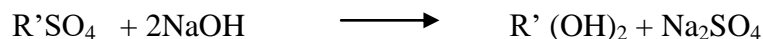
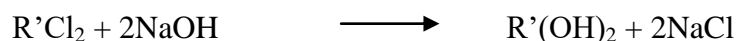
Regeneration of cation exchanger resins

To regenerate the resins, the deionization process is stopped. Dilute HCl solution is poured over the exhausted cation exchanger to regenerate. Washings of this resin are released from bottom and are passed to sink. Washings contains chlorides of metals.



Regeneration of anion exchanger resins

To regenerate anion exchanger resins, dilute NaOH is poured over it. Because of high concentration of OH⁻ of NaOH, the captured Cl⁻, HCO₃⁻ etc get removed. Washings of this resin are released from bottom and contain sodium salts and are passed to sink.



Advantages of deionization process

- 1) This process can be used for purifying highly acidic or alkaline water.
- 2) Water of zero hardness is obtained.
- 3) Treated water contains negligible amount of total dissolved solid i.e upto 2 mg/lit.
- 4) Water obtained can be used in high pressure boilers.
- 5) Easy to operate.
- 6) Method self adjusts with water of all types and different hardnesses.
- 7) Gives best quality water similar to distilled water.

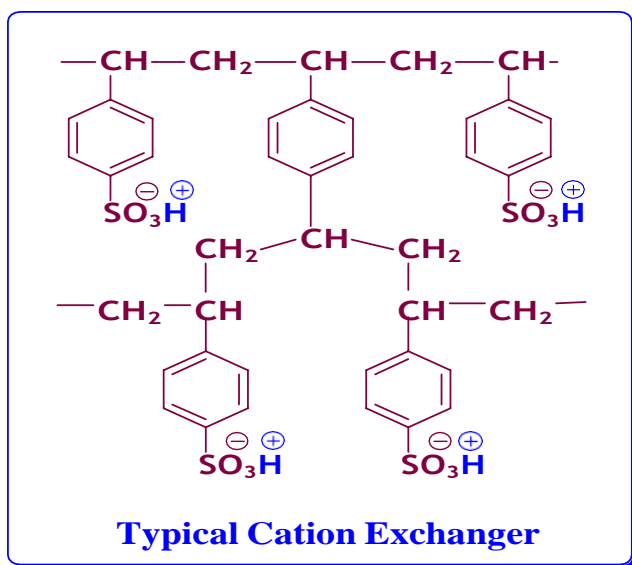
Limitations

- 1) Method can not be used for getting deionised water on large scale.
- 2) Initial investment is high (low running cost)

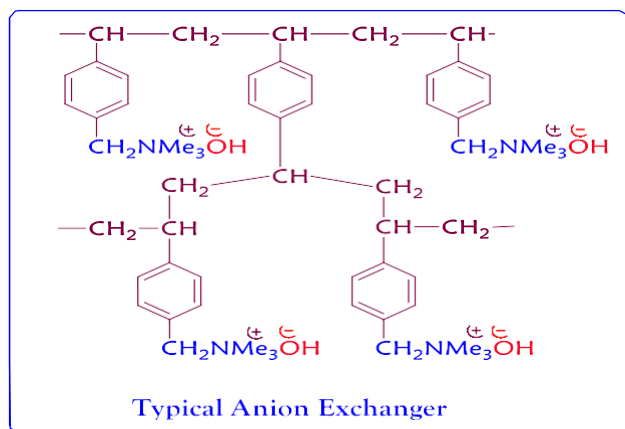
- 3) If water containing colloidal impurities is treated for long, the impurities block the micropores of resin, which then needs replaced by fresh resin and such impurities are removed first by coagulation and filtration.

Additional Notes

Cation exchanger resin $R(H^+)_2$ are high molecular weight, cross linked polymers containing sulphonic, carboxylic, groups (Acidic functional group). 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.



Anion exchange resin: $R'(OH^-)_2$ is a polymers containing amine groups as integrated parts of the polymers lattice and an equivalent anions such as chlorides, hydroxide or sulphate ions. These are styrene – divinyl benzene or amine formaldehydecopolymers, which contains amino or quaternary ammonium or quaternary phosphonium groups as an integral parts of resin.



Give reason for

De-mineralised water is softened water but vice versa is not true.

De-mineralised water means water free from all minerals or ions .

Soft water means water free from Ca^{++} / Mg^{++} ions.

Water obtained by zeolite process is soft water as Ca^{++} / Mg^{++} ions (cations) are removed by it but anions remains in water means it is not demineralised water.

In water obtained by ion exchange process cations as well as anions are removed by it so it is demineralised as well as soft water.

So we can say demineralised water is softened water but vice versa is not true.

Name and describe the process of water softening recommended (with reason) for obtaining feed water for High Pressure boilers.

There are 3 methods of softening

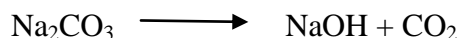
Lime soda process

Zeolite Process (or Permutit Process)

Ion Exchange Process (or demineralization or Deionization process)

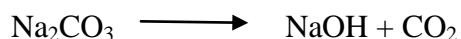
But only **Ion Exchange Process** of water softening is recommended for obtaining feed water for high pressure boiler as it removes **cations** as well as **anions** and **dissolved gases** also.

In Lime soda process, slight excess of lime is used than the calculated amount of lime .Hence it consists of Ca^{++} ions & excess Na_2CO_3 may cause caustic embrittlement.



So this process cannot be used in high pressure boiler.

The water softened by zeolite process consists of sodium salts like NaHCO_3 , Na_2CO_3 . If such water is used in boiler for steam generation, NaHCO_3 decomposes producing CO_2 which causes boiler corrosion by formation of carbonic acid H_2CO_3 and Na_2CO_3 hydrolyses to NaOH which causes caustic embrittlement in boiler.



So this process cannot be used in high pressure boiler.

