Module - II : Water and its treatment

→ **Sources of water**

1. Surface water
2. Underground water
3. Rain water

→ **Common impurities of water**

1. Dissolved impurities
2. Colloidal impurities
3. Suspended impurities

→ **Standards for drinking water**

Parameter	BIS standards	WHO standards
pH	6.5 - 8.5	6.5 - 8.5
Total Solids	500 - 1000	500
Total hardness	200 - 250	200

BIS - Beureau of Indian standards.

WHO - World Health Organisation.

chloride	200	150
fluoride	1.0 - 1.5	1.0

→ **Definition of Hardness**

Its defined as the characteristics of water that prevents lathering of soap. Hardness of water is due to presence of certain insoluble salts of calcium and Magnesium in water.

A sample of water when treated with soap (sodium salts of oleic, palmitic or stearic acids) doesn't form lather or foam but forms a white precipitate insted. This is because of the formation of insoluble salts of calcium and Magnesium.

Equ: $2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\ (ppt) + 2NaCl$

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* **Types of Hardness**

→ Temporary hardness :

Its also called carbonate or alkaline hardness. Due to the presence of bicarbonate, carbonate and hydroxide. Can be determined by titration with HCl using methyl orange as indicator.

Equ : $\boxed{Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow}$

Can be removed by boiling.

→ Permanent hardness :

Its also called non-carbonate or non-alkaline hardness. Due to the presence of dissolved chlorides, sulphates and nitrates of Calcium and Magnesium and other heavy metals. It cannot be removed by boiling but can be removed by lime-soda process, ion-exchange process or zeolite process.

* Degree of Hardness

[16 sept]

Hardness is always calculated in terms of equivalence of $CaCO_3$, based on :

i) Molecular weight is 100 and equivalent weight is 50.

ii) It is the most insoluble salt that can be precipitated in water treatment.

→ Calculation of Equivalents of $CaCO_3$

$$\text{Equivalents of } CaCO_3 = \frac{\text{Mass of Hardness producing Substance} \times 50}{\text{chemical equi. of hardness prod. substance}}$$

$$\text{Expression of Hardness of water} = \frac{\text{Mass of hardness producing substance} \times 100}{\text{M.W of hardness producing substance}}$$

→ Units of hardness of water and their interrelationship.

1. ppm
2. mg/lit
3. Cl° clarke degree
4. Fr° french degree

$$\boxed{1 \text{ ppm} = 1 \text{ mg/lit} = 0.07°\text{cl} = 0.1\ °\text{Fr}}$$

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* Disadvantages of hard water

1. For industries, if hard water is used, the salts present in water causes problems in sugar, paper, dyeing and pharmaceutical industryies.

2. Steam generation in boilers : The use of hard water in boilers causes problems like scale and sludge formation, boiler corrosion, caustic embrittlement, priming and foaming.

3. In domestic use :

a. Drinking - Hard water can have bad effect on our appetite and digestive system. Sometimes it produces calcium oxalate that causes different urinary problems.

b. Cooking - The BP of hard water increases because of the presence of various salts. This causes wastage of time and fuel.

c. Bathing and washing - As hard water does not form lather with soap, lot of water is wasted.

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* **Determination of hardness of water by complexcometric methods.**

The ethylene diamine tetracetic acid (EDTA) forms stable soluble complex with Ca^{+2} and Mg^{+2} ions in the pH 8 - 10 range.

EDTA is a chelating ligand and it acts as a hexadentate ligand coordinating through two Nitrogen atoms of amine group and four oxygen atoms of carboxylic acid with Ca^{+2} and Mg^{+2} ions at a pH of 8 - 10.

The structure of metal - EDTA complex is octahedral. To maintain the ~~buffer~~ pH of 8-10, ammonical buffer is added.

Even though EDTA contains 8 O atoms [7 OCT] and 2 Nitrogen atoms, it can not use its four Oxygen atoms of CO group for coordination due to steric effect.

To maintain pH 8-10, ammonical buffer is added.

Indicator is Eriochrome black -T, is metal-ion indicator. wine red to blue colour.

The indicator also forms complexes with metal ions at a pH of 8-10, However, indicator metal complex is less stable when compared to EDTA-metal complex.

