

2. Water Treatment

Introduction, types of water, Impurities in water and their consequences. Hardness of water, units of hardness, disadvantages of hardness, measurement of hardness by EDTA method, numerical problems on measurement of hardness of water, boiler troubles- priming & foaming, scales & sludge, caustic embrittlement, boiler corrosion, softening of water- Ion exchange process, zeolite process, desalination of brackish water by reverse osmosis, **Drinking water treatment- Ozonisation & chlorination, specifications of potable water as per WHO and BIS standards.** Fluoride in ground water: Effects on human health, defluoridation method – Nalgonda method; merits and demerits of various defluoridation methods.

Introduction: "Water is the driver of nature". Nearly three-fourths of the earth's surface is covered with water. Water is also found below the earth's surface. It is present in air in the form of water vapor. The bodies of all plants and animals contain water.

Water is our most important food stuff: An adult should drink at least 2 liters of liquid per day. The recommended liquid drink is water, because water contains mineral nutrients and trace elements. Moreover, it is the perfect drink for meeting our daily fluid requirements. And furthermore, water does not contain calories.

The role of water in human body: Roughly 60% of an adult's body is composed of water and this reaches as much as 70 to 80% in newborns. Quantitatively speaking, this makes water is the most important building block of the human body.

Particularly, water maintains the physical and mental health. For example:

- i) During physical exercise or in the case of fever, water acts as a heat conductor as a result body temperature returns to normal by sweating
- ii) Water acts as transport and a solvent in living cells.
 - Water transports mineral (e.g. magnesium, sodium, potassium and calcium) nutrients contained within the diet to cells and removes the unwanted by-products of metabolic processes through excretion
 - Bio-chemical reactions continuously take place in live cells, which occurs only in presence of water. *i.e.* water acts as solvent / reagent in these reaction.
- ❖ With this it is clear that life is possible on earth due to the presence of water. Water is not only essential for lives of animals, plants, but also occupies a unique position in industries.
 - i. Industry like textile, paper, sugar, atomic energy, steel, ice etc. needs water to function.
 - ii. As a coolant in power and chemical industry.
 - iii. Stream is needed for manufacturing of Engineering Materials.

Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources are available for ready use. Hence it is required to use it carefully and economically.

Requirements for Drinking Water:

- It should be clear and odorless.
- It should be devoid of any unpleasant taste.
- It should be devoid of heavy metals and arsenic.
- pH should be about 8.
- Suspended matter should not exceed 10 ppm.
- Content of dissolved salts should not exceed 50 ppm.
- Lastly, it should be free from pathogenic (disease causing) microorganisms

Types of water (or) Sources of Water:

Rainwater, oceans, rivers, lakes, streams, ponds and springs are natural sources of water. Dams, wells, tube wells, hand-pumps, canals etc, are man-made sources of water.

The natural source of water is divided into two types. 1) Surface water 2) underground water

1) Surface Water:

Water present on the surface of the earth in the form of oceans, rivers, lakes, ponds and streams is called surface water. The water in rivers and lakes comes from rain and melting of snow on mountains. These rivers flow into the sea. Normally, surface water contains many impurities, suspended matter, and also disease producing microorganisms.

- i) Rain Water is obtaining as a result of evaporation from the surface water, so the rain water is the purest form of natural water. However, during raining, the rainwater journey downwards through atmosphere, as result it dissolves an industrial gases (CO_2 , SO_2 , NO_2 etc) and suspended solid particles of organic and inorganic.
- ii) River water is obtained from rains and springs. River water contains many dissolved minerals of the soil with which it has come in contact during its journey from source. River water also contains the organic matter derived from the decomposition of plants and small particles of sand and rock in suspension.
- iii) Lake water has more constant chemical composition. It, usually, contains much lesser amount of minerals than river water, but contains high concentration of organic matter.
- iv) Sea water is the most important form of natural water. Sea water contains about 3.5% of dissolved salts out of which about 2.6% is NaCl . It is too saline and not fit for industrial uses, but can be used as cooling purpose in thermal and nuclear power plants.

Sea water is very impure due to two reasons:

- Continuous evaporation increases the dissolved impurities content.
- Impurities thrown by rivers as they join sea.
- Due to the excretory impurities released by sea animals.

2) Underground Water:

- Some of the rainwater seeps through the earth soil onto the non-porous rocks below. As result sometimes a high pressure may develop and as a result this water sprouts out in the form of springs.
- Rain water comes in contact with a number of mineral salts present in the soil and dissolves some of them during its journey downwards in the earth. As result, underground water is rich with large amount of dissolved salts.
- Underground water can be obtained by digging wells, sinking tube wells, etc.
- Normally, underground water is clear in appearance due to the filtering action of the soil
- Moreover, it is free from organic impurities.

❖ However, now days both surface and ground water contains many impurities, microorganisms, pathogens and toxic materials due to rapid industrialization. So the water must be purifying for safety before its use.

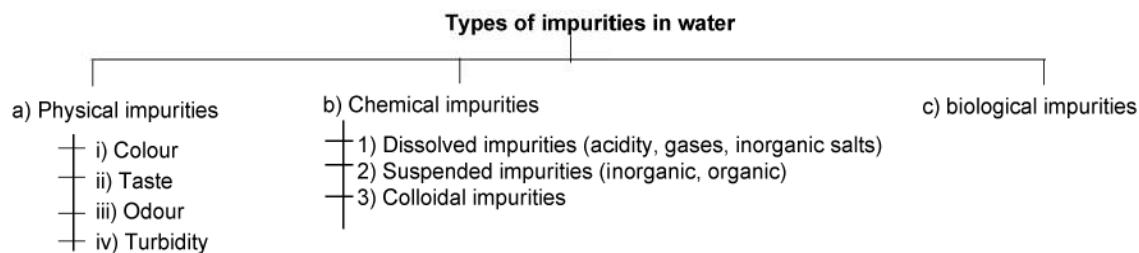
Types of impurities in water (or) Characteristics imparted by impurities in water (or) Impurities in water and their consequences

The natural water is usually contaminated with many types of impurities.

Sources of impurities in water:

- (i) Gases (O_2 , CO_2 etc.) are picked up from the atmosphere by rainwater.
- (ii) Rain water dissolves impurities when it comes in contact with ground, soil or rocks
- (iii) Decomposition of plants and animals remains introduce organic impurities in water
- (iv) When water comes in contact with sewage or industrial waste.

The most important are the following three types: a) Physical impurities b) Chemical impurities
c) biological impurities



a) **Physical impurities:** Generally the pure water has no colour, taste and odour.

(i) Colour in water is caused by metallic substances, algae, weeds, protozoa, industrial wastes etc. however, change in colour of water is not harmful, unless it is associated with toxic chemical impurities.

- Yellowish tinge indicates the presence of chromium or presence of organic matter
- Yellowish red colour indicates the presence of iron
- Red brown colour indicates the presence of peaty matter (vegetable matter)

(ii) Taste is due to the presence of dissolved mineral in water

- Bitter taste: due to the presence of iron, aluminum, manganese, sulphate or excess of lime.
- Soapy taste: due to the presence of large amount of sodium bicarbonate.
- Brackish taste: due to the presence of unusual amount of salts.
- Pleasant taste: due to the presence of dissolved gases and minerals like nitrates in water

(iii) Odour in water is undesirable for domestic as well as industrial use. The cause of odour in polluted water is due to the

- presence of organic and inorganic impurities of N, S and P
- Industrial effluents containing organic substances such as aldehydes, phenols, esters, ketones etc
- Presence of algae in water gives grass odour
- Growth of iron, phosphorus and sulphur bacteria produces offensive odour

(iv) Turbidity is due to the colloidal, extremely fine suspension such as clay, finely divided organic and inorganic matters and microorganisms etc. Turbidity expresses the optical properties of

water. Turbid water scatters light rather than transmit it in straight line. Turbidity in water can be eliminated by sedimentation, followed by coagulation, filtration etc.

b) Chemical impurities in water: DSC-AGI

1) Dissolved impurities:

(i) Acidity: Surface waters and ground waters attain acidity from industrial wastes like acid, and free CO_2 . Acidity is, usually expressed in terms of ppm (or) mg/L of calcium carbonate equivalent.

(ii) Gases: Generally the dissolved gases in water are O_2 , CO_2 , NH_3 , H_2S etc. However, their solubility depends upon temperature, pressure and dissolved mineral content of water.

- a) The dissolved oxygen (DO) in water is essential to the life of aquatic organisms such as fishes. Same time, the water with excess of 'DO' promotes corrosion.
- b) All natural waters contain dissolved atmosphere CO_2 . As result water become acidic and promotes corrosion when it comes in contact with metals.
- c) Dissolved NH_3 in water arises due to the decomposition of nitrogenous organic compounds like urea. The NH_3 gives pungent odour to water.

(iii) Inorganic salts: they are released from industrial wastes.

- (a) Cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , Mn^{2+} , Al^{3+} etc.
- (b) Anions: CO_3^{2-} , SO_4^{2-} , NO_3^- , Cl^- , F^- etc.

2) Suspended Impurities:

- (a) Inorganic: Clay and sand.
- (b) Organic: Oil, vegetables, and animal material.

3) Colloidal Impurities

Finally divided clay, silica, Al(OH)_3 , Fe(OH)_3 , organic waste products, colouring matter, amino acids etc. Their particles size in between 1 nm to 1 μm .

c) Biological impurities:

Micro-organisms like bacteria, algae, fungi, different worms etc. grow in water. The source of these contaminations is discharges of domestic and sewage wastes. The contaminated water is not only harmful to aquatic animals like fish, but also to human health. The growth of micro-organisms is more at 20-35 °C. These micro-organisms can be controlled by chlorination.

HARDNESS OF WATER

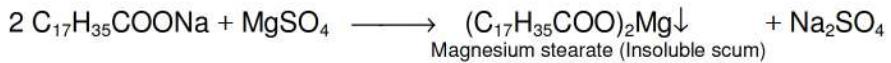
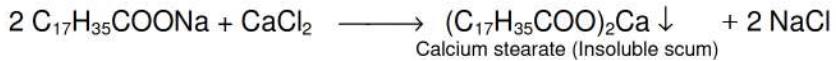
The water consist of excess of minerals is called as "hard water". The characteristic property of hard water is prevention of the lathering of soap.

Reason for Hardness: Hardness is due to presence of certain salts of Ca^{+2} , Mg^{+2} and other heavy metal ions like Al^{3+} , Fe^{3+} and Mn^{2+} in water. Hardness of water can be explained by the reaction of soap in soft and hard water.

Reaction of soap in soft water: When 'soft water' is treated with soap, lather is produced according to the following reaction:



Reaction of soap in hard water: Lather does not form, when hard water is treated with soap. But a water insoluble white scum or precipitate forms, which do not possess any detergent action.