Comparison of the water softening Processes

Sr.No	Lime soda Process	Permutit Process	Ion Exchange Process
1	Through study of water w.r.t amounts of various salts necessary.	Self adjusts with different hardness waters.	Self adjusts with different hardness waters
2	Treated water contains lesser quantity of total dissolved solids than original water.	Treated water contains almost equal quantity of total dissolved solids as in original water.	Treated water contains almost zero total dissolved solids.
3	Residual hardness 25-50 ppm CaCO_3 equivalent	Residual hardness is almost zero.	Residual hardness is almost zero.
4	Water containing suspended, colloidal impurities can be softened.(Pretreatment is not necessary)	Water containing suspended, colloidal impurities can not be softened.(Pretreatment is necessary)	Water containing suspended, colloidal impurities can not be softened.(Pretreatment is necessary)
5	Lower initial investment but running cost higher.	High initial investment but lower running cost .	Higher initial investment but lower running cost
6	Acidic water can be treated	Acidic water can not be treated	Acidic water can be treated
7	Involves problem of settling, filtration and disposal of precipitates formed.	Involves no precipitates.	Involves no precipitates.
8	Large scale treatment possible with batch process	Method applicable for small scale treatment of water.	Method applicable for small scale treatment of water.

What is the difference in quality of treated water from lime soda process, zeolite process and ion exchange process?

Boiler Troubles

The major boiler troubles caused by the use of unsuitable water are

- | | |
|-----------------------------------|-------------------------|
| 1 Carry Over: Priming and foaming | 2 Scale formation |
| 3 Corrosion and | 4 Caustic embrittlement |

All these troubles increase with increasing operating pressure of the boilers.

Scale formation

In a boiler, water is continuously converted into steam. This results in the concentration of the dissolved impurities until the water becomes saturated. Then the salts start separating out from the solution in order of their solubility, the least soluble one separating out first.

Some of the solids separate in the body of the liquid in the form of soft and muddy deposits or in the form of suspension which can be flushed out easily. Such deposits are known as **sludges**.

On the contrary, some of the solids deposit on a solid surface to form a sticky and coherent **scale**.

The limits of tolerance for boiler feed waters take into account that

Reduction in hardness, silica and alumina decrease scale formation

Causes of scale formation

1 Increase in concentration

The normal increase in concentration that occurs due to continuous evaporation of water in the boiler.

2 Decrease in solubility

The decrease of solubility of some dissolved substances e.g. CaSO_4 or CaCO_3 at high temperature.

3 Chemical Decomposition

By the reactions that produce insoluble salts, such as by the decomposition of soluble bicarbonates, e.g. $\text{Ca}(\text{HCO}_3)_2$ forming insoluble carbonates, e.g. CaCO_3

Disadvantages of scale Formation

1 Wastage of Fuel

Scale is a bad conductor of heat and the heat given to boiler water does not transfer completely. Higher the thickness of scale ,greater is the wastage of fuel.

2 Over Heating Of Boiler

Scale being bad conductor of heat, it reduces transfer of heat from boiler to water. To regulate the steam supply ,we need to overheat the boiler. This makes the boiler material soft and weak and may cause bursting of boiler tubes. This lowers safety of boiler.

3 Boiler safety

In addition to the loss of strength due to overheating, rapid reaction between water and iron occurs at high temperatures, causing additional thinning of the tube wall.



4 Danger of Explosion

When thick scale cracks due to uneven expansion the water comes suddenly in contact with the overheating boiler metal. This causes large amount of steam formation suddenly and sudden high pressure is developed. Due to sudden high pressure the softer boiler metal may burst with explosion.

5 Decrease in Efficiency

Scales may sometimes deposit in the valves and condensers of the boiler and choke them This results in decrease of efficiency of boiler.

6 Reduction in life of boiler

If salt like MgCl_2 is present in water then it will cause corrosion of boiler to a large extent as it reacts with water and HCL is produced again and again (Chain reaction)



Prevention of scale Formation

Scale formation can be prevented by the following methods

A) External Treatment

This involves removal of hardness causing impurities (such as calcium and magnesium salts) and silica from the water before entering the boiler. methods like lime soda process, zeolite process, ion exchange process are used for this.

B) Internal Treatment

Internal treatment consists of adding chemicals directly to the water in the boiler for removing dangerous scale forming salts which were not completely removed in the external treatment for water softening.

The internal treatment methods involve

1 Carbonate conditioning

2 phosphate conditioning

3 Colloidal conditioning

4 calgon conditioning

5 conditioning with EDTA

6 Boiler compounds

C) Blow Off

Frequent blow down operations to remove the scales when they are thin.

D) adding sod. aluminate which can trap the scale forming particles.

E) Adding organic chemicals like tannin which forms coating on the scale forming particles. This matter becomes easily removable by blow down operations.

Removal of scales

Scales are removed from time to time by different ways-

i) By use of suitable chemicals , the scales can be dissolved and removed (Internal treatment)

ii) Use of scraper or wire brush to remove thin scales.

iii) Thick scales may be removed by hammer and chisel.

iv) Thermal shocks technique is used to remove hard brittle scale. In this method empty boiler is heated and cooled by cold water suddenly. While sudden cooling, the contracting boiler metal exerts pressure on scales to crack them.

v) Blow down operation used if scales are loosely adhering.

Difference between scale and Sludge

Scale	Sludge
1. Scale is hard coating	Sludge is a loose deposit of slimy matter
2. Scale is strongly adhered to boiler metal and difficult to remove	Scale is less adherent on boiler metal and can be removed easily by brushes, detergents.
3. Being bad conductor, heat transfer to boiler water is affected largely.	3. Heat transfer to boiler water is affected slightly.
4. Scale is formed at hotter parts	Sludge is formed at cooler parts and where flow rate is low.
5. Scale may lead to bulging of metal tube , its bursting or explosion.	Sludge may lead to chocking
6. Scales are formed due to CaSO_4, CaCO_3, $\text{Mg}(\text{OH})_2$, MgSiO_3, CaSiO_3, SiO_2 etc	Sludge formation is due to an increase in concentration of salts in boiler water.

