

Unit-1

Water



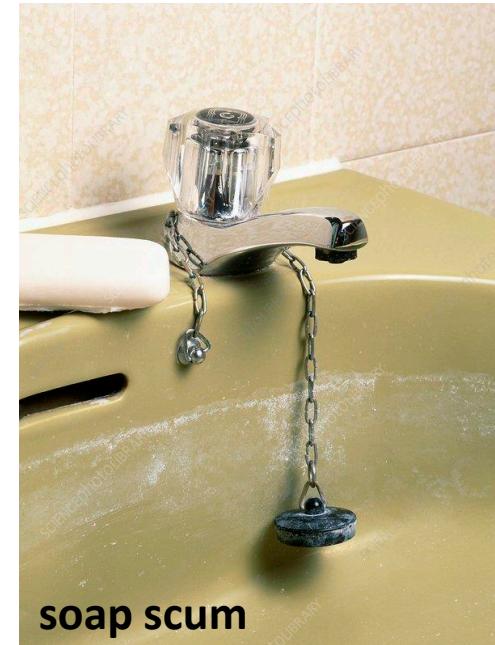
Topics: Structure of water, physical and chemical properties, Hydrogen bonding, Specifications for water in industries, types of water (raw water, cooling water, boiler water, nuclear water), Hardness of water, Estimation and units of Hardness, Boiler feed water, Boiler Problems - Scales & Sludge, Priming, Foaming, Carryover, Caustic Embrittlement, Boiler corrosion, Desalination. Water softening (lime-soda, zeolite and ion-exchange) methods.

Hardness of water

- Hardness of water is the characteristic of preventing lather formation of water with soap. Generally salts like chlorides, bicarbonates and sulfates of Ca^{2+} , Mg^{2+} and Fe^{2+} make water hard.
- This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.

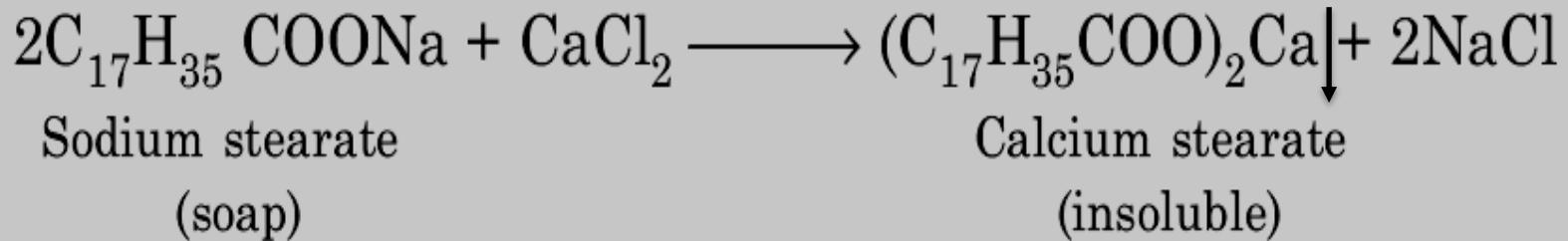
Hardness Scale

mg/L \& ppm CaCO_3	Classification
Less than 17.1	Soft
17.1 - 60	Slightly Hard
60 - 120	Moderately Hard
120 - 180	Hard
over 180	Very Hard



Hardness of water

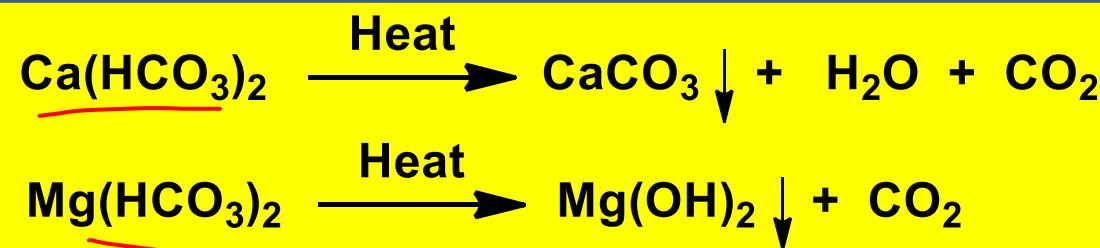
- Hardness of water is the characteristic of preventing lather formation of water with soap. Generally salts like chlorides, bicarbonates and sulfates of Ca^{2+} , Mg^{2+} and Fe^{2+} make water hard.
 - This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.



- Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

Types of Hardness

- o Hardness of water is due to dissolved salts of mainly calcium and magnesium as well as iron and other heavy metals.
- o Hardness is two types:
 - a) **Temporary :**
 - Due to dissolved **bicarbonates** of calcium and magnesium and carbonates of iron and other heavy metals. Hence it is also called as carbonate hardness.
 - Can be easily removed by boiling where CO_2 gas gets expelled removing the hardness.



b) Permanent:

- Due to dissolved **chlorides** (Cl^-) and **sulphates** (SO_4^{2-}) of calcium and magnesium. Also called