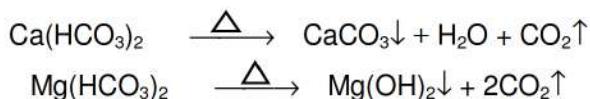


Types of Hardness

Water shows two types of hardness. 1) Temporary Hardness 2) Permanent Hardness

1. Temporary Hardness

- (a) Temporary hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonates of iron and other metals.
 - (b) The main salts responsible for temporary hardness are $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.
 - (c) Temporary hardness can be easily removed by boiling the water. On boiling bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust(cover)at the bottom of vessel.



- (d) Temporary hardness is also known as *carbonate hardness* or alkaline hardness.

2. Permanent Hardness

- (a) Permanent hardness is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals.
 - (b) The salts responsible for permanent hardness are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ etc.
 - (c) Unlike temporary hardness, permanent hardness is not removed by boiling.
 - (d) Permanent hardness is also known as non-carbonate or non-alkaline hardness.
 - (e) Permanent hardness = Total hardness — Temporary hardness

Disadvantages of Hard Water (or) Effect of Hardness

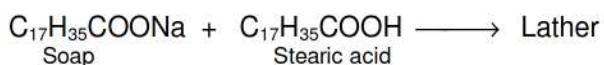
Hardness causing impurities present in the hard water shows effects both on *domestic* and *industries*.

A) Effect on domestic uses:

(a) Washing: hard water reduces the efficiency of soap. Because hard water does not produce lather freely. Same time it produces sticky precipitate (*i.e.* scum) of calcium stearate or magnesium stearate.



The formation of such insoluble sticky precipitates continues till all calcium and magnesium salts present in water are precipitated. After that, the soap (*i.e.*, sodium stearate) gives lather with water. As a result the consumption of soap increases. This causes wastage of soap. The sticky precipitate adheres on the fabric giving spots and streaks. Finally shows effect on economy.



Stains: If hard water contains iron salts, these salts may cause staining on cloth during washing.

(b) Bathing: Hard water does not give lather freely with soap, but produces sticky scum on the body and bath-tub. As a result, the cleaning quality of soap depresses and a lot of soap is wasted.

(c) Cooking:

- The boiling point of water increases, due to the presence of hardness producing salts in dissolved form. As result, more fuel and time are required for cooking.
 - Certain foods such as pulses, beans and peas do not cook soft in hard water.
 - Tea or coffee, prepared in hard water, has an unpleasant taste and muddy looking extract.
 - Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

(d) Drinking: Consumption of hard water adversely affects digestive system and increases possibilities of forming calcium oxalate crystals in the urinary track on drinking.

B) **Effect on industries:** Following adverse effects on various industries can appear, due to presence of hardness producing salts in water

(i) Textile industries: The $\text{Ca}^{+2}/\text{Mg}^{+2}$ adhered on fabrics reduces quality of the colour shade. Further, salts like iron may cause colored spots on fabrics, thereby spoiling their beauty.

- (ii) *Sugar industries*: Difficulties in crystallization of sugar and further the produced sugar may be deliquescent.
- (iii) *Dyeing industry*: Dissolved salts may react with costly dyes, as result impure shade and spot on fabric may develop.
- (iv) *Paper industry*: Dissolved salt react with the chemicals used to give shining to paper. As result, paper quality may fall down. Further, iron salts affect the colour of paper.
- (v) *Effect on laboratories*: Hardness causing ions interference in various reactions, therefore hard water is not a suitable solvent.
- (vi) *Concrete making*: the presence of Cl^- , SO_4^{2-} affects the hydration of cement and reduces the final strength of the hardened concrete.
- (vii) *Effect on steam generation in boilers*: For steam generation, boilers are widely used in various industries. If the hard water is fed directly to the boilers it may cause a boiler trouble known as sludge and scale formation, caustic embrittlement, boiler corrosion and also causes priming

Boiler troubles

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

Requirements for boiler water:

S.No	Requirements for boiler water	If not, it causes
1.	Free from hardness causing salts	Sludge & scale
2.	Free from dissolved salts (Na_2CO_3)	Caustic embrittlement
3.	Free from dissolved gases (DO , CO_2), suspended salts	Boiler corrosion
4.	Free from oil and greases	Foaming & Priming

1) Sludge & scale, 2) caustic embrittlement, 3) boiler corrosion, 4) priming & foaming, occurs in boilers are collectively known as boiler troubles.

1 Sludge and Scale formation

In boilers, water gets evaporates continuously as a result, if water contains hardness causing salts like MgCO_3 , MgCl_2 , MgSO_4 , $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 , CaCl_2 and the concentration of these dissolved salts increases progressively. As a result at one stage, dissolved salts concentration reaches a saturation point and at this stage these dissolved salts thrown out of water in the form of precipitates (scale and sludge) on the inner walls of their boiler.

- i) **Sludge** is a soft, loose, slim and non-sticky precipitate formed within the boiler. Sludge is formed by substances which have grater solubility in hot water than in cold water. eg: MgCO_3 , MgCl_2 , MgSO_4 , CaCl_2 etc

Disadvantages due to sludge formation:

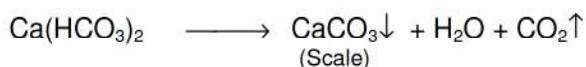
- a) Sludge is a bad conductor of heat, hence requires, more amount of fuel for the generation of steam.
- b) Excessive sludge formation reduces the efficiency of the boiler.

Prevention and removal of sludge formation:

- a) Sludge can be easily scrapped off with a wire brush
 - b) Frequent blow-down operation.
 - c) By using well softened water.
- ii) **Scales** are hard deposits, which stick very firmly to the inner surfaces of the boiler.

Formation of scales may be due to following reasons:

- a) Decomposition of $\text{Ca}(\text{HCO}_3)_2$:



But in high pressure boilers, CaCO_3 soluble in water and forms soft scale



- b) Deposition of CaSO_4

The solubility of CaSO_4 in water decrease with rise of temperature, consequently, CaSO_4 gets precipitated as hard scale on the heated portion of the boiler.

- c) Hydrolysis of magnesium salts

Dissolved magnesium salts undergo hydrolysis and forms soft type of scales.



- d) Presence of Silica

Presence of SiO_2 in water causes the formation of calcium silicates (CaSiO_3) and magnesium silicates (MgSiO_3). These silicates adsorbs strongly on the inner walls of the boilers. These silicates scales are very difficult to remove. The formation silicates can be prevented just by removing silica by using sand filters.

Disadvantages due to scale formation:

- i) Wastage of fuel:

Scales acts as a bad conductor of heat. In order to provide steady supply of heat to water, excessive heating is done and this causes increase in fuel consumption. The wastage of fuel depends on the thickness of scale

Thickness of scale (mm)	0.3	0.6	1.2	2.5	12
Wastage of fuel (%)	10	15	50	80	150

- ii) Lowering of boiler safety:

Due to scale formation overheating is done for the production of steam, because of this overheating the boiler material becomes soft and weaker. This makes the boiler unsafe to bare the pressure of the steam.

iii) *Danger of explosion:*

At high temperature, cracks may be formed on scale and due to the formation of uneven scales inside the boiler, causes the formation of large amount of steam suddenly. This develops the high pressure, which may even cause explosion of the boilers

iv) *Decrease in efficiency:*

Scales may sometimes deposit in the valves of boilers, this results in decrease in efficiency of the boilers.

Removal of scales:

- a) scales can be removed by thermal shocks
- b) scales can be removed with the help of a scraper or piece of wood
- c) CaCO_3 scales can be dissolved by using 5-10% HCl.
- d) CaSO_4 scales can be dissolved by adding EDTA, which forms soluble complex.

Prevention of scales formation: By using the soft water and this can be done in two ways;

- i) External treatment
- ii) Internal treatment.

2 Caustic embrittlement : This type of corrosion caused by the NaOH formed in the boilers.

- i) Generally, scale formation can be avoided by adding Na_2CO_3 to boiler water (Carbonate conditioning).



As a result, there is a chance for the presence of free Na_2CO_3 in small proportion in the softened water. In boilers these Na_2CO_3 decomposes to give NaOH.



This NaOH passes into the minute hair cracks present on the boiler by a capillary action and reacts with iron present in the surrounding area. As a result the iron converts into sodium ferroate (Na_2FeO_2) flakes, which weakens the boiler walls. This causes the formation of irregular intergranular cracks on the inner walls of the boiler which is known as embrittlement. This type of embrittlement always occurs at highly stressed parts like bends, rivets, and joints etc. causing failure of boilers.



Prevention of embrittlement:

- a) by using Sodium hexameta phosphate (calgon) as softening agent instead of Na_2CO_3



- b) The hair line cracks of boilers can be sealed by waxy materials like Tannin and Lignin.

3 Boiler corrosion:

"Decay of boiler material by a chemical or electrochemical attack by its environment" is known as boiler corrosion.

This boiler corrosion is due to the presence of

- i) Dissolved oxygen (DO)
- ii) Dissolved CO₂
- iii) Acids from dissolved salts (MgCl₂) in water.

i) Dissolved oxygen (DO): water usually contains 8 mg/L of dissolved oxygen at room temperature. It attacks boiler material causing rust formation.



Removal of DO: a) by mechanical de-aeration

b) by adding calculated quantity of Na₂SO₃ or Na₂S or N₂H₄



ii) Dissolved CO₂:- Water contains some dissolved CO₂ and bicarbonates present in water also produce CO₂. This CO₂ dissolves in water forming carbonic acid which causes local corrosion called pitting.



Removal of dissolved CO₂: a) by mechanical de-aeration

b) by adding calculated quantity of ammonia



iii) Acids from dissolved salts:- Water from industries contains acidic waste and also magnesium salts present in water liberate acids on hydrolysis.



The liberated HCl reacts with iron in chain like reactions producing HCl again and again. So the presence of even small amount of MgCl₂ can cause corrosion of iron to a large extent. This type of corrosion may be avoided by neutralization with alkali.



4 Priming and foaming:-

Priming:

- Due to rapid boiling, the steam may carry some water droplets along with it. This is called 'wet steam' or 'carry over'.
- Production of wet steam by rapid boiling of water in boilers is called **priming**.
 - It may be due to i) Very high steam velocity ii) High water level
iii) Uneven boiling due to oil layers, slats etc iv) Improper boiler design

Impacts of priming: Priming reduces the heat of the steam and causes corrosion in the pipeline

Priming can be avoided by – i) Fitting mechanical steam purifiers ii) Maintaining low water level iii) using softened water iv) using well designed boiler

Foaming:

- The production of continuing bubbles or foam in boiler, which do not break easily is known as foaming.
- It may be due to i) The presence of oil or soapy substances,
ii) more amount of salts.