$M^{2+} + EBT \rightarrow [M(EBT)_2]$ $(M = Ca \text{ or } Mg)$

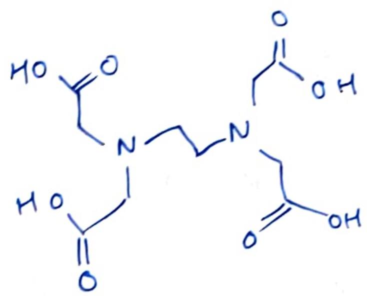
wine red colour

$[M(EBT)_2] + EDTA \rightarrow [M(EDTA)] + 2EBT$

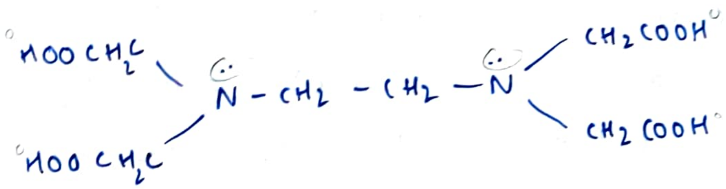
blue colour

This is the best method to determine the hardness. We can determine temperorg, permanent and total hardness of water.

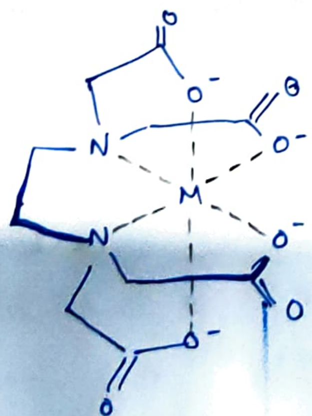
→ Structure of ethylene diamine tetracetic acid.



6 lone pairs are used in compound formation.

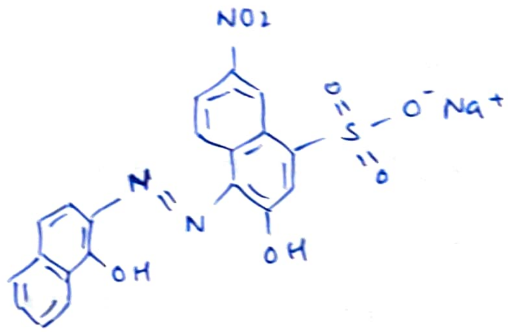


→ Structure of metal EDTA complex.



Hexadentate ligand EDTA forms a complex with the metal ion.

→ Structure of Erichrome black T inductor



* Molecular weight of hard salts

$Ca(HCO_3)_2$ = 162

$Mg(HCO_3)_2$ = 146

$MgCl_2$ = 95

$MgSO_4$ = 120

$CaCl_2$ = 111

$CaSO_4$ = 136

* Numericals on hardness of water.

1. one liter of water sample collected from a water source in Telangana has shown the following analysis. $Mg(HCO_3)_2$ = 14.6 mg, $MgSO_4$ = 12 mg, $Ca(HCO_3)_2$ = 16.2 mg, $CaCl_2$ = 22.2 mg, $MgCl_2$ = 9.5 mg and organic impurities = 100 mg. Calculate temporary and permanent hardness in degree french.

Sol Given data :

$Mg(HCO_3)_2$ = 14.6 mg

$MgSO_4$ = 12 mg

$Ca(HCO_3)_2$ = 16.2 mg

$CaCl_2$ = 22.2 mg

$MgCl_2$ = 9.5 mg

$$\text{Hardness of the hardness causing salt} = \frac{\text{Amount of the hardness causing salt in terms of } CaCO_3}{\text{M.W of hardness causing salt}} \times 100$$

$Mg(HCO_3)_2 = (14.6 / 146) \times 100 = 10$ ppm

$Ca(HCO_3)_2 = (16.2/162) \times 100 = 10$ ppm

$MgSO_4 = (12 / 120) \times 100 = 10$ ppm

$CaCl_2 = (22.2 / 111) \times 100 = 20$ ppm

$MgCl_2 = (9.5 / 95) \times 100 = 10$ ppm

Temporary Hardness $= Mg(HCO_3)_2 + Ca(HCO_3)_2 = 10 + 10 = 20$ ppm

Permanent hardness $= CaCl_2 + MgCl_2 + MgSO_4 = 20 + 10 + 10 = 40$ ppm.

Temporary hardness $= 20 \times 0.1 = 2\,°Fr$

permanent hardness $= 40 \times 0.1 = 4\,°Fr$

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2. one liter of water from Tirupati shows following analysis : Calc. temp and perm hardness. of 10,000 l of water.