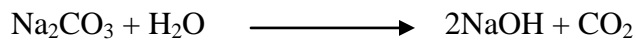
Caustic Embrittlement

1) Caustic embrittlement is a fast type of boiler corrosion caused by a high concentration of **sodium hydroxide** (highly alkaline condition) in boiler water especially in those boilers operating at **higher pressures**.

In this phenomenon the boiler material becomes brittle due to the accumulation of caustic substances.

It is characterized by the formation of irregular inter-granular cracks on the boiler metal, particularly at places of high local stress, such as riveted seams, bends and joints. It is caused by the high concentration of NaOH which is capable of reacting with steels stressed beyond their yield point.

2) Water softened by lime soda process may contain the slight un-reacted quantity of **Na₂CO₃**. Due to evaporation of water in boilers, the concentration of sodium carbonate increases and thus it undergoes hydrolysis to form sodium hydroxide in the boiler.

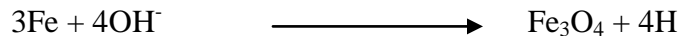
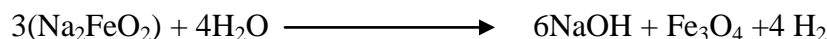


The formation of NaOH makes the water highly alkaline or caustic. The water containing NaOH penetrates in intergranular spaces or minor cracks on the inner surface of boiler by capillary action.

Water evaporates, as a result NaOH conc.increases progressively.

3) NaOH attacks the given boundaries chemically.

NaOH reacts with iron forming magnetic oxide and hydrogen.



This causes embrittlement of boiler parts particularly stressed parts like bends, joints, rivets etc and may lead to failure of boiler.

4) The extent of hydrolysis increases with temperature. The rate and extent of corrosion by caustic embrittlement increases with the conc. of NaOH & temp. & hence with increasing operating pressure.

Under normal conditions in unstressed metal a fairly continuous film of oxide is produced. When the metal is stressed beyond its yield point, the oxide coating cracks and chemical attack continues into the metal mainly along grain boundaries. This may be due to the energy stored

there and partly to the increased E.M.F. produced as a result of the stress. The products of the reaction viz., Fe_3O_4 and hydrogen also tend to favour penetration along grain boundaries. The attack is considerable under these conditions because of the large area of the metal exposed.

5) Caustic embrittlement is caused due to combination of following factors

- a) High tensile stress in the metal
- b) Leakage in the cemented joints
- c) Presence of sodium carbonate in the boiler feed water.

6) Two types of cells are formed during this type of corrosion

Galvanic cell in which stressed part acts as anode and unstressed part acts as cathode.

Another is **Concentration cell** in which higher conc. of NaOH in minor cracks of stressed parts acts as anode and lower conc. of NaOH parts as cathode.

In both the cases, **anodic part gets corroded.**

7) To avoid caustic embrittlement

Use sodium phosphate for water softening instead of sodium carbonate.

Add some tannin or lignin to boiler water, which will block the minor cracks.

Internal treatments

This involves addition of specific chemicals directly into the boiler water. These chemicals either do not allow the scale formation to take place or they attack on the previously formed scales to convert them into sludges.

Need for internal treatment

The soft water obtained by external treatment methods always contains some small quantities of residual impurities like hardness causing salts, O_2 , CO_2 , colloidal impurities etc.

The quantities of the impurities go on increasing during the continuous operation of boiler and the increased quantities of them in boiler causes the troubles like boiler corrosion, caustic embrittlement, scale formation, priming etc. Therefore it is necessary to add specific chemicals in boiler water so that the troubles are overcome. The important internal treatment methods are given below, along with the action of chemical added.

1. Phosphate conditioning

Principle

Hard adherent scale forming calcium and magnesium salts are converted into their phosphates by treatment with sodium phosphate. Addition of phosphate increases the ionic product of $[Ca^{2+}] [PO_4^{3-}]^2$. Due to this effect, $Ca_3(PO_4)_2$ is precipitated which is non adherent and can be removed as sludge by blow down operation.

By this method scale formation in all types of boilers can be avoided but this method is costly so it is used for high pressure boilers only.

Process and reaction

The scale contains $CaCO_3$, $Mg(OH)_2$, $CaSO_4$, SiO_2 fused together as coating.

Sodium orthophosphates can attack scales to convert them to sludges. When scale is formed in boiler, proper quantity of sodium phosphate is added in feed water.

Depending upon the quality of feed water, choice of a particular orthophosphate is made. For instance, if boiler tends to produce acidic condition, then alkaline orthophosphate Na_3PO_4 is preferred., Na_2HPO_4 is used if water is neutral and if water treatment is producing highly alkaline condition, then acidic NaH_2PO_4 is selected.

Type of Sod Phosphate used**Nature of boiler feed water**Na₃PO₄ Trisodium phosphate

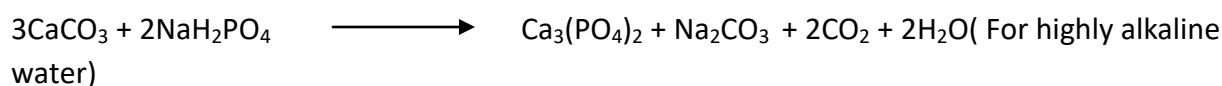
(For acidic water)

Na₂HPO₄ Disodium Hydrogen phosphate

(For neutral water)

NaH₂PO₄ sodium dihydrogen phosphate

(For highly alkaline water)



Use of such treatment combined with blow down operations frequently , helps even high pressure steam boilers work without scale formation.

Phosphate conditioning treatment converts

Scale inside the boiler to sludge and

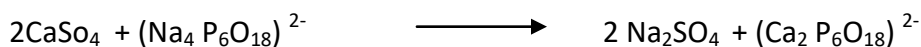
Hard water to soft water during external treatment.

At high pressure , sod.phosphates do not undergo hydrolysis to form NaOH (like hydrolysis of Na₂ CO₃) as well as soft adherent sludge of Ca & Mg phosphates are stable.