Impacts of Foaming: This foaming reduces both quality and quantity of steam

Foaming can be avoided by –

- i) By adding antifoaming agents like cotton seed oil and castor oil
- ii) Adding sodium aluminate (NaAlO_2) or aluminium hydroxide coagulates the oily or soapy substances.

Units of hardness: Both temporary and permanent hardness is principally expressed in Parts Per Million (ppm) units.

◆ ppm is defined as "the parts of CaCO_3 equivalent per 10^6 parts of water. i.e. 1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water".

$$1\text{ppm} = \frac{1 \text{ part of hardness}}{10^6 \text{ parts of water}}$$

The choice of CaCO_3 is due to the fact that its mol. wt. is 100 and equivalent weight is 50 and it is the most insoluble salt in water.

$$\begin{aligned}\text{Equivalent of } \text{CaCO}_3 &= \frac{(\text{Mass of hardness producing substance}) \times (\text{Chemical equivalent of } \text{CaCO}_3)}{\text{Chemical equivalent of hardness producing substance}} \\ \text{Equivalent of } \text{CaCO}_3 &= \frac{(\text{Mass of hardness producing substance}) \times (50)}{\text{Chemical equivalent of hardness producing substance}}\end{aligned}$$

- ❖ Other units for hardness are mg/L, meq/L, degree French (${}^\circ\text{Fr}$), Clarke's degree (${}^\circ\text{Cl}$).
- ❖ Relationship between various hardness units:

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.02 \text{ meq/L} = 0.1 {}^\circ\text{Fr} = 0.07 {}^\circ\text{Cl}$$

- Milligrams per liter (mg/L): is the number of milligrams of CaCO_3 equivalent hardness present per liter of water.

1 mg/L = 1 mg of CaCO₃ equivalent of 1 L of water

But 1 Lit of water = 1 kg = 1000g = 1000 x 1000 mg

$\therefore 1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water}$

= 1 part of CaCO_3 equivalent per 10^6 mg of water = 1 ppm

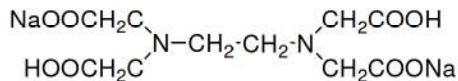
- Milliequivalent per liter (meq/L): is the number of milliequivalents of hardness present per liter.
 - Degree French ($^{\circ}\text{Fr}$): is the parts of CaCO_3 equivalent per 10^5 parts of water.
 - Clarke's degree ($^{\circ}\text{Cl}$): It is parts of CaCO_3 equivalent hardness per 70000 parts of water.

Problems relating to hardness of water: Refer Text book and class note book.

<u>Hardness</u>	<u>Category Equivalent Concentration of CaCO₃</u>
Soft	< 60 ppm
Medium hard	60 ppm to < 120 ppm
Hard	120 to < 180 ppm
Very hard	180 ppm or greater

Estimation of hardness of water sample by EDTA method:

Estimation of hardness of water sample by EDTA (Ethylene Diamine Tetra Acetic acid) is a complexometric titration method. In this method disodium salt of EDTA is used as a complexing agent for Ca^{2+} , Mg^{2+} .



Titrations involving the use of complexing agents are known as complexometric titrations.

Chemicals required:

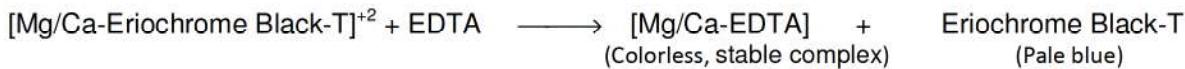
(a) EDTA solution, (b) Ammonical Buffer solution (pH = 10) (c) Eriochrome Black-T (EBT indicator): (d) Water sample: 1 liter (e) Standard hard water: Dissolve 1 g pure dry CaCO_3 in 1 L distilled water. i.e 1 mL of the solution contains 1 mg CaCO_3 equivalent hardness.

Principle:

'Eriochrome Black-T' indicator, which is a blue colored dye, forms an unstable complex with Calcium or Magnesium ions in hard water at pH of 9-10 (using $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer Solution). The complex is wine red in color.



As this solution is titrated against EDTA, the free Ca^{2+} and Mg^{2+} ions in water forms stable Mg/Ca -EDTA complex (colorless). Once all the free metal ions (Ca^{2+} and Mg^{2+}) are complexed, the EDTA replaces Ca^{2+} and Mg^{2+} ions from the unstable indicator complex, with the result, the indicator is set free. Consequently, the colour of the solution changes from wine red to blue at the end point.



Finally, temporary hardness can be removed by boiling and after the removal of precipitate by filtration; the permanent hardness in the filtrate is determined by titration with EDTA as above.

Procedure:

Part 1: Standardization of EDTA solution: Since EDTA is non-primary standard solution it must be standardized. The burette is rinsed and filled with EDTA solution. 20 mL of standard hard water is pipette out into a clean conical flask. To this 2 mL of ammonical buffer and two drops of EBT indicator are added and then titrated against EDTA solution until the wine red colour changes to deep blue colour which indicates the endpoint. Let the volume of EDTA used be V_1 mL. i.e. 20 mL of standard hard water consumes V_1 mL of EDTA.

$$20 \text{ mL of standard hard water} = V_1 \text{ mL EDTA}$$

$$\text{But } 1 \text{ mL of standard hard water} = 1 \text{ mg CaCO}_3 \text{ equivalent}$$

$$\therefore V_1 \text{ mL of EDTA} = 20 \text{ mg of CaCO}_3 \text{ equivalent} \quad \text{eq.1}$$

$$1 \text{ mL EDTA} = \frac{20}{V_1} \text{ mg of CaCO}_3 \text{ equivalent} \quad \text{eq.2}$$

Part 2: Estimation of Total hardness: 20 mL of a given sample of hard water is pipette out into a 250 mL clean conical flask. To this 2 mL of ammonical buffer and two drops of EBT indicator are added and then titrated against EDTA solution until the wine red colour changes to deep blue colour which indicates the endpoint. Let the volume of EDTA used be V_2 mL. i.e. 20 mL of given hard water sample consumes V_2 mL of EDTA.

$$20 \text{ mL of given hard water} = V_2 \text{ mL EDTA} \quad \text{eq.3}$$

$$\text{Then } 1000 \text{ mL of above hard water} = \frac{V_2}{20} \times 1000 \text{ mL of EDTA}$$

$$\text{From eq.2; } 1 \text{ mL EDTA} = \frac{20}{V_1} \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\frac{V_2}{20} \times 1000 \text{ mL of EDTA} = \dots? \dots \text{mg of CaCO}_3 \text{ equivalent}$$

$$= \frac{20}{V_1} \times \frac{V_2}{20} \times 1000 \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\therefore 1 \text{ L (1000 mL) of given hard water} = \frac{V_2}{V_1} \times 1000 \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\text{i.e. Total hardness} = \frac{V_2}{V_1} \times 1000 \text{ mg/L} \quad \text{eq.4}$$

Part 3: Estimation of permanent hardness: 250 mL of the hard water sample is taken in 1 L beaker, heated strongly and evaporated nearly 50 mL. As a result all bicarbonates decompose to insoluble CaCO_3 . Filter off CaCO_3 and make-up the filtrate to 250 mL with distilled water. 20 mL of make-up solution is pipette out into a clean conical flask. To this 2 mL of ammonical buffer and two drops of EBT indicator are added and then titrated against EDTA solution until the wine red colour changes to deep blue colour which indicates the endpoint. Let the volume of EDTA used be V_3 mL. i.e. 20 mL of boiled water sample consumes V_3 mL of EDTA.

$\therefore 20 \text{ mL of boiled water} = V_3 \text{ mL EDTA}$ ----- eq5

Then $1000 \text{ mL of above boiled water} = \frac{V_3}{20} \times 1000 \text{ mL of EDTA}$

From eq.2; 1 mL EDTA = $\frac{20}{V_1}$ mg of CaCO_3 equivalent

$\frac{V_3}{20} \times 1000 \text{ mL of EDTA} = \dots? \dots \text{mg of } \text{CaCO}_3 \text{ equivalent}$

$$= \frac{20}{V_1} \times \frac{V_3}{20} \times 1000 \text{ mg of } \text{CaCO}_3 \text{ equivalent}$$

$1 \text{ L (1000 mL) of boiled water} = \frac{V_3}{V_1} \times 1000 \text{ mg of } \text{CaCO}_3 \text{ equivalent}$

i.e. Permanent hardness = $\frac{V_3}{V_1} \times 1000 \text{ mg/L}$ ----- eq 6

Part 4: Temporary hardness = Total hardness – Permanent hardness

$$= \left(\frac{V_2}{V_1} \times 1000 \right) - \left(\frac{V_3}{V_1} \times 1000 \right) \text{----- (from eq 5 and 6)}$$

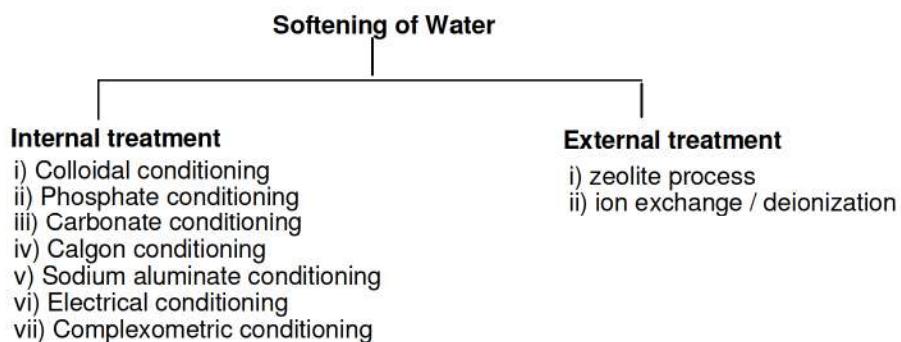
$$\text{Temporary hardness} = \left(\frac{V_2 - V_3}{V_1} \right) 1000 \text{----- eq 7}$$

Advantage of EDTA method:

- i) greater accuracy ii) more rapid iii) simple and convenience
-

Softening of Water:

Softening of water means the removal of calcium, magnesium, iron salts and similar other metallic ions. This can be done by internal treatment or by external treatment. However, importantly external treatment is adopted by most of industries because of their repeated use.



Internal treatment:

This process is more familiar with boilers, normally internal treatment done by adding proper chemicals to the boiler water. As a result following two conditions may observed

- i) converts scale formed substances into sludge which can be removed by blow-down operation
- ii) By keeping the scale forming substances in soluble state by means of complexation.

(Sledge: A soft, loose and slimy precipitate formed within the boiler or water storage tanks.