$Mg(HCO_3)_2 = 42$ mg

$Ca(HCO_3)_2 = 146$ mg

$CaCl_2 = 71$ mg

$MgSO_4 = 48$ mg

$$\text{Hardness of the hardness causing salt} = \frac{\text{Amount of the hardness causing salt in terms of } CaCO_3}{\text{M.W of hardness causing salt}} \times 100$$

$Mg(HCO_3)_2 = (42 / 146) \times 100 = 28.76$ ppm

$Ca(HCO_3)_2 = (146 / 162) \times 100 = 90.12$ ppm

$CaCl_2 = (71 / 111) \times 100 = 63.96$ ppm

$MgSO_4 = (48 / 120) \times 100 = 40$ ppm

temp. hardness $= 28.76 + 90.12 = 118.88$ ppm permanent = 40 + 63.96 = 103.96 ppm

total = 118.88 + 103.96 = 222.84 ppm

Permanent hardness = 103.96 × 10000 = 10,39,600 ppm

temporary hardness = 118.88 × 10000 = 11,88,800 ppm

total hardness = 222.84 × 10000 = 22,28,400 ppm

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3. A sample of hard water contains following /L.

$Mg(HCO_3)_2$ = 14.6 mg

$Ca(HCO_3)_2$ = 16.2 mg

$CaCl_2$ = 111 mg

$CaSO_4$ = 1.36 mg

Silica = 40 mg

Turbidity = 10 mg

Calc. temp, perm and total hardness in ppm, °Cl and °Fr.

$Mg(HCO_3)_2$ = (14.6 / 146) × 100 = 10 ppm

$Ca(HCO_3)_2$ = (16.2 / 162) × 100 = 10 ppm

$CaCl_2$ = (111 / 111) × 100 = 100 ppm

$CaSO_4$ = (1.36 / 136) × 100 = 1 ppm

perm hardness = 100 + 1 = 101 ppm = 10.1 °Fr = 7.07 °Cl

temp hardness = 10 + 10 = 20 ppm = 2 °Fr = 1.40 °Cl

total hardness = 101 + 20 = 121 ppm = 8.47 °Cl

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4. Calculate temp and perm hardness of a water sample which contains :

$CaSO_4$ = 6.8 mg

$CaCl_2$ = 33 mg

$MgCl_2$ = 40 mg

$MgSO_4$ = 24 mg

$CaSO_4$ = (6.8 / 136) × 100 = 5 mg

$CaCl_2$ = (33 / 111) × 100 = 29.72 mg

$MgCl_2$ = (40 / 95) × 100 = 42.10 ppm

$MgSO_4$ = (24 / 120) × 100 = 20 ppm

temporary hardness = 0 mg = 0 ppm

permanent hardness = 20 + 42.1 + 29.72 + 5 = 96.82 ppm

5\. A sample of water of 100 ml required 12.6 ml of 0.02 M EDTA solution with EBT as indicator and 8.4 ml of 0.02 M EDTA for the same volume of water after removing the carbonate hardness. Calculate the total, permanent hardness in terms of calcium carbonate equivalents.

Sol: Given for 100 ml of sample → 12.6 ml of 0.02 M EDTA.

Then, $M_1V_1 = M_2V_2$

$M_1 = M_2V_2 / V_1$

$= 0.02 \times 12.6 / 100$

$= 0.00252$ M

Again, given for 100 ml of sample → 8.4 ml of 0.02 M EDTA after removing carbonate hardness

then, $M_3V_3 = M_2V_2$

$M_3 = M_2V_2 / V_3$

$M_3 = 0.02 \times \cancel{12.6}\ 8.4 / 100$

$= 0.00168$ M

Now, total hardness is, $M_1 \times 100 \times 1000$

$= 0.00252 \times 100 \times 1000$

$= 252$ ppm

Permanent hardness $= M_3 \times 100 \times 1000$

$= 0.00168 \times 100 \times 1000$

$= 168$ ppm

temporary hardness = total − perm = 252 − 168 = 84 ppm

6. A sample of water of 20 ml required 17.2 ml of 0.01 M EDTA solution with EBT as indicator and 4.6 ml of 0.01 M EDTA for the same volume after the removal of carbonate hardness. Calculate the total, permanent and temporary hardness in terms of calcium carbonate equivalents

Sol: Given 20 ml sample → 18.2 ml of 0.01 M EDTA

$M_1 V_1 = M_2 V_2$

$M_1 = M_2 V_2 / V_1$

$M_1 = 0.01 \times 18.2 / 20$

$M_1 = 0.0091$ M

Again, given 20 ml sample → 4.6 ml of 0.01 M EDTA

$M_3 = M_2 V_2 / V_3$

$= 0.01 \times 4.6 / 20$

$= 0.0023$ M

total hardness

$= M_1 \times 100 \times 1000$

$= 0.0091 \times 100 \times 1000$

$= 910$ ppm

Permanent hardness

$= M_3 \times 100 \times 1000$

$= 0.0023 \times 100 \times 1000$

$= 230$ ppm

temporary hardness $= 910 - 230 = 680$ ppm

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7. A sample water of 20 ml required 22.5 ml of 0.02 M EDTA sol. with EBT indicator and 14.5 ml of 0.02 M EDTA for the sam volue after removing carbonate hardness. Calc. the total, temp and perm.