2.Calgon Conditioning

Scale forming salts can be converted into highly soluble complexes which are not easily precipitated under the boiler conditions. In order to achieve this , sodium hexameta phosphate Na₂ (Na₄ P₆O₁₈) (its trade name is calgon) is generally employed.0.5 to 5.0 ppm.

This substance interacts with the residual calcium ions forming highly soluble calcium hexa meta phosphate and thus prevents the precipitation of scale forming salts.



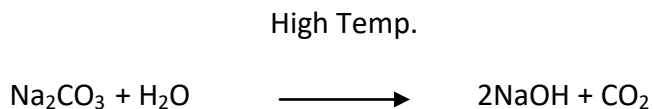
Calgon conditioning method is suitable for high pressure boiler because calgon anion & soluble complex anion of Ca or Mg are stable for high pressure.

3. Carbonate Conditioning

In low pressure boilers, it is possible to prevent scale formation, by addition of appropriate quantity of Na_2CO_3 in the feed water. Na_2CO_3 reacts with the scale forming CaSO_4 in water into CaCO_3 as long as loose precipitate which can be removed by blow down operation.

However, in high pressure boiler, Na_2CO_3 cannot be used as conditioning or treating agent because it is risky to use. If any excess quantity of Na_2CO_3 is added, it causes caustic embrittlement (fast corrosion of boiler metal due to highly alkaline condition of water)

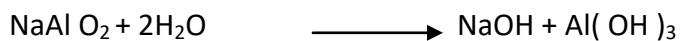
Na_2CO_3 is converted into NaOH due to hydrolysis as follows.



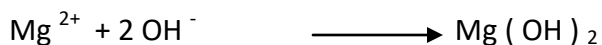
Thus added Na_2CO_3 in boiler feed water in high pressure boiler will not convert hard adherent scale of CaSO_4 into soft scale of CaCO_3 . So this method is suitable only for low pressure boilers.

4. Sodium Aluminate Treatment (NaAlO_2)

Sodium aluminate gets hydrolysed in presence of water at a boiler temp. to form gelatinous ppt. of $\text{Al}(\text{OH})_3$ and NaOH .



The sodium hydroxide formed in the above reaction reacts with magnesium ions present in boiler water to form magnesium hydroxide.



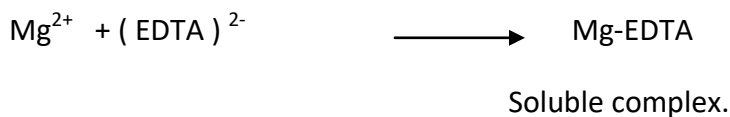
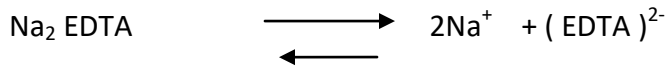
The flocculent precipitate of $\text{Mg}(\text{OH})_2$ and gelatinous ppt of

$\text{Al}(\text{OH})_3$ entraps finely divided silica and oil droplets and forms a sludge which can be removed from the boiler by blow down operation.

5. EDTA Conditioning

This method is based upon formation of soluble complexes by addition of complexing agent like EDTA, into the boiler water.

The complexation is quite effective and a scale free and sludge free boiler operation is possible. EDTA disodium has the property to form water soluble complexes easily with the hardness causing ions like Ca^{2+} , Mg^{2+} , Fe^{2+} etc.



6. Colloidal conditioning

This method involves addition of certain organic substances in the form of colloids like tannin, agar-agar gel, kerosene, glue starch etc. into the water during boiling in the boiler.

These colloidal substances get coated over the surface of particles of scale forming precipitate, thereby converting into non sticky and loose deposits (as that of sludge) which can be removed by blow down operations. Thus scale formation can be avoided. This method is suitable only for low pressure boilers, because at high pressure, colloidal substances get decomposed i.e. colloidal substance will not form coating on the surface of particles of scale forming ppt. i.e. scales are not converted to sludge.

Drinking Water or Municipal Water

Municipalities have to supply potable water i. 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 perfectly clear and odourless.
- 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 H_2S .
- 6) It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
- 7) Its alkalinity should not be high.
- 8) Its PH should be about 8.0
- 9) It should be reasonably soft.
- 10) Its total dissolved solids should be less than 500 ppm.
- 11) It should be free from disease producing micro-organisms.

Domestic water treatment or Purification of Water for Domestic Use

Natural water from rivers, lakes, canals etc consist of impurities such as floating matters, colloidal particles, Bacteria etc.

For removing all these impurities, following treatment processes are used.

1. Screening-

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

2. Sedimentation-

The process of removing suspended impurities by allowing the water to stay undisturbed for hours (or several days in large tanks when most of the suspended particles settle down due to force of gravity) is called as sedimentation.

Sludge settled at the bottom of the tank can be removed periodically. The clear water i. e sedimented water can be taken out from tank with the help of pumps.

Factors affecting to sedimentation-

1. The horizontal or vertical flow velocity of the water.
2. The size of the particle
3. The specific gravity of the particle
4. The shape of the particle
5. The temperature of the water.

The sedimentation tanks commonly used are of horizontal flow rectangular type and circular shaped upward flow type.

Sedimentation takes a long time, requires large capacity settling tanks and cannot ensure complete removal of coarse-dispersed impurities from water. Plain sedimentation usually removes only **70 to 75 %** of the suspended matter.

3) Coagulation

Finely divided silica, clay and organic matter does not settle down easily and hence cannot be removed by simple sedimentation. Most of these are in colloidal form (e.g. sols, gels or emulsions) and are generally negatively charged and hence do not coalesce because of mutual repulsion. Such impurities are generally removed by chemical assisted sedimentation, in which certain chemicals are added which produce ions of right electrical charge that neutralize the oppositely charged colloidal particles and brings about their coalescence. This process is called **coagulation**. This permits the particles to aggregate together until a denser particle is formed which falls through still water at a reasonable rate and is called **flocculation**.