Scale hard deposits, which stick very firmly to the inner surfaces of the boiler or water storage tanks)

Important internal treatment /internal conditioning methods are:

i) Colloidal conditioning:

Organic substances like kerosene and agar-agar are added to the water to avoid scale formation. They form a coating over the scale forming precipitate, thereby yielding non-sticky and loose deposits which can be easily removed by blow-down operations.

ii) Phosphate conditioning:

Sodium phosphate reacts with scale forming $\text{Ca}^{2+}/\text{Mg}^{2+}$ salt and converts them into loose sludge, which can be easily removed by blow-down operation.



iii) Carbonate conditioning:

Scale formation can be avoided by adding Na_2CO_3 to boiler water



iv) Calgon conditioning:

Sodium hexameta phosphate (calgon) is added to boiler water to prevent the scale formation.



v) Sodium aluminate conditioning:

Sodium aluminate (NaAlO_2) gets hydrolyzed yielding NaOH precipitates the magnesium present in hard water as $\text{Mg}(\text{OH})_2$



vi) Electrical conditioning: A Sealed glass bulbs, containing mercury connected to a battery, are set rotating in the boilers/water tanks. When an electrical discharge emitted through these mercury bulbs, they attract all the scale forming particles present in water and this prevents scale/sledge formation.

vii) Complexometric conditioning: This method involves with addition of alkaline solution of EDTA to hard water. EDTA binds the scale forming cations in hard water and this prevents scale/sledge formation.

External treatment: the most important and the best external treatment methods are

- i) zeolite process ii) ion exchange process

Zeolite process (or) Permutit process: Zeolites in Greek it means “boiling stone”.

Zeolites is hydrated sodium alumina silicate ($\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, x\text{SiO}_2.y\text{H}_2\text{O}$ where $x = 2-10$ and $y=2-6$). zeolites are insoluble in water and have the property of exchanging ions (Na^+) present in them with the ions ($\text{Ca}^{2+}, \text{Mg}^{2+}$) present in the hard water. Zeolite is of two types **a)** natural zeolite and **b)** artificial zeolite

Natural zeolite (natrolite, $\text{Na}_2\text{O Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) is hard and nonporous. So it cannot be used for water softening.

Artificial zeolite is prepared by heating together with china clay (Al_2O_3 mineral), feldspar (silicate minerals) and soda ash (Na_2CO_3). These are porous and glassy and have greater softening capacity

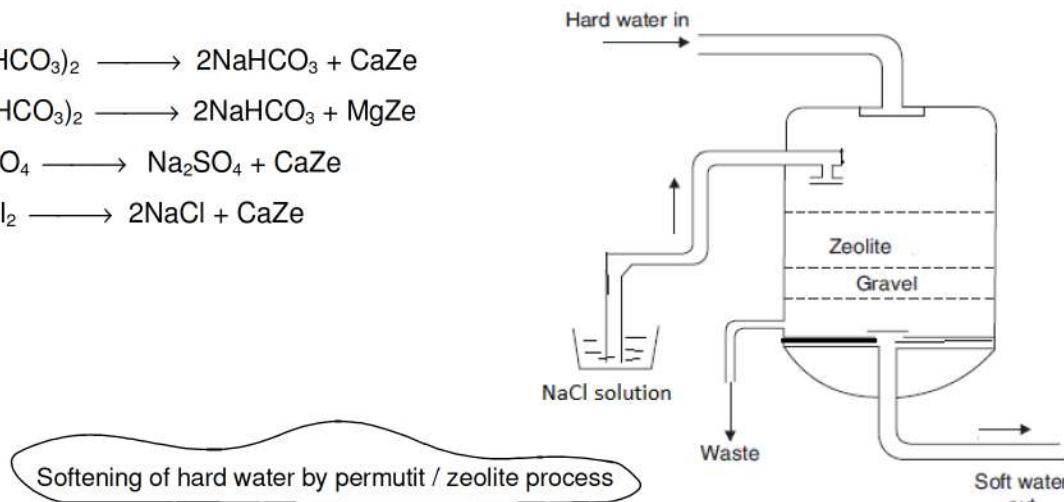
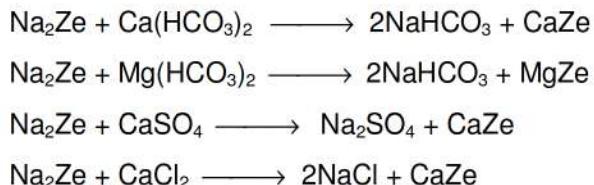
Feldspar ($\text{KAlSi}_3\text{O}_8 - \text{NaAlSi}_3\text{O}_8 - \text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}$)

Artificial zeolite used for softening purpose and this process is also called as **permutit process**.

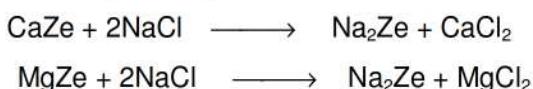
Principle: A slow stream of hard water is passed through artificial zeolite. As a result, Ca^{2+} and Mg^{2+} ions present in hard water are exchanged with Na^+ ions in the Zeolite. The outgoing water contains sodium salts, which do not cause hardness.

Method of softening in zeolite process: Hard water is passed through a bed of zeolite packed in a suitable container at a specific rate at ordinary temperature. The hardness causing cations (Ca^{2+} and Mg^{2+}) are exchanged by Na^+ of zeolite and as a result the artificial zeolite is converted to CaZe and MgZe . ($\text{Ze} = \text{O. Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$; where $x = 2-10$ and $y = 2-6$).

Following reactions taking place during softening of water in zeolite process:



Regeneration of Zeolite: After some days, the zeolite is completely converted into Ca/Mg zeolites and as a result further it cannot soften the water. Such Ca/Mg zeolites are called as exhausted zeolites, which can be regenerated by treating the bed with 10% of brine (NaCl) solution.



The washings containing CaCl_2 (or) MgCl_2 are discarded.

Advantages:

- (i) The water softened by this process can be used for laundry purposes
- (ii) Hardness of water can be removed completely up to about 10 ppm
- (iii) The equipment used is small and easy to handle
- (iv) It requires less time for softening
- (v) Easy to regenerate the exhausted zeolite

Disadvantages / limitations:

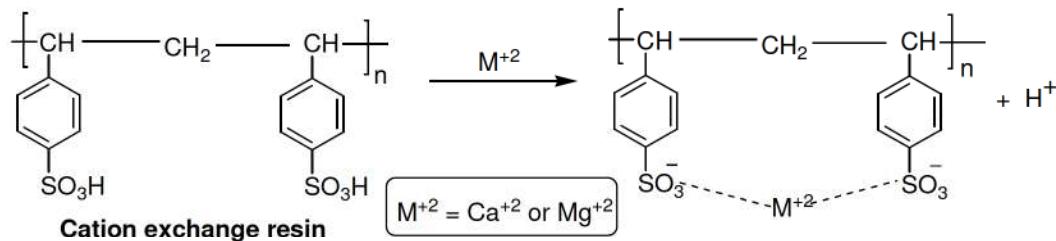
- (i) Coloured water due to Mn^{+2} and Fe^{+2} cannot be used as such. Because these ions reacts with zeolite and produces manganese and iron zeolite, which cannot be easily regenerate.
- (ii) water containing suspended impurities cannot be used without filtration
- (iii) Water with acidic nature cannot be used for softening; as acidity destroys the zeolite
- (iv) In this method only Ca^{2+} and Mg^{2+} ions are replaced by Na^+ ions leaving all acidic ions like HCO_3^- , CO_3^{2-} . When this water is used in boilers on heating liberates CO_2 , which causes corrosion in the boilers and hence this soft water is not suitable for boilers.

Ion Exchange Resins / ion-exchange polymer / Demineralization of water

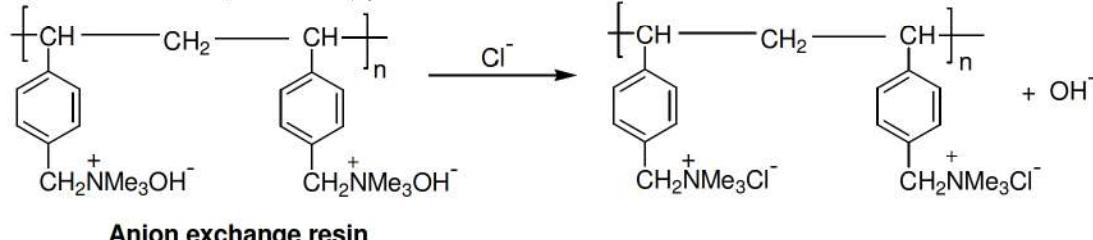
For many laboratory and industrial applications, high-purity water which is essentially free from ionic contaminants is required. Water of this quality can be produced by deionization. This can be done by using ion exchange resins. Normally ion exchange is widely used in the food & beverage, chemical, pharmaceutical, sugar, nuclear plants, thermal power plants, and a host of other industries.

Giant organic molecules with acidic (or) basic groups are known as *Ion-exchange resins*. They are two types. i) Cation exchange resins ii) Anion exchange resins. The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter and then the Cation exchange / Anion exchange resin chambers are field with the corresponding beds.

- (i) Cation exchange resins (RH) contain the acid group which exchange their H^+ ions with the cations (Ca^{2+} and Mg^{2+}) present in the water.

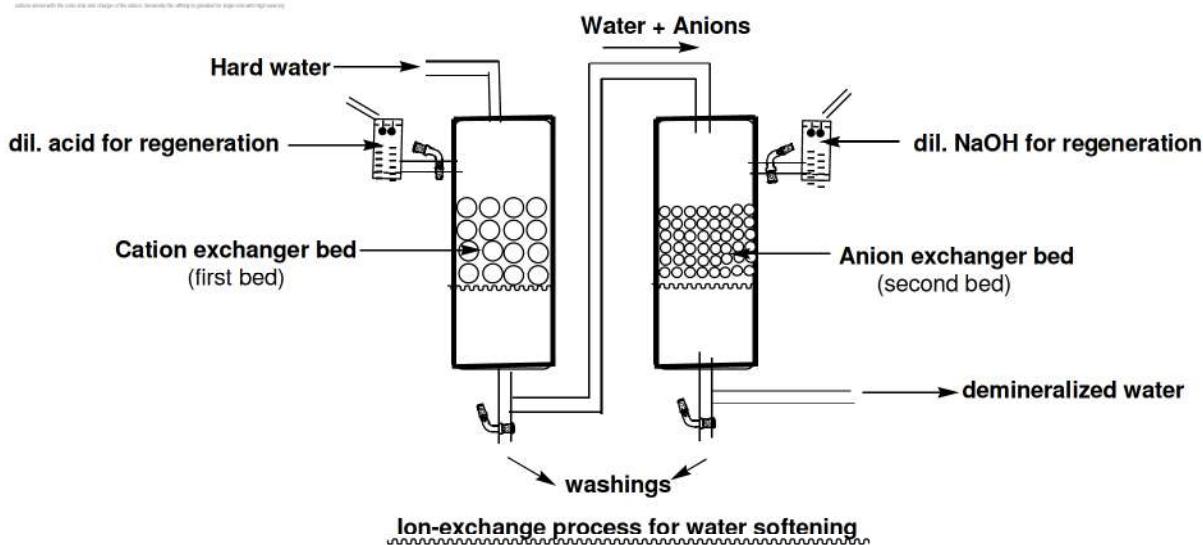


- (ii) Anion exchange resins (R'OH⁻) contain basic group which exchange their OH^- ions with the anions (Cl^- , SO_4^{2-}) present in the water.