Sol: Given 20 ml sample → 22.5 ml of 0.02 M EDTA

$M_1 V_1 = M_2 V_2$

$M_1 = M_2 V_2 / V_1$

$M_1 = 0.02 \times 22.5 / 20$

$= 0.0225$

Again, given 20ml sample → 14.5 ml of 0.02 M

$M_3 V_3 = M_2 V_2$

$M_3 = M_2 V_2 / M_3$

$M_3 = 14.\cancel{8} \times 0.02 / 20$

$= \cancel{5.8} \quad 0.0145$

total hardness
$= M_1 \times 100 \times 1000$
$= 0.0225 \times 100 \times 1000$
$= 2250$ ppm

Permanent hardness
$= M_3 \times 100 \times 1000$
$= \cancel{5.8} \times 100 \times 1000$
$= \cancel{5,80,000}$ 1450 ppm

temporary = 2250 − 1450 = 800 ppm

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* Portable water

Common requirements for portable water is :

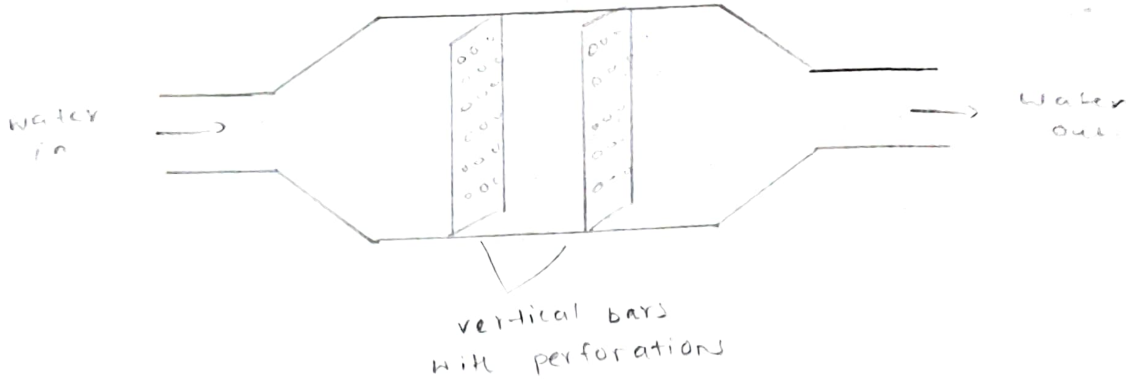
- should be clear, colourless
- should be odourless
- should be soft
- should be abundant and cheap
- organism and disease causing bacteria shouldn't be present.
- The dissolved oxygen should be 5−7 ppm.

→ Water treatment for domestic use employs following steps :

1. Screening

It is used to remove suspended impurities by passing water through screens having large number of holes when the floating matter is retained by them.

Screens are vertical bars with perforations. Water is passed through them where the suspended and floating impurities are removed.



2. Segmentation

Process of removing fine, suspended colloidal impurities by allowing water to stand undisturbed in a 5m deep big tank.
Most particles settle down at the bottom by gravitational force. The clear water is then drawn from the tank with pumps.
The retention period in a segmentation tank ranges from 2 - 6 hrs.
Fine suspended particles like mud particles & colloidal mater present in the water cannot settle by plain segmentation.

→ **Sedimentation with coagulation**

Coagulants, when added to water, form an insoluble gelatinous flocculent precipitate which trap the very fine suspended impurities forming bigger flocs, which settle down.

Coagulants used are : alum, ferrous sulphate, sodium aluminate etc.