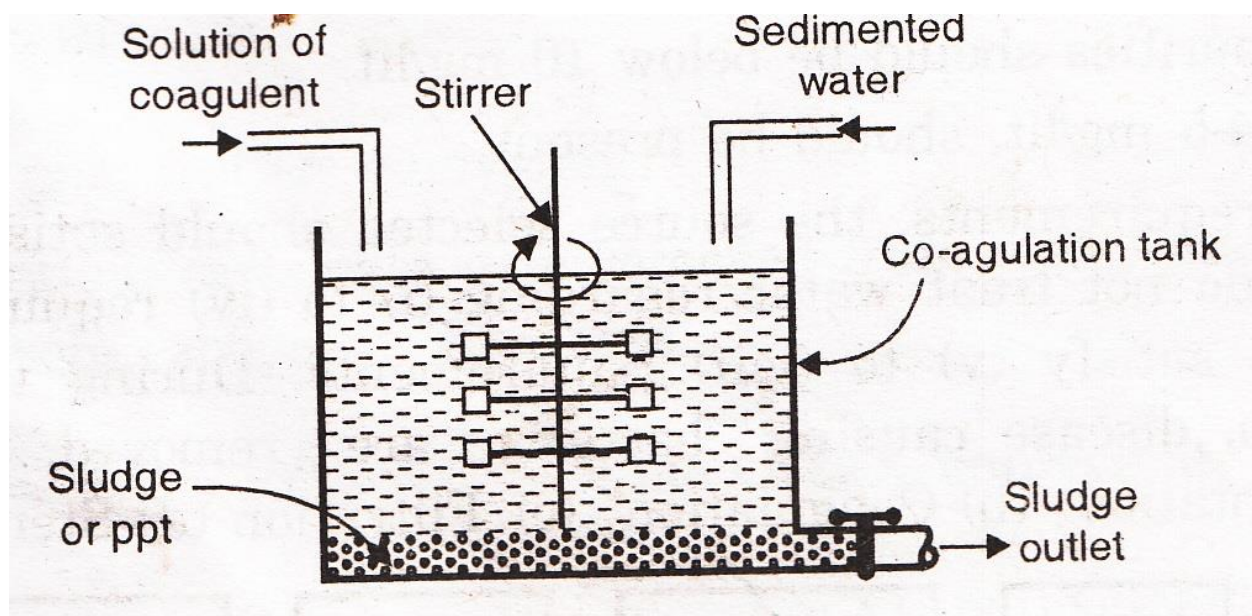
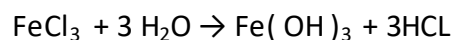
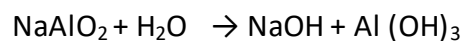
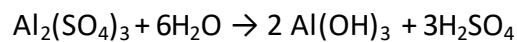


Fig: Coagulation

Examples of coagulants are FeSO_4 , alums, $\text{Al}_2(\text{SO}_4)_3$, sodium aluminate NaAlO_2 etc



The most commonly used coagulants and their ideal pH range of use are as follows

Chemical coagulants	Ideal pH range
$\text{Al}_2(\text{SO}_4)_3$ Alum	6.5-8.5
NaAlO_2	5.5-8.0
FeSO_4	➤ 8.8

Most commonly used coagulants are

- Alum (K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$)

Alum is the most widely used coagulant in water treatment plants.

Alum reacts with water in the presence of alkalinity of water.



Present in water Coagulant Flocculant ppt



The insoluble aluminium hydroxide forms the floc, which adsorbs and entangles the fine suspended and colloidal impurities. The floc becomes heavy and settles down due to the force of gravity.

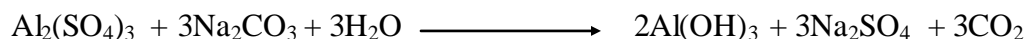
For best results, the pH of water should be between the range 6.5 to 8.5

The dose of alum varies from 5 mg/liter for relatively clear water to about 80 mg/liter for very turbid water (the average dose is 20mg/liter).

The $\text{Al}(\text{OH})_3$, so formed acts as a floc which has an enormous surface area per unit volume and removes the finely divided and colloidal impurity by neutralizing the charge on them (particles of ppt of $\text{Al}(\text{OH})_3$ are positively charged due to adsorption of Al^{3+} ions on their surface. Colloidal particles of clay possess negative charge. Positively charged ppt particles of $\text{Al}(\text{OH})_3$ neutralize the negative charge of colloidal particles. As the charge is removed from the clay particles, they come nearer and combine to form bigger particles, which settle down at the bottom of the container due to gravitational force.

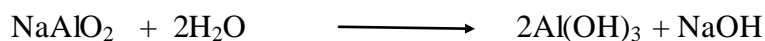
As well as by other mechanisms like adsorption and mechanical entrainment. Thus the smaller particles join together to form denser particles which settle down to the bottom due to gravitational force.

With waters having a little or no natural alkalinity, an alkali such as sodium carbonate is added.



- **Sodium aluminate (NaAlO_2)**

It can very easily be used for treating water having no alkalinity (i.e pH < 7). For best results, the pH range is 5.5 to 8.0

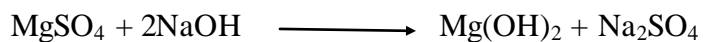


Coagulant

floc

The floc settles down by adsorbing fine suspended and colloidal impurities.

The sodium hydroxide thus produced, precipitates magnesium salts as $\text{Mg}(\text{OH})_2$.

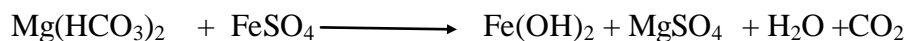


Thus sodium aluminate decreases magnesium hardness, besides removing fine suspended and colloidal impurities. It has further advantage of removing corrosive qualities of the water.

But due to comparatively high cost, it is not widely employed in water works practice.

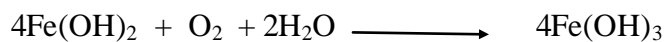
- **Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)**

It gives good results above pH value of 8.5 (i.e slightly alkaline)



Present in water Coagulant

Ferrous hydroxide



Dissolved Oxygen

Ferric hydroxide (Heavy floc)

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

It is cheaper than alum and can be used over a wider range of pH values, gives good results in the pH range 8.5 to 11.0.