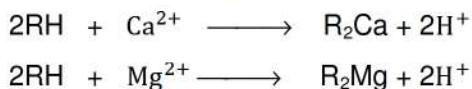
Principle: Raw water is passed via ion exchange resins beds. During this process the cations get exchanged with H^+ in first bed, the anions are exchanged with OH^- in the second one. This exchange can be done because, while hard water passed down a resin bed, it flows through the

cross-linked polymer. This helps to bring intimate contact between the exchange sites.

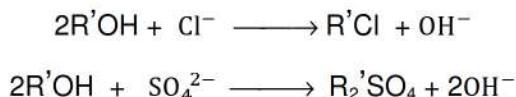


Method of Softening in ion exchange resin process:

Removal of cation: The hard water is passed first through *cation exchange resin bed* (RH), where all the cations like Ca^{2+} , Mg^{2+} are removed from the hard water.



Removal of anions: After removal of cations, this hard water is again passed through *anion exchange resin bed* ($\text{R}'\text{OH}$), where all the anions like SO_4^{2-} , Cl^- , CO_3^{2-} are removed from the hard water. The water becomes soft after this process.



These H^+ and OH^- produced in *cation exchange resin bed* and *anion exchange resin bed* respectively are combined to form water molecule in *anion exchange resin chamber*. Thus the water coming out finally from the two exchangers is ion free and called deionized (or) demineralized water. This is as good as distilled water.



With the continuity of above reactions at one stage the both the resins get exhaustion. This exhaustion of demineraliser is usually detected by an electrical conductivity cell installed at the outlet. When the conductivity rises to indicate ionic break through, a regeneration cycle can be initiated automatically.

Regeneration of cation and anion exchange resin:

The inactivated or exhausted cation exchange resin is regenerated by dil. H_2SO_4 / HCl



Similarly, the exhausted anion exchange resin is regenerated by dil. NaOH



The columns are finally washed with deionized water and the washings are discarded.

Advantages:

- This method can be used to soften highly acidic **or** alkaline waters.
- By this method the hardness of the water can be brought to low (2 ppm). So this water is good for high pressure boilers.
- A bed of resin not only helps to remove unwanted ions from a solution passed through it, but also helps to accumulate the valuable mineral which can be recovered from the resin.

Disadvantages:

- The equipment is costly and more expensive chemicals are to be used.
- The water used for purification must be free from turbidity.

Note: If Anion exchanger is used before cation exchanger in water treatment system then following problem occurred.

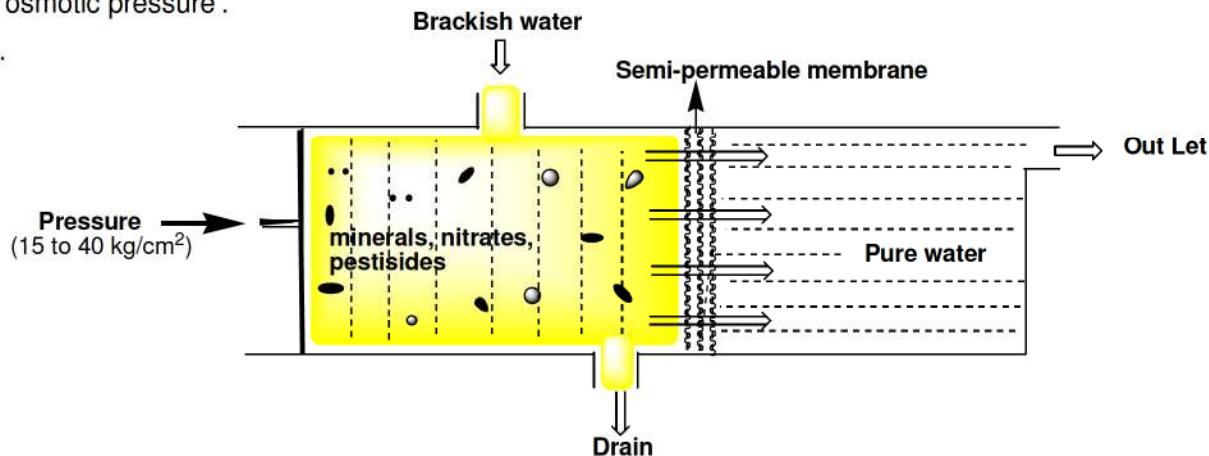
As a result, there is a chance for release of more OH^- as shown in chemical equation. Deposition of sulphate in bed at high pH as a result formed sludge reduces the efficiency of resin. In normal procedure in second stage these OH^- get neutralized by H^+ .

Desalination of Brackish Water:

The water containing dissolved salts and having very salty taste like the sea water is called brackish water, and it is not suitable for drinking. The process of removal of common salt (NaCl) from this brackish water is called desalination. Generally, desalination can be done by either reverse osmosis methods **or** by electro dialysis.

The popularity of reverse osmosis water (R.O. water) has steadily grown since it was first introduced as a home water purification system in the 1970s.

Reverse osmosis (RO): To understand reverse osmosis, it is necessary to understand natural osmosis. Osmosis describes the flow of solvent from dilute solution to concentrated solution through a semi-permeable membrane. The pressure that developed during osmosis is called 'osmotic pressure'.



Reverse osmosis (RO) is a water purification technology that uses a semi-permeable membrane. The semi-permeable membrane is made with polymers like cellulose acetate **or** polyamide. Semi-permeable membrane can allow only solvent but not solute particle through pores. So, this 'membrane filtration' is also called as 'super-filtration' or 'hyper-filtration'.

Principals involved in RO:

- i) In reverse osmosis the flow of solvent is in opposite direction to osmosis process i.e. solvent from concentrate solution to dilute solution across the semi-permeable membrane. In reverse osmosis, an applied pressure (15 to 40 kg/cm²) is used to overcome osmotic pressure as a result the solvent flow reverse. cm² = Square centimetre
- ii) Moreover, reverse osmosis involves a diffusive mechanism, so that separation efficiency is dependent on solute concentration, pressure, and water flux rate. An RO membrane rejects contaminants based on their size and charge. (Flux: flow rate of water based on the pressure applied per unit area) diffusion mechanism: which oxygen enters the body during external respiration.
- iii) RO depends on physical force only and no chemical reaction is observed during the entire process of RO. Further, no chemical reagents are required.

Method: In this process, 15 to 40 kg/cm² pressure is applied on the feed water in RO tank. This applied pressure force the solvent only to pass through the semi-permeable membrane leaving behind the dissolved salts.

Advantages by reverse osmosis purification process:

- (i) The main health advantage R.O. water has over tap water is that an R.O. system removes many unhealthy contaminants.
- (ii) Reverse Osmosis is capable of removing up to 99%+ of the dissolved salts (ions), non-ionic, colloidal particles, high molecular weight solutes, organics, bacteria and pathogens from the feed water.
- (iii) A good R.O. system can remove contaminants such as fluoride, nitrates, arsenic, sodium, copper, lead, and some organic chemicals.
- (iv) Easy replacement of the semi-permeable membrane and life time of membrane is high.
- (v) Uninterrupted supply of large volume of water for industrial or domestic purpose can be obtained.
- (vi) Reverse osmosis is largely used for purification of sea water for domestic use.

Disadvantage due to reverse osmosis purification process:

- a) Drinking de-mineralized water is not healthy. According to 'WHO' risks include gastrointestinal problems, bone density issues, joint conditions, and cardiovascular disease. .
- b) Further, removing the minerals makes the water acidic (often well below 7.0 pH). Drinking acidic water affect the healthy pH balance (7.35 - 7.45) in the blood. In fact, in 1931, Dr. Otto Warburg won the Nobel Prize for discovering the cause of cancer. According to him lack of cellular oxygenation is main reason for cancer; this situation is just due to acidosis in body.
- c) Removing the naturally occurring minerals also leaves the water tasteless.
- d) It is recommended to add a remineralization cartridge (such as Trace Minerals Ionic Tonic,) to existing R.O. system.
- e) Reverse osmosis membrane alone does not remove volatile organic chemical (VOCs) found in municipal water.

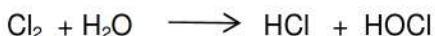
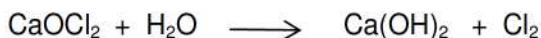
Drinking water treatment or Removal of micro-organisms (Ozonisation & chlorination)

The water obtained after removal of suspended impurities may contain small percentage of pathogenic bacteria, micro-organisms. The process of destroying/killing the disease producing bacteria and micro-organisms from water and making it safe for use is called 'disinfection'. The chemical substances added to water for killing the bacteria and micro-organisms are known as 'disinfectants'.

(I) By boiling: Water on boiling for 10-15 min, all the disease producing bacteria are killed and water become safe for use. Solar power can be used for boiling the water now-a-days.

(II) Chlorination: The process of adding chlorine to water is called chlorination. This is not only for disinfection action on raw water but also to oxidize (i) organic matter (ii) reducing substances (iii) free ammonia in raw water. Chlorination can be done by the following methods

(a) By adding bleaching powder: The disinfecting action of bleaching powder is due to the formed hypochlorous acid (HOCl).

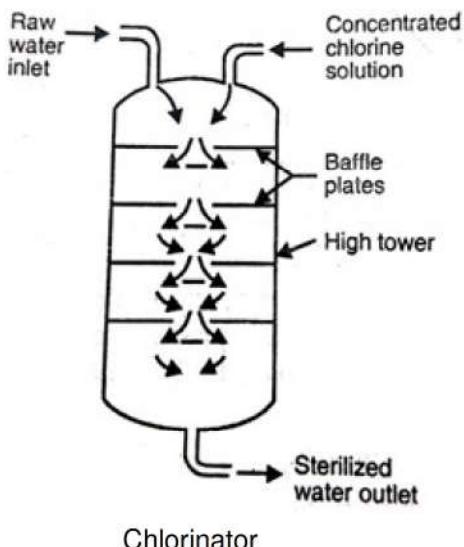


About, 1 kg of bleaching powder per 1000 kg of water is mixed and resulted water allowed to stand undisturbed for several hours. The disadvantage is the bleaching powder introduces calcium into water.