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

$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

3. Filteration

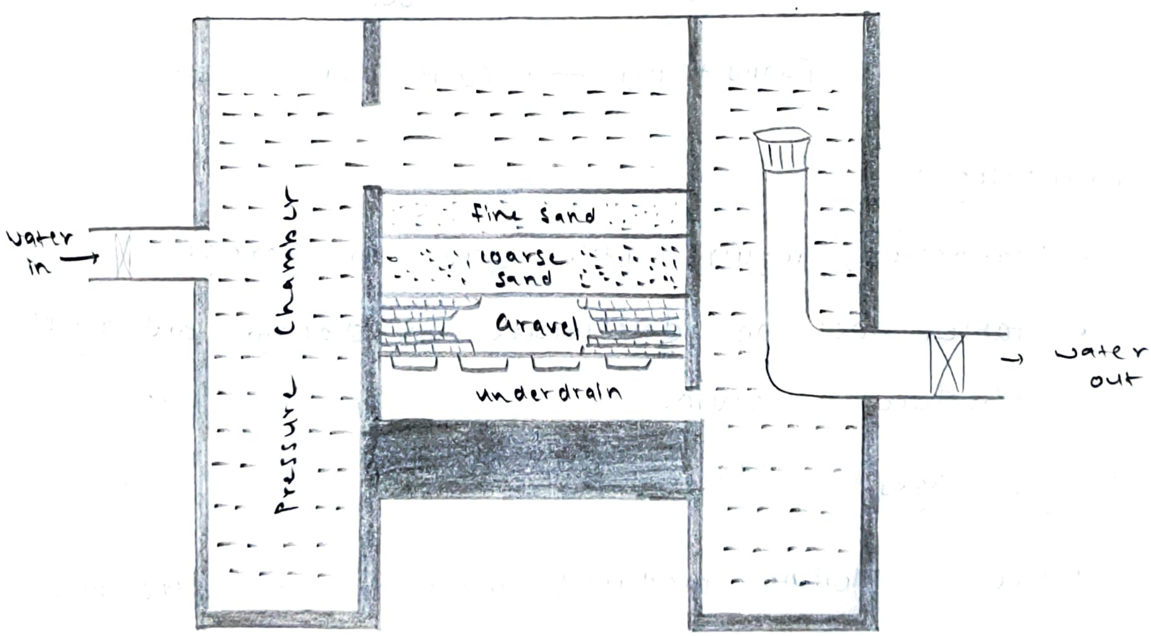
It is the process of separating colloidal and suspended impurities from water by passing it through a porous bed made of fine sand and other proper sized granular materials.

Filteration is carried out in a sand filter. It consists of a top thick layer of fine sand, placed over coarse sand layer followed by gravel.

Water comes from the top. The suspended particles present in water are of bigger size than the voids in the sand layer are retained itself and water becomes free of them.

The sand layer maye get choked after sometime and then it is to be replaced with clean sand for further action.

Advantages : Removes all suspended particles, colloidal impurities and organic matter.



4. Disinfection

[9 oct]

It is the process of removing pathogenic bacteria, viruses and protozoa. from water. There are several methods to achieve this :

- Boiling
- By adding bleaching powder
- By direct chlorination
- By adding chloramines
- Ozonization
- By adding $KMnO_4$

→ **Direct chlorination**

Chlorine, in either gas or concentrated solution form, produces hypochlorous acid which is a powerful germicide.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$HOCl \rightarrow H^+ + OCl^-$$

$$\text{Germs} + OCl^- \rightarrow \text{Germs are killed}$$

Advantages

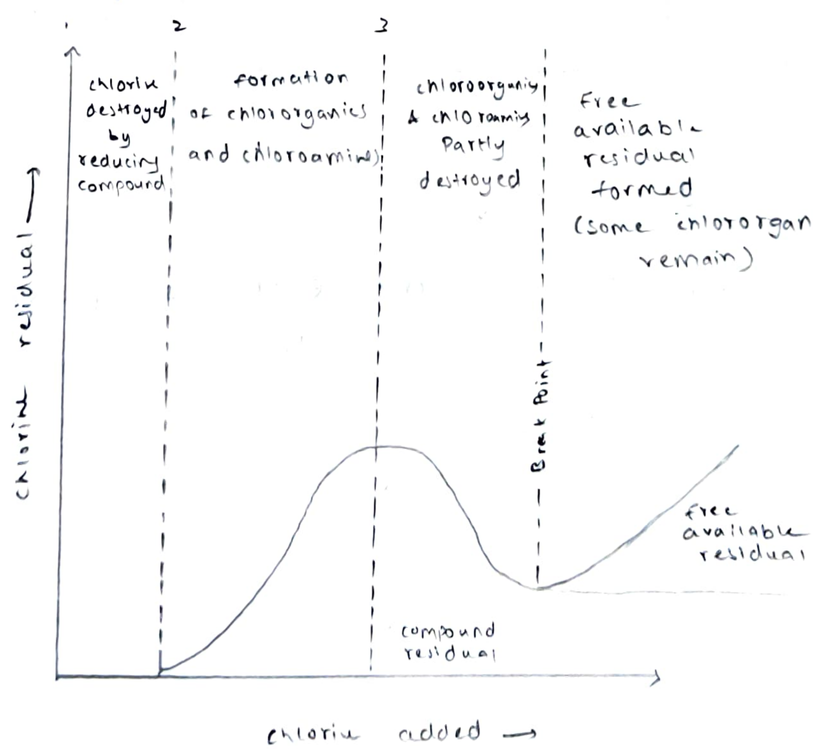
- Economical, require little space for storage
- Stable does not deteriorate on storage and doesn't introduce calcium.