But for coloured raw water it is not used.

4) Filtration

Filtration 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 sized granular materials.

Two types of filters are commonly used in domestic water treatment.

i) Gravity Sand filter ii) Pressure filter.

i) Gravity Sand filter-

It is used for large scale water treatment for municipal water supply. It consists of a thick top layer of fine sand (about 50 cm thick) placed over coarse sand layer (about 20 cm thick) and gravels (about 30 cm thick). At the bottom of the tank, there is a channel of bricks through which filtered water goes out. The rectangular tank has an inlet for entering sedimented water.

Sedimented water enters the sand filter from the top. As the water percolates through the fine sand bed, colloidal particles, most of the germs and bacteria's are retained by the top sand layer. Clean filtered water is collected in the under-drain channel from where it is drawn out.

After 24 hours of use of this filter, the rate of filtration becomes slow due to clogging of pores of the fine sand layer by the impurities retained in the pores. Therefore, the portion of the top fine sand layer (about 2 to 3 cm) is scrapped off and replaced by a new sand layer. Then the same filter is used again.

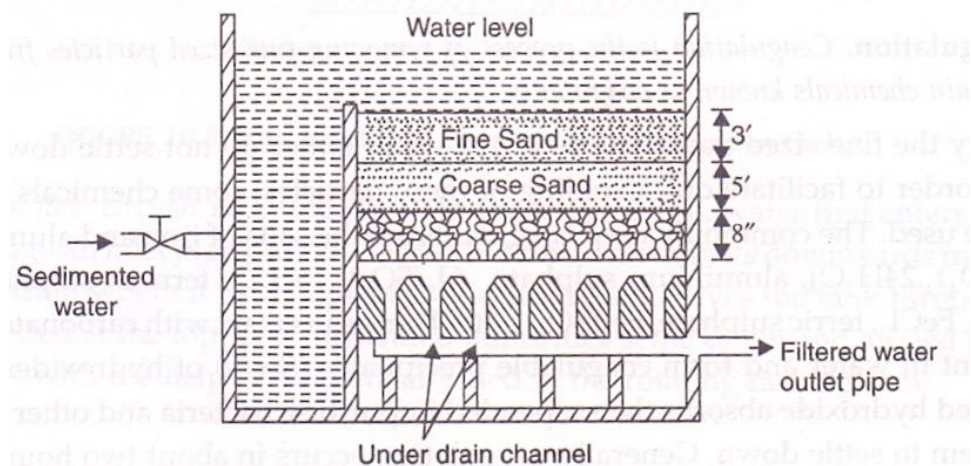


Fig: Gravity sand Filter.

ii) Pressure Filter or vacuum filter

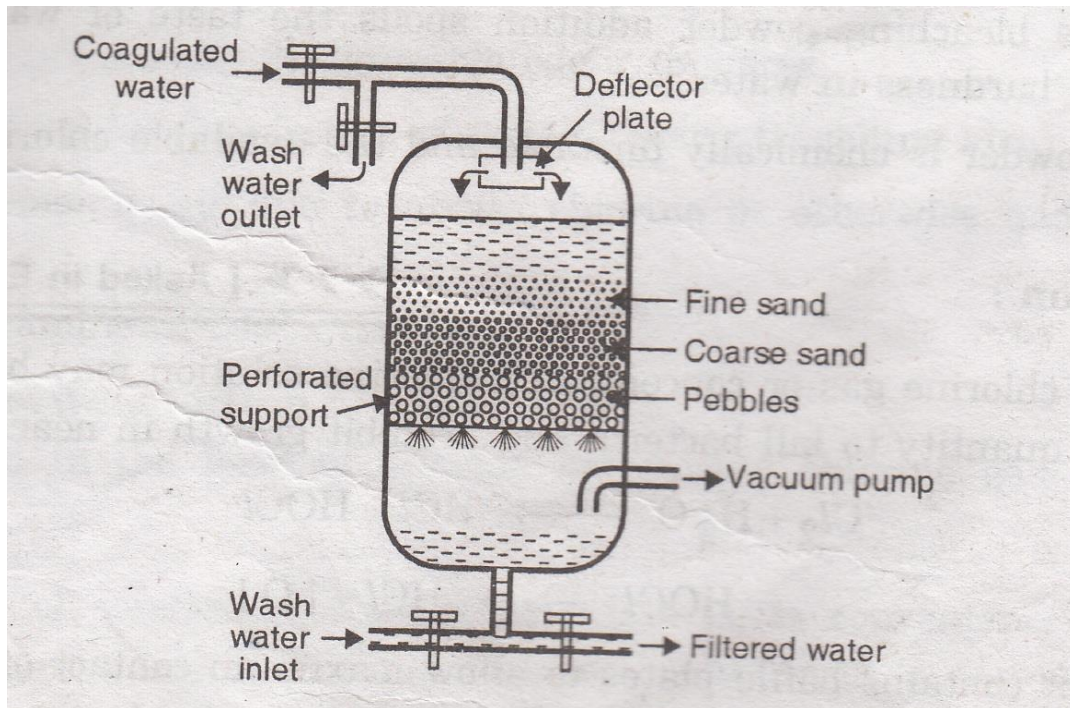


Fig: Pressure Filter

5) Sterilization of Water-

The process of destroying or killing the disease producing bacteria's , micro-organisms etc, from the water and making it safe for use ,is called disinfection or sterilization.

The chemicals or substances which are added to water for killing the bacteria's etc are known as disinfectants

The disinfection of water can be carried out by following methods.

- a) Boiling-
- b) Chlorination-
- c) Ozonisation –
- d) Sterilization by using Ultra Violet (UV) rays-

- Apparatus used for chlorination is known as chlorinator 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.