(b) By chlorine: Chlorine gas is a very good disinfectant, which can be bubbled in the water. In this process calculated amount of chlorine gas is passed in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid (HOCl) and nascent oxygen, which acts a powerful oxidizing agent and kills the bacteria.



Procedure for chlorination:



Liquid chlorine is most effective and adequate mixing is required when it applied to the filter water. The apparatus used for this purpose 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 tower, they get thoroughly mixed. The treated water collected from the bottom. For filter water, about 0.3 to 0.5 ppm of chlorine is sufficient.

Factors affecting efficiency of chlorine:

- i. Time of contact: the number of micro-organisms destroyed is proportional to number of unit time in contact.
- ii. pH value of water: at lower pH values (5-6) a small contact period is required to kill same percentage of organisms.
- iii. Temperature of water: the death rate of micro-organisms by chlorine increases with rise in water temperature.

Advantage of chlorine:

- It is effective and economical
- It can be used at low as well as at high temperature
- It does not introduce salt impurities in the treated water.

Disadvantage of chlorine:

- If excess of chlorine is added it produces a characteristic unpleasant taste and odour
- More over 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

(c) By using chloramines: When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine (CINH_2) is formed.



Chloramine (CINH_2) is a better bactericidal than chlorine. Chloramine compounds decompose slowly to give nascent oxygen which will act as good disinfectant than the Chlorine. Chloramine gives good taste to the treated water.



Mechanism of action chlorine/bleaching powder/ Chloramine:

In the earlier it was believed that the disinfection action of Chlorine was due to the nascent oxygen, which oxidizes the harmful bacteria. But in later stage the experiments proved the chemical action of hypochlorous acid with enzymes in the cell of bacteria results the death of these micro-organism.

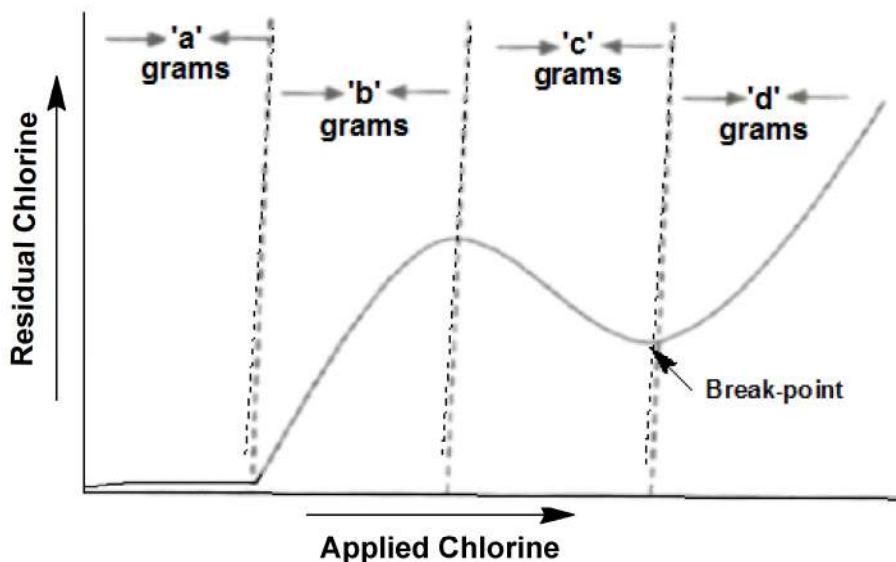
What is Breakpoint chlorination (or) free-residual chlorination?

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

'Residual chlorine' is the amount of chlorine that remains in the water after a certain period or contact time. Residual chlorine is an important measurement to safeguard against microbial contamination.

The free residual chlorine begins to appear during chlorination is only after the break-point chlorination.

The water sample is treated with chlorine and estimated the residual chlorine in water. The plotted graph shown below gives the information of break-point chlorination and residual chlorine.



From graph it is clear that:

- 'a' gms of chlorine added oxidizes reducing impurities of water.
- 'b' gms of chlorine added forms chloramines and other chloro compounds.
- 'c' gms of chlorine added causes destruction of bacteria.
- 'd' gms of chlorine is residual chlorine. After the break-point, further addition of chlorine is not at all utilized and simply increases the residual chlorine level.
- 'c' gms is the break point for addition of chlorine to water. This is called **break- point chlorination**.

Advantages of break-point chlorination:

- i) It removes bad taste, odour, colour, from the water
- ii) It oxidizes completely organic compounds, ammonia and other reducing impurities
- iii) It destroys completely (100%) the pathogenic bacteria
- iv) It prevents the growth of any weeds in water

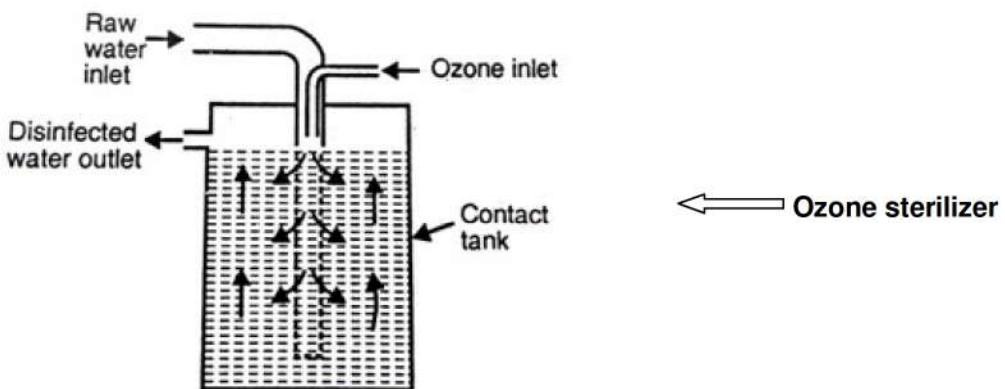
(III) **Disinfection by Ozone (ozonation):** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable gas and breaks down to give nascent oxygen [O]. The nascent oxygen is very powerful oxidizing agent and kills the bacterias as well as oxidizes the organic matter present in water.



The nascent oxygen is very powerful oxidizing agent and kills the bacterias as well as oxidizes the organic matter present in water.

During ozonation, due to the low stability of O_3 , it is synthesized by using ozonizer instantaneously and immediately released into the water in a specially designed sterilizing tank. Both water and O_3

are allowed to come in contact in this tank about 10-15 minutes and the usual dose strength is 2-3 ppm. The disinfected water is removed from the top.



Disadvantage of ozonation: This method is quite expensive, not employed for disinfection of municipal water supply. Due to unstable of ozone cannot be stored for long time

Advantage of ozonation: More effective than chlorination and simultaneously removes colour, odour and taste. Further, its excess is not harmful and do not leave harmful residues.

Specifications of potable water as per WHO and BIS standards.

A report prepared by the World Health Organization (WHO) in cooperation with the World Bank showed that in 1975, some 1230 million people were without safe water supplies. Therefore, the standard was formulated by WHO in 1981 with the objective of assessing the quality of water resources, and to check the effectiveness of water treatment and supply by the concerned authorities. Indian Standard (1983) was adopted by the Bureau of Indian Standards (BIS), after the draft finalized by the Drinking Water Sectional Committee had been approved by the Food and Agriculture Division Council - India, where the WHO standard uses as the basis.

Potable water (Drinking Water) and its specifications

- i. Water free from contaminants or water that is safe for human consumption is called potable water. The following are the specifications of water drinking.
- ii. The water should be clear (colorless), odorless and pleasant taste.
- iii. The hardness of water must be 300 ppm
- iv. The acceptable limit of Total alkalinity of water 200 ppm
- v. The acceptable limit of fluorides of water 1.5 ppm
- vi. The quantity of free chlorine in treated water should not exceed 0.1 to 0.2 ppm
- vii. The recommended concentration of *total dissolved solids (TDS)* is 500 ppm
- viii. The *turbidity* in drinking water should not exceed 25 ppm.
- ix. The pH of potable water should be 7.2 to 8.5.
- x. The water must be free from *heavy metals* like Lead, Arsenic, Chromium and Manganese.
- xi. The water must be *free from pathogenic bacteria*
- xii. The water must be *free from dissolved gases* like H_2S , CO_2 and NH_3 .

Fluorides in water:

- Fluorine is a common element that does not occur in the elemental state in nature because of its high reactivity.
- It accounts for about 300 mg/kg of the Earth's crust and exists in the form of fluorides in a number of minerals, of which fluorspar (CaF_2), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and cryolite (Na_3AlF_6) are the most common.
- In groundwater, fluoride concentrations vary with the type of rock the water flows.
- In seawater, a total fluoride concentration was found as 1.3 mg/liter.
- Fluorides may also enter a river as a result of industrial discharges.

Effects of fluorides on human health can be studied as their importance and their adverse effects related to human health:

A) ***Importance of fluoride:***

- Fluoride may be an essential element for animals and humans. Normally, minimum oral doses of at least 1 mg of fluoride per kg of body weight were required.
- As per medical research reports, low concentrations of fluoride intake by water provide protection against dental caries, especially in children.
- The pre- and post-eruptive protective effects of fluoride involving the incorporation of fluoride into the matrix of the tooth during its formation. In this way fluoride prevents tooth decay.
- Though fluoride is necessary for the body function the WHO limits fluoride concentrations in drinking and cooking water to 1.5 mg/liter.

B) ***Adverse effects of fluoride:*** In case the fluoride concentrations exceed above 1.5 mg/liter in drinking water leads to fluorosis in fluorotic areas. Therefore, there is a great need for education and awareness of fluorosis. .

Fluorosis means adverse changes in bone structure and finally weakens the bone strength, which leads to a serious bone disease. Fluorosis is non-curable, thus efforts should be directed toward prevention.

i) **Dental fluorosis:**

- Dental fluorosis is the most common in fluorotic areas due to over-consumption of fluoride. If the fluoride concentrations in drinking-water is above 1.5 mg/liter shows adverse effect on tooth enamel.
- Dental fluorosis is visible by white, yellow, and brown streaks on the teeth, characteristic of the hypoplasia (teeth formation is not perfect) and hypo calcification (damage to enamel). This damage is more than cosmetic, as it tends to be associated with painful "cavity-like" feelings.

ii) **Skeletal fluorosis:**

- Skeletal fluorosis is a bone disease caused by excessive accumulation of fluoride in the bones leading to changes in bone structure and making them extremely weak and brittle.

Normally it is observed on consumption of drinking-water contains 3–6 mg of fluoride per liter over a long period of time.