Disadvantages

- Excess chlorine produces upleasant taste and odor.
- Excess produces irritation on mucous membrane.

→ Break point chlorination

- It is a controlled process, in which suitable amount of chlorine is added to water, in order to kill all the bacteria present in the water. It oxidizes the entire organic matter and reacts with free ammonia when the chlorine required is appropriate.
- Break-point determines wether the chlorine is further added or not. By chlorination, organic matter and disease producing bacteria are completely eliminated which are responsible for bad taste and bad odour in water. When certain amount of chlorine is added to the water, it leads to the formation of chloro-organic compounds and chloramines.
- The point at which free residual chlorine begins to appear is termed as "Break-point".



→ Ozonization

- Ozone is produced by passing silent electric discharge through cold and dry oxygen.

$$3O_2 \longrightarrow 2O_3$$

- Ozone is highly unstable and breaks down liberating nascent oxygen.

$$O_3 \rightarrow O_2 + O \text{ (Nascent oxygen)}$$

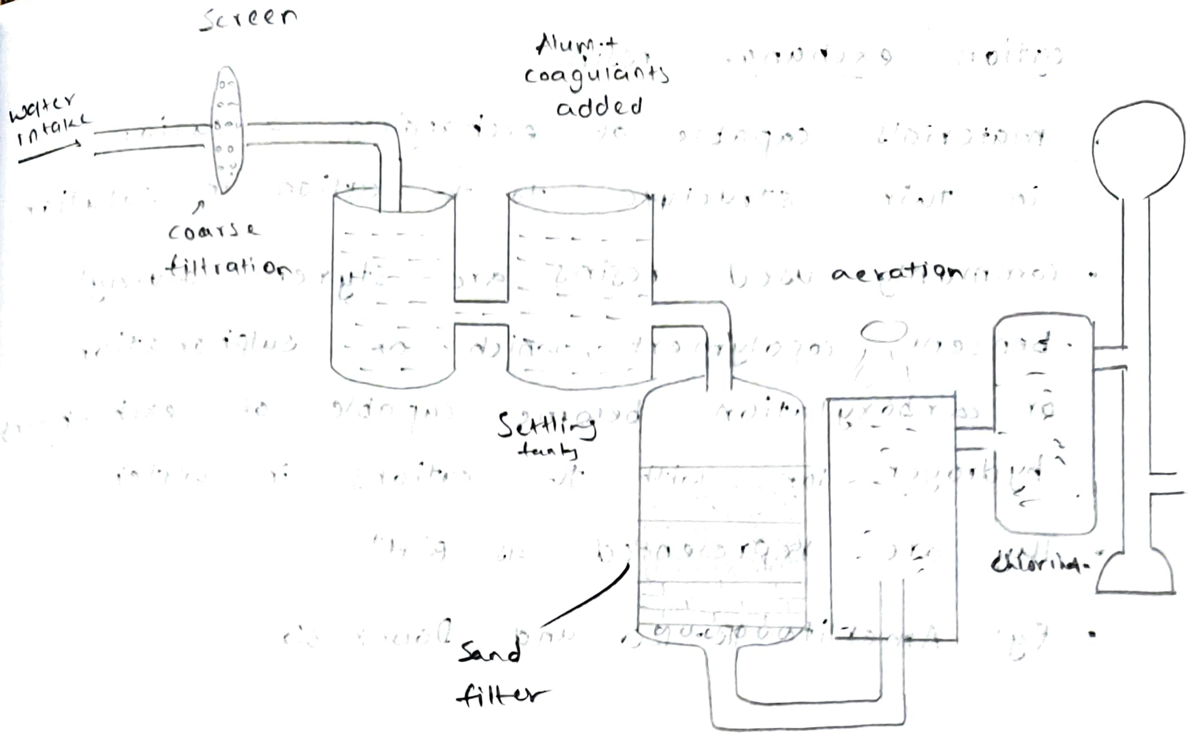
- Nascent oxygen is a powerful oxidizing agent and kills all the bacteria as well as oxidizes the organic matter present in water.
- The contact period is about 10 - 15 mins and dose is 2-3ppm

Advantages

- Ozone sterilizes, bleaches, deodorizes and decolorizes water.
- Excess of ozone in water is not harmful as it decomposes to give oxygen.
- Ozone improves the taste of water. Highly portable water is thus sterilized with ozone.

Disadvantages

- Ozonization is a very expensive process. Ozone is also corrosive agent. It corrodes stainless steel, cast iron, copper and rubber.



* Water softening methods [10 oct]

→ Internal methods - conditioning in the boiler itself.
→ External methods - treatment before entry in boiler.

The process of removal of hardness causing salts from the sample of water.

External Treatment methods

1. Ion-exchange / Deionization / Demineralization :

- Defined as the reversible exchange of ions in the structure of an ion exchanger to ions in solution that is brought in contact with it.
- The resin used for the purpose are called ion exchange resins. They are porous, insoluble, cross linked, long chain organic polymers capable of exchangiong ions.

cation exchange resin

- materials capable of exchanging a cation in their structure to the cation in solution.
- commonly used resins are styrene divinyl benzene copolymers, which on sulphonation or carboxylation become capable of exchanging hydrogen ion with the cations in water.
- They are represented as R^-H^+
- Eg: Amerlite IR-120 and Dowex 50

Anion exchange resin

- These materials are capable of exchanging an anion (OH^-) in their structure, to anion in solution.
- Aion exchangers employed for water softening are styrene divinyl benzene or amine formaldehyde copolymers which contain basic functional group as amino.
- They are represented as R^+OH^-
- Eg: Amberlite 400 and Dowex-3

→ Process [11 oct]

The hard water is passed through a column containing cation exchange resin.

All cations are removed and equivalent amount of H^+ ions are released from this column to water.

water coming out of this chamber has low pH.

$$2RH + Ca^{2+} \rightarrow R_2Ca + 2H^+$$

$$2RH + Mg^{2+} \rightarrow R_2Mg + 2H^+$$

Then the water is passed into second column containing anion exchange.
All the anions are removed and an equivalent amount of OH^- ions are released.

$$ROH + Cl^- \rightarrow RCl + OH^-$$

The H+ ions released from cation exchange column and OH^- ions released from anion exchange column combine to produce water molecules. The water coming out of the exchanger is free from all cations and anions. The ion free water is known as deionized water or demineralized water.

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

→ Regeneration

After some time the resin loses all their H^+ and OH^- ions and then their capacity to exchange ions is lost.
In such a condition, the resins are said to be exhausted.
The exhausted cation exchange resin is regenerated by passing a dilute solution of HCl.

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

The anion exchange resin is regenerated by passing a dilute solution of NaOH. ~~and~~

$$RCl + NaOH \rightarrow ROH + NaCl$$

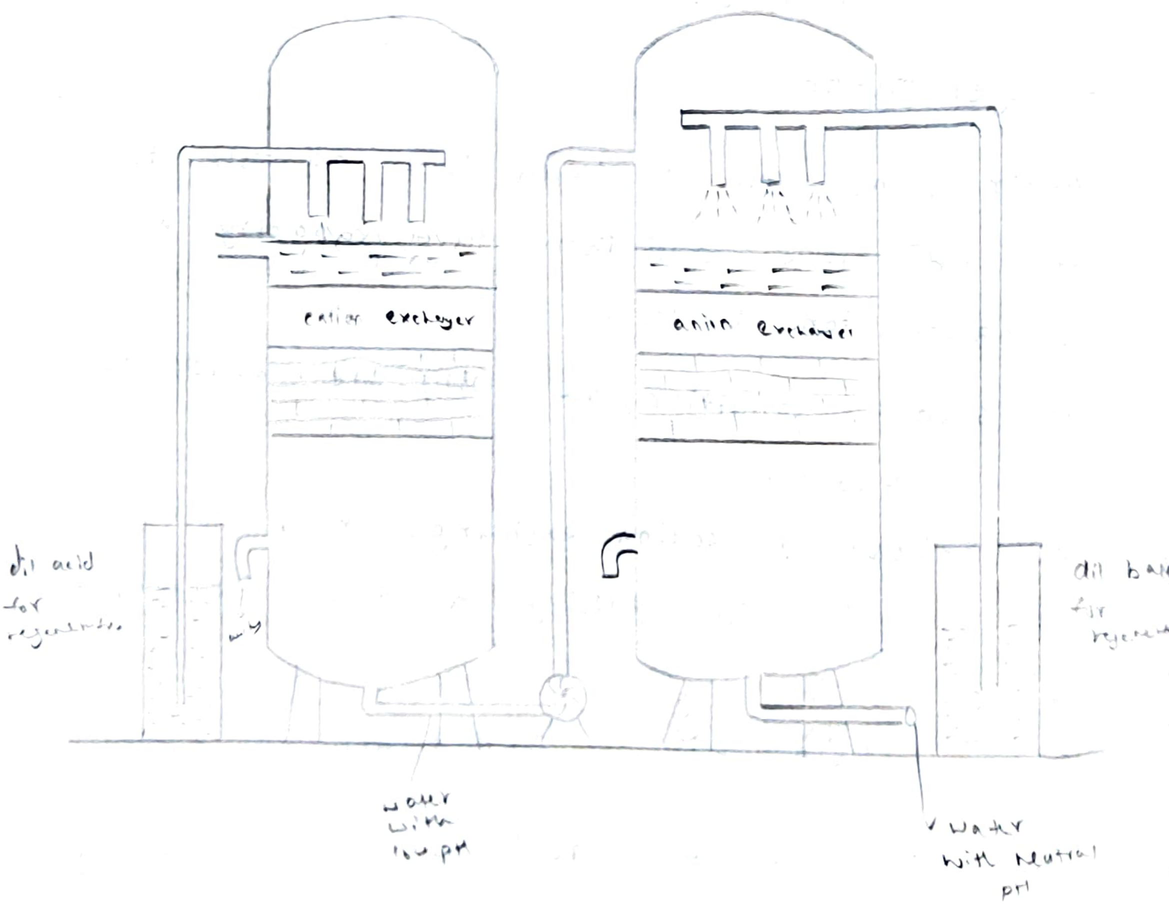
The salts formed are removed by washing with distilled water.

→ **Advantages**

- The process produces water of very low residual hardness (about 2 ppm).
- The process can be used to soften highly acidic or alkaline water.
- It removes all cations and anions.

→ **Disadvantages**

- The process is expensive, both the equipment and resin are costly.
- Turbid water decreases the efficiency of the process.



Q. 1 gm of $CaCO_3$ was dissolved in HCl and th Soln. was made upto 1 litre with distilled water, 50 ml of th above solution required 30 ml of EDTA soln on titration. 50 ml of hard water sample require 40 ml of th same soln of EDTA for titration 50 ml of hard water boiling, filtering etc. required 30 ml of th same EDTA soln for titration. Calculate th temporary hardness of th water.

Sol 1 gm $CaCO_3$ → suitable HCl make up 1 litre

$$(M_1) = \frac{wt}{G.M.wt} \times \frac{1000}{V} = \frac{1}{100} \times \frac{1000}{1000} = 0.01\,M$$

Titration ① ⇒

$$\underset{\text{water}}{M_1V_1} = \underset{\text{EDTA}}{M_2V_2}$$

$$0.01 \times 50 = M_2 \times 30$$

$$M_2 = \frac{0.01 \times 50}{30}$$

$$M_2 = 0.0167\,M$$

Titration ② ⇒

$$\underset{\text{Hard water}}{M_3V_3} = \underset{\text{EDTA}}{M_2V_2}$$

$$M_3 \times 50 = 0.0167 \times 40$$

$$M_3 = \frac{0.0167 \times 40}{50}$$

$$M_3 = 0.0133\,M$$

Total molarity $(M_3) = 0.0133\,M$

Total hardness $(M_3 \times 10^5) = 0.0133 \times 100 \times 1000$

$= 1330\,ppm$

Titration ③ ⇒ Boiled hard water EDTA

$$M_4 V_4 = M_2 V_2$$

$$M_4 \times 50 = 0.0167 \times 30$$

$$M_4 = \frac{0.0167 \times 30}{50}$$

$$M_4 = 0.0100\ M$$

Permanent molarity (M_4) = 0.0100 M

Permanent hardness $= M_4 \times 100 \times 1000$

$= 0.0100 \times 100 \times 1000$

$= 1000$ ppm

Temperory hardness = total - permanent hardness

$= 1330 - 1000$

$= 330$ ppm.