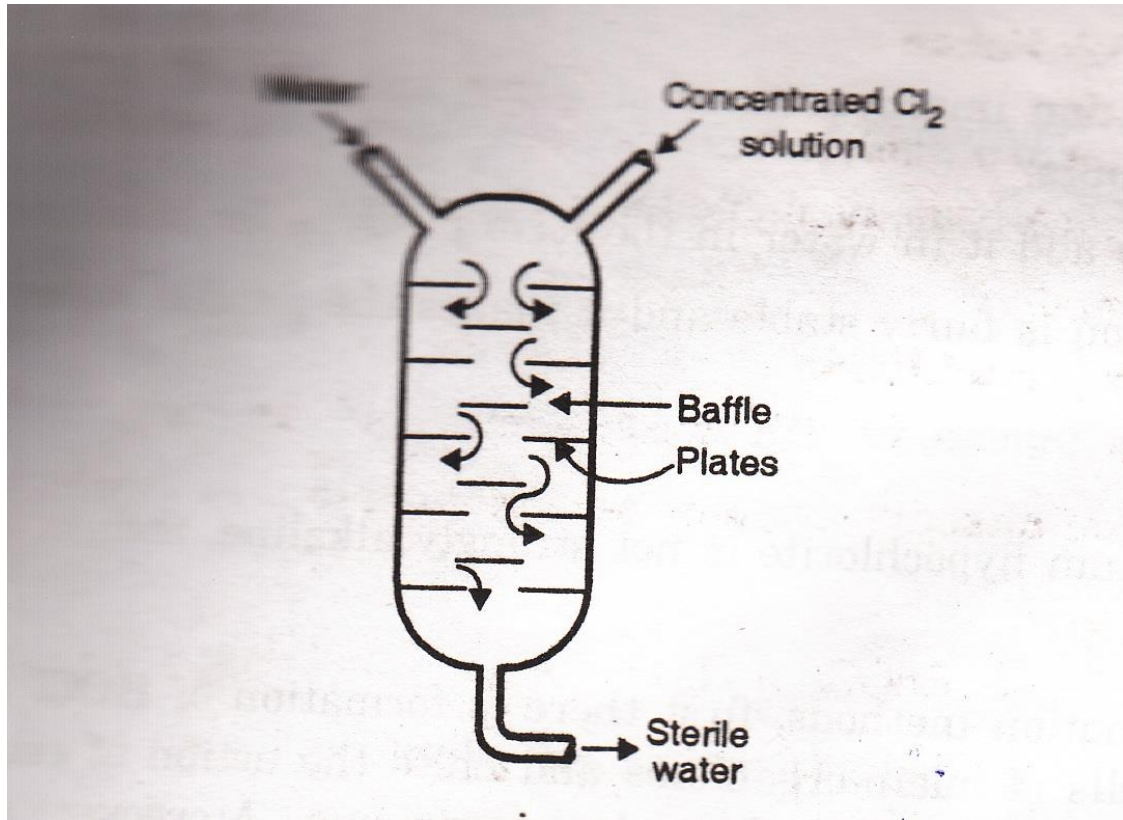


Fig: Chlorination pot

Factors affecting Chlorination

i)Time of Contact

The death rate of microorganisms is maximum at initial stage and it goes on decreasing with increasing time.

ii)Temperature

The death rate of microorganisms by chlorine increases with rise in temperature

iii) PH Value of water

At lower PH values of water (PH 5.0 to 6.5) a small contact period is required to kill the same percentage of organisms.

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 introduces no salt impurities in the treated water.

It is most ideal disinfectant.

Disadvantages Of chlorine

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

It is more effective below 6.5 PH and less effective at higher PH values.

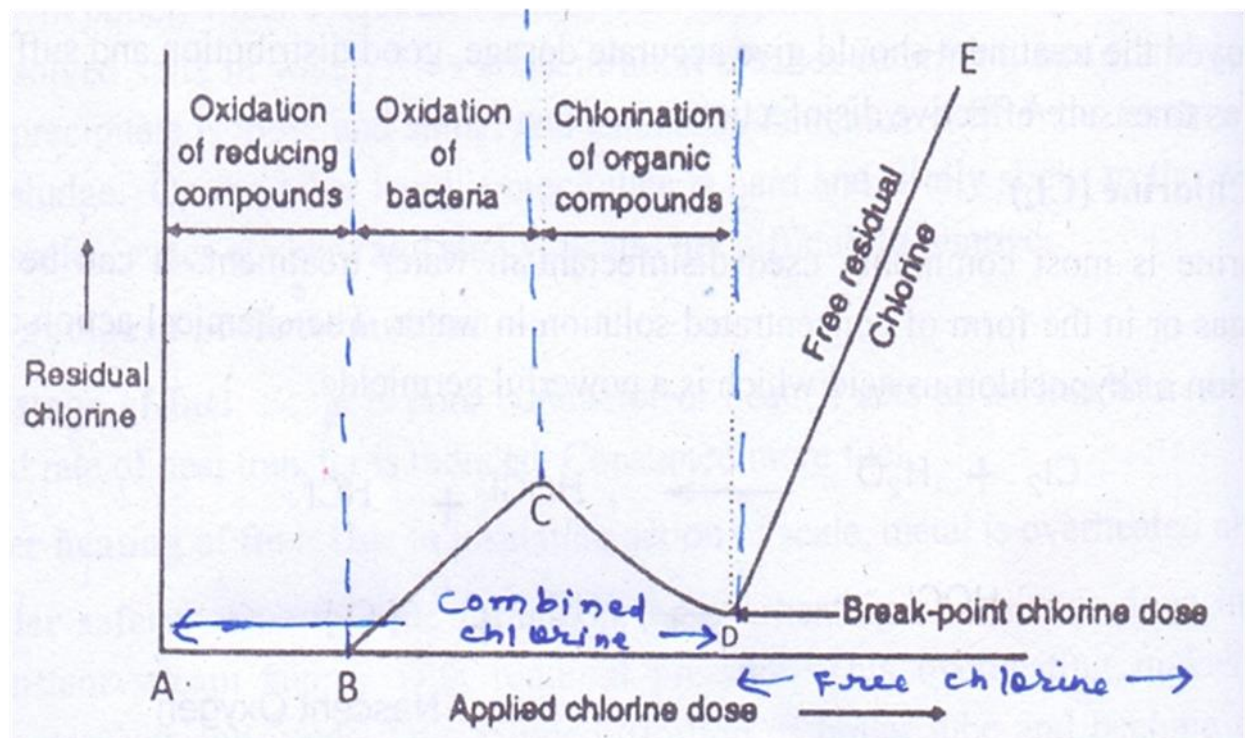
Break Point Chlorination or Free Residual chlorination

Break point chlorination is a more precisely controlled process in which just sufficient chlorine is added to oxidize all the organic matter, destroy bacteria and react with any ammonia, leaving a slight excess of free chlorine (up to 0.1 ppm)

The break through point i. e the appearance of free chlorine in the water must be determined experimentally as follows.

If chlorine is added to a sample of water and after a few minutes, the residual chlorine available in the water is estimated, it will be found that the residual chlorine in water is less than the amount added initially. This is due to the fact that some of the chlorine added initially is consumed by oxidizing bacteria and other organic matter. Now if we take a few more aliquots of the same volume of the water sample and add increasing doses of chlorine to different samples and analyse the residual chlorine after the same interval of time (a few minutes) a curve of the type shown below is obtained.

Fig Break Point Chlorination



It can be seen from fig that the quantity of residual chlorine increases with increasing dose of chlorine added giving a straight line until at a definite chlorine dose; a sudden decrease in the residual chlorine is noticed. This is known as the break point, after which the residual chlorine appearing more or less agrees with the chlorine dose added.

The reason for such a behavior is due to the fact that some organic compounds which defy oxidation at lower chlorine concentrations get oxidized when the break point chlorine concentration is reached.

Since it is these organic compounds which are generally responsible for bad tastes and odours in water, it is obvious that break point chlorination eliminates bad tastes and odours.

Advantages of break point Chlorination

It oxidizes completely organic compounds ammonia and other reducing compounds.

It removes colour in water, due to the presence of organic matters.

It destroys completely all the disease producing bacteria's.

It removes both odour and taste from the water.

It prevents the growth of any weeds in water.

Dechlorination

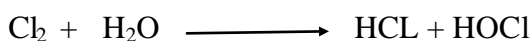
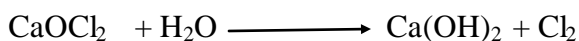
The water treated by the process of break point chlorination may be filtered through activated carbon, in order to remove the decomposition products formed and the excess chlorine remaining. Other methods of dechlorination include treatment with SO_2 or Na_2SO_3 sod.sulphite or $\text{Na}_2\text{S}_2\text{O}_3$ Sod.thiosulphate.



Sod.Tetrathionate

ii) Chlorination by adding bleaching Powder

In small water works, about 1Kg of bleaching powder per 1,000 kilolitres of water is mixed and water allowed to stand undisturbed for several hours. The chemical action produces hypochlorous acid (powerful germicide)



Hypochlorous acid



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

Drawbacks

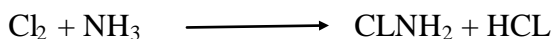
Bleaching powder introduces calcium in water, thereby making it more hard.

Bleaching powder deteriorates due to its continuous decomposition during storage. So, whenever it is to be added, it has to be analysed for its effective chlorine content.

Only calculated quantity of bleaching powder should be used as an excess of it gives a bad taste and smell to treated water.

iii) By using chloramines (ClNH₂)

When chlorine and ammonia are mixed in the ratio 2:1 by volume, a compound chloramines is formed.



Chloramine

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



Disinfectant

Nowadays chloramines is used for disinfection of water, because its excess does not produce any irritating odour. Moreover it imparts a good taste to treated water.

Limitation -It is costly.

c) **Ozonisation** –

Addition of ozone gas O_3 in water for sterilization is called ozonisation.

Ozone is unstable. When O_3 is added in water, O_3 decomposes to O_2 and nascent oxygen (O). Nascent oxygen kills bacteria.



Process – In ozonisation, water is allowed to percolate through a tower having perforated partitions. Ozone is allowed to enter from the bottom which kills the germs when they come in contact with water. Sterilized water is collected at the bottom of the tank.

Advantages of Ozonisation

- 1) Ozone not only acts as a sterilizing agent but also as a bleaching decolorizing and deodourising agent.
- 2) It improves the taste of water
- 3) In excess, it is not harmful because on decomposition O_3 gives O_2

Disadvantages of Ozonisation-

This method is quite expensive and hence generally it is not used for municipal water supply.

d) **Sterilization by using Ultra Violet (UV) rays -**

Ultra-violet rays are obtained from mercury lamps enclosed in a quartz globe. U.V rays are invisible. U.V rays are very effective in killing all types of bacteria. This method is widely used for the sterilization of swimming pool of water, because it does not require any chemicals to be mixed with water.

This method is very costly and can not be used for municipal water supply.

(It is also used in equipment like “Aqaguard” where the water filtered through charcoal is allowed to get exposed to uv rays.)

e) **Aeration**

Water is allowed to spray in air due to which water is converted into small drops and comes in contact of oxygen of air, which can kill bacteria. Taste of such water is good, temperature of the water decreases on aeration but has limited use.

Other chemicals available for sterilization are KMnO_4 , H_2O_2 etc: but they are strong oxidizing agents and are not desirable to use as they make taste of water very bad and their excess quantity in water is harmful for body.

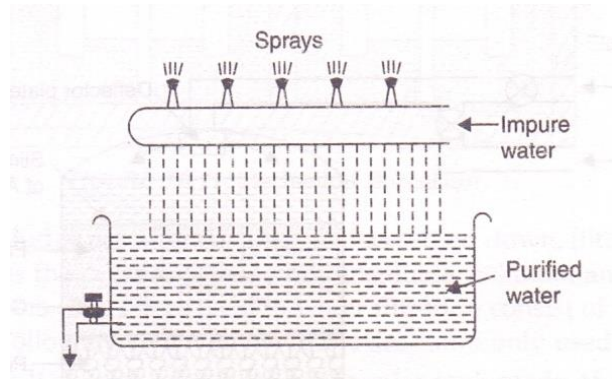


Fig: Aeration