- Skeletal fluorosis is characterized by deformation of bone structure. The early stages of skeletal fluorosis are characterized by decrease of bone mass, detectable by x-ray. Skeletal fluorosis causes pain and damage to bones and joints

iii) Crippling skeletal fluorosis: Crippling means to become unable to walk or move properly.

- The most severe form of skeletal fluorosis is known as "crippling skeletal fluorosis," which may result in calcification of ligaments, immobility, and neurological problems related to spinal cord compression.
- In this case the bone loses its elastic nature. This results an increased frequency of fractures.
- Usually Skeletal fluorosis develops on consumption of drinking-water contains over 10 mg of fluoride per liter over a long period of time.

iv) Neurological complications:

- It is suspected that these complications are caused by fluorides effects on the spine and compression on the spinal cord.
- Studies have shown that high levels of fluoride can cause headaches, insomnia (habitual sleeplessness), and reductions in the IQs of children.

v) Persons suffering from the renal problems have a lower margin of safety even with low concentration of fluorides in water.

vi) High fluoride concentrations also effect the functioning of thyroid gland, pineal gland and even blood sugar levels.

vii) Effects on animals: The histological changes which are induced through fluorine on rats resemble those of humans.

viii) Fluorosis has significant economic impacts in the developing world. In addition, fluorosis removes people from the workforce.

Mechanism of action to explain fluorosis:

The mechanism of action of fluorine to break down bones, which leads to skeletal fluorosis can be explained in stepwise fashion.

1. Fluorine enters the body through the fluoride water and they leave F^- free to pass further into the body.
2. F^- reacts with the concentrated HCl in the stomach to form the weak acid, HF.
3. This formed HF is then absorbed by the gastro-intestinal tract and passes into the liver ...
4. The HF is now free to pass into the blood stream and be distributed to all tissues including bones. Since elemental F is one of the strongest oxidizer, the anion F^- generally involves in metabolic oxidation reactions leads to formation of harmful biotransform.
5. Bones are largely composed of 'Ca' based compounds, particularly hydroxyapatite ($Ca_5(PO_4)_3OH$). The reaction of Ca^{2+} ions and HF forms an insoluble CaF_2

salt, this results calcium deficient hydroxyapatite. Finally, this weakens the strength of the bone.

6. The formed CaF_2 must be cleared by the body, otherwise it deposits between joints and gives pain because of non-lubrication.

Treatments for fluorosis patients:

- As of now, there are no established treatments for fluorosis patients.
- However, depending on the progression (process of developing) of the disease, i.e. in early stage, if fluorine intake is stopped, the fluorine existing in bone structures will deplete and be excreted via urine. However, it is a very slow process to eliminate the fluorine from the body completely. Minimal results are seen in patients.
- Further, treatment of side effects is also very difficult. For example, a patient with a bone fracture cannot be treated according to standard procedures, because the bone is very brittle. In this case, recovery will take a very long time moreover, healing cannot be guaranteed. *So prevention is better than cure.*

Defluoridation:

- Defluoridation is a process of removing the excess of fluoride from water.
- Generally, 60% of fluoride intake is only through drinking. The concentration of the fluorides in the body rises, due to the continuous consumption of fluoride contaminated water. This results several biological problems in humans. By considering these serious effects it is advised to take water free from fluorides.
- So, it is highly essential to have knowledge on defluoridation methods.

Steps to reduce fluoride exposure:

- Do not take fluoride supplements
- Read labels on bottled beverages – should not consume, unless they are made using distilled or reverse-osmosis water. Because, they are probably made with fluoridated water
- Consider to used unfluoridated toothpaste
- Avoid drinking black or red tea - There are many health benefits associated with chemical compounds found in tea. But this may be a beverage to avoid if one needs to reduce fluorine intake. Because, black and red tea come from two different types of plants, but both leaves naturally contain high amounts of fluoride content
- Be wary of tinned fish and canned food items – because, fluorides are used as preservatives.
- Avoid using chewing tobacco, which is rich with fluorides.
- Avoid long term use of medication that contains fluorine - Certain antidepressants

These do not remove Fluoride:

- Boiling Water - This will concentrate the fluoride rather than reduce it
- Freezing Water - Freezing water does not affect the concentration of fluoride. i.e. remains same .

Ways to Remove Fluoride from Water: The important ways are

- i. **Nalgonda Technique** employs flocculation principle. In this method Alum (hydrated aluminium salt) commonly used as coagulant agent to flocculate fluoride ions in the water. This method is simple and effective. No special skills are required, as result this method is in wide use.
- ii. **Bone Char** produced by carbonizing bone at a temperature of 1100-1600 °C used as defluoridating agent.
- iii. **Contact precipitation** is a technique by which fluoride is removed from the water through the addition of calcium and phosphate compounds and then brings the water in contact with an already saturated bone charcoal medium.
- iv. **Activated Alumina Defluoridation Filter** - They are relatively expensive and require frequent replacement, but it is an option for home water filtration.
- v. **Brick:** In this method, brick powder is applied as defluoridating agent. Fluoride contaminated water is passed through the long glass columns filled with brick powder. This heat treated soil acts as good fluoride removal.
- vi. **Reverse osmosis** is a water purification technology that uses a semipermeable membrane to remove ions, molecules, and larger particles from drinking water. RO will provide delicious and healthy drinking water. However, brackish water only used in reverse osmosis.

Comparison of merits and demerits of various Defluoridation methods:

S.No.	Method	Merits	Demerits	Estimated relative cost
1	Nalgonda Alum used as coagulant agent	❖ Low cost technology ❖ Adaptable for domestic use ❖ No skill required	• Large quantity of sludge • High chemical dose depend on F⁻ level • Daily addition of chemicals • Mechanical stirring	Low to medium
2	Bone Char Bone charcoal used as defluoridating agent.	❖ for Domestic use ❖ Local available media	• unhygienic due to the contamination of water with charcoal • Requires regeneration periodically • Effected by high alkalinity • Cultural and religious objections	Low to medium
3	Contact precipitation Ca and P compounds bring to contact with bone charcoal medium	❖ Low cost ❖ recommendable for domestic use	• Algae growth can occur in phosphate solution • Bone char used as a catalyst may not be acceptable in many countries	Low to medium

4	Activated Alumina activated Alumina filters are used	<ul style="list-style-type: none"> ❖ Effective for community scale and for domestic use ❖ High F removal 	<ul style="list-style-type: none"> • increase of Al^{+3} ions in water, this results anemia, hair loss and Alzheimer • Periodic regeneration • Required skilled persons for plant operation 	Medium to High
5	Brick powder is applied as defluoridating agent.	Low cost technology <small>Why we use glass column? It is just because glass doesn't leach F. But remaining materials absorb F.</small>	<ul style="list-style-type: none"> • Brick powder must be replaced from time to time • chance for breakage of columns 	Low to medium
6	Reverse osmosis: A semipermeable membrane used to remove fluorides in water	<ul style="list-style-type: none"> ❖ High fluoride removal ❖ Can remove other ions 	<ul style="list-style-type: none"> • High maintenance costs makes unaffordable for personal use. • requires skilled operation • originally designed for brackish water treatment 	Very High

Nalgonda method: The National Environment Engineering Research Institute (NEERI), in Nagpur, India has evolved an economical and simple method of defluoridation since 1961, which is referred to as the Nalgonda technique. This technique employs flocculation principle.

- Nalgonda Technique involves addition of aluminum salts (alum), lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection.
- Aluminium salt may be added as aluminum sulphate or aluminum chloride or combination of these two. Aluminum salt is only responsible for removal of fluoride from water. The dose of aluminium salt increases with increase in the fluoride and alkalinity levels of the raw water. The selection of either aluminum sulphate or aluminium chloride also depends on sulphate and chloride contents of the raw water to avoid them exceeding their permissible limits.
- **Note:** The amount of alum added must be carefully monitored, because the left over aluminum can cause significant health problems including neurological, cardiovascular, and respiratory problems.

This can be done based on the Freundlich equation, to obtain water with acceptable limit of fluoride.

$$A = \frac{(F_r - F_t) \times V}{m \times F_t^{1/n}}$$

A = amount of Alum to be added (grams)

V = volume of water to be treated in liters

F_r = fluoride concentration (mg/L) in raw water

m = sorption capacity constant

F_t = fluoride concentration (mg/L) in treated water

n = sorption intensity constant

(**m** = 6 and **n** = 1.33 under near neutral pH and concentrations of fluoride is 1.5 mg/L)

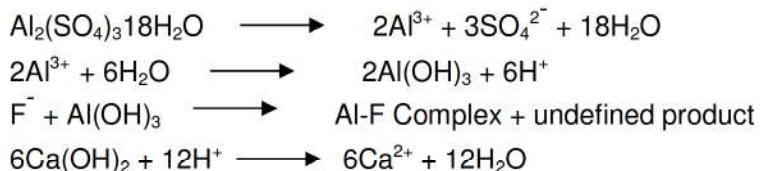
- Since this process is best carried under alkaline condition, lime $[Ca(OH)_2]$ is added. Further, lime facilitates forming dense floc. The dose of lime is empirically $1/20^{\text{th}}$ that of the dose of aluminum salt.
- For the disinfection purpose bleaching powder is added to the raw water at the rate of 3 mg/liter for disinfection.

Mechanism involved in Nalgonda technique: The following five stages occur in this technique. i) rapid Mix, ii) flocculation, iii) sedimentation, iv) filtration, v) disinfection and distribution

Rapid Mix: Provides thorough mixing of aluminium salts, lime and bleaching powder with the water for 1 minutes, continue stirring slowly for 5 minutes, and then let it allowed to settle for 1 hour.

Flocculation: The flocculation period permits close contact between the fluoride in water and polyalumemic species formed in the system.

- The chemical reaction involving fluorides and aluminium species is complex. Further, turbidity, colour, odour, pesticides and organics are also removed due to their adsorption on polymeric aluminium hydroxides (floc).
- Simultaneous disinfection is achieved with bleaching powder which also keeps the system free from undesirable biological growths.



Additionally, some of the fluoride is able to form precipitate with calcium.



Sedimentation: In sedimentation floc loaded with fluorides, turbidity, bacteria, and other impurities get settled down. This process helps to reduce the concentration of suspended solids that must be removed in filtration.

Filtration: Rapid gravity sand filters are used to remove coagulated and settled materials from water. Even sand bed can be used for filtration.

Disinfection and Distribution: The filtered water collected in the storage water tank is chlorinated with bleaching powder before distribution.

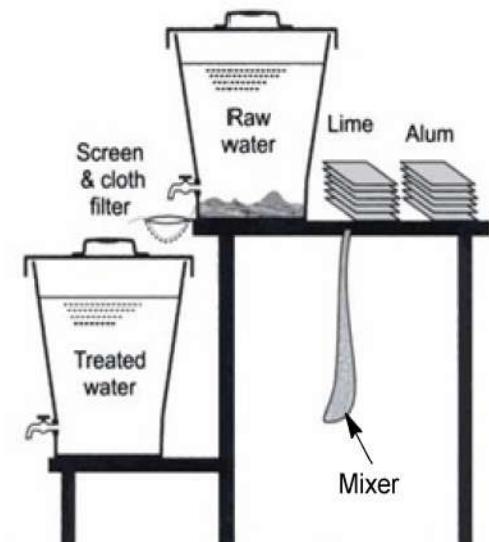
Limitations of Nalgonda technique:

- Nalgonda Technique not sufficient for the treatment of water with a fluoride concentration greater than 10 mg/L.
- Difficult to maintain alkalinity with the addition of lime.
- Sludge created needs to be properly disposed.
- The calculated quantity of alum must be added, in order to avoid significant health problems

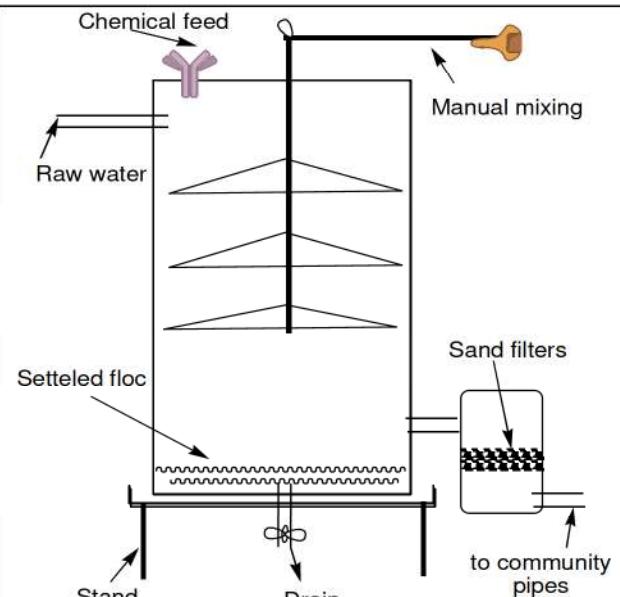
- Though often considered to be a cheaper defluoridation method available, it is not necessarily cheaper everywhere, particularly where necessary materials are not readily available, such as East Africa.

Salient features of Nalgonda technique

- Simplicity of design, construction, operation and maintenance
- Adaptable to domestic use and it can be easily scalable
- No handling of acids and alkalies.
- Simultaneous removal of colour, odour, turbidity, bacteria and organic contaminants.
- Little wastage of water and least disposal problems .
- This process can be used both for “domestic level” and “community level”.
 - i) **Domestic Level:** can be carried out in a bucket (container) of 60 liter capacity with a tap 3-5 cm above the bottom of the container for the withdrawal of water after precipitation and settling.
 - ii) **Community level:** this process can be scale up easily for community use. The raw water taken in the container is mixed with adequate amount of aluminiumsulphate (alum) solution, lime and bleaching powder depending upon its alkalinity and fluoride content. Then the water stirred slowly for 20 minutes and allowed to settle for nearly one hour. The settled sludge is discarded. Finally, water is filtered through sand filters and the obtained defloridated water supplied through community pipes.



Domestic defluoridation by Nalgonda technique



Apparatus for using Nalgonda Technique on community level from 1993

When to adopt Nalgonda technique?

- Absence of low fluoride water source within transportable distance.
- Raw water fluorides ranging should be not more than 10 mg/L.

- Total dissolved solids below 1500 mg/L
- Total hardness is below 600 mg/l.

Indian traditional defluoridation methods:

Tulsi (holy basil): Rajasthan University, India has discovered that the Tulsi plant can be used to significantly reduce the amount of fluoride in drinking water.

Tamarind seed powder: Fluoride contains water was passed over the Tamarind seed powder packed into a glass column, where major amount of Fluoride content will be removed from water.

Tea ash: The activated tea ash powder material was subjected to various physico-chemical parameters and used for sorption

EXERCISES

1. What is desalination? Name the different methods of desalination and describe any one.
2. What are boiler troubles? Why are they caused? What are the methods of their elimination?
3. Distinguish between:
 - (a) Temporary and permanent hardness. (b) Sludge and Scale. (c) Softening and demineralization.
4. Write notes on: (i) Caustic embrittlement, (ii) Reverse osmosis, (iii) Priming and foaming, (iv) Boiler corrosion
5. What is the principle involved in the determination of total hardness of water by EDTA method? (June-17)
6. Why does hard water consume more soap?
7. During deionization process, water is first passed through cation exchanger and then through anion exchanger, why?
8. Compare the merits and demerits of various defluoridation methods?
9. Explain Nalgonda method.
10. Engineer is asked to explore the suitability of SVEC ground water to startup a mine steam power plant in the college campus. Water sample is observed to contain the following CaCl_2 , NaCl , MgCO_3 , MgSO_4 , O_2 , HCl , SiO_2 and oil. Your answer should contain definition, disadvantages, reactions and removal methods for the predicted boiler operation troubles. (Dec-16)
11. "Reverse osmosis is advantages over ion-exchange process" Justify the statement. (June-17).
12. What is the principle of reverse osmosis? Explain the process of reverse osmosis. (June-17)
13. Rishika want to investigate the reason for unpredicted explosion at home boiler. After explosion the following deposits were found on analysis of boiler pieces. CaSO_4 , CaSiO_3 , MgSiO_3 , Fe_2O_3 , Mg(OH)_3 , Na_2FeO_2 , CaCO_3 . Looking at this data Rishika discussed about how boiler has suffered before explosion predicting the impurities present in water. Can you write the report discussing the attributes for explosion?
14. What are the water quality physical parameters? Explain their significance.

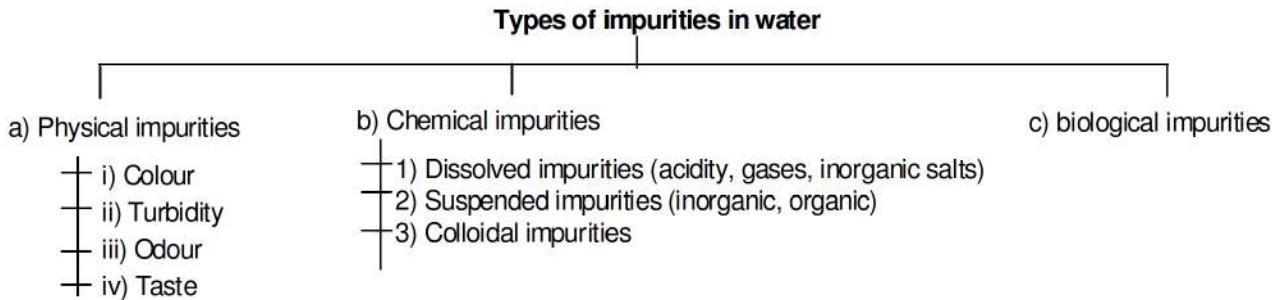
-
- 1) **This material gives you a basic information**
 - 2) **Refer text book for more details**

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Points to memorize

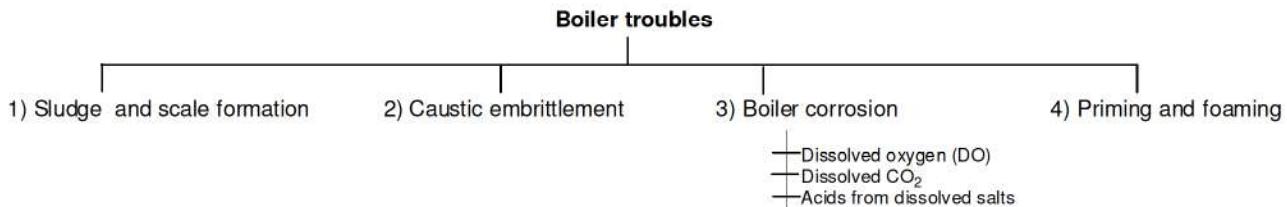
Source of water 1) Surface water 2) underground water

Types of impurities in water



Hardness of water- temporary and permanent hardness

Disadvantages of hard water i) *Effect on domestic uses* ii) *Effect on industries*



Requirements for boiler water	If not, it causes
Free from hardness causing salts	Sludge & scale
Free from dissolved salts (Na_2CO_3)	Caustic embrittlement
Free from dissolved gases (DO, CO_2), suspended salts	Boiler corrosion
Free from oil and greases	Foaming & Priming

Units of hardness

Problems on hardness (Refer class note book (or) text book)

Estimation of hardness by EDTA method

Softening of Water:

Internal treatment

External treatment: zeolite process, ion exchange process,

Desalination of Brackish water by Reverse osmosis.

Fluorides in water

Nalgonda technique

Comparison of merits and demerits of various Defluoridation methods

General information

Differences between Hard Water and Soft Water

S.No	Criteria	Hard Water	Soft Water
1	Definition	<ul style="list-style-type: none"> Water that has high mineral content is hard water Hard water does not produce lather with soap, but forms a white scum 	<ul style="list-style-type: none"> Water that has low mineral content is called soft water Soft water gives lather easily with soap
2	Dissolved Salt	Salt of Ca and Mg and other heavy metals are present	Does not contain such salts
3	Water of soap	Soap is wasted to get desired results	Does not waste
4	Cleansing quality of soap	It is depressed due to hardness and a lot of soap is wasted during washing and bathing	It is good in soft water has kit gives lather easily
5	Taste of water	It is usually better than soft water. The label or the better of mineral water shows that it contains Mg^{2+} and Ca^{2+} ions.	Less batter as ions like Ca^{2+} and Mg^{2+} are not present in soft water.
6	Strong tooth and bones	It helps in producing strong teeth and bones due to presence of Ca^{2+}	Does not help as such
7	Prevention of lead dissolution	Lead piping used for distribution of water in old house are coated with insoluble $CaCO_3$ present in hard water. This prevents any of the poisonous led dissolving in the drinking water.	Does not help as such
8	Elevation of boiling point of water	Due to the presence of dissolved salts the boiling point of water is elevated consequently more fuel and time are required for cooking. Moreover the dissolved salts are deposited as carbonates on the inner walls of the water heating materials.	Less time and fuel are required and no deposition of Calcium bicarbonates on the inner wall of heating materials
9	Effect health on	It causes bad effect on our digestive system moreover the possibility of forming the calcium oxalate crystals in urinary track is increased.	No such effect is observed
10	Effect steam generation in boilers	Direct use of hard water in boiler creates following troubles <ul style="list-style-type: none"> Scale and sludge formation Corrosion Caustic embrittlement 	No such effect is observed
11	Effect industries on	Shows bad effect on textile, Sugar, paper industries, etc.	No bad effects Moreover, soft water is used in these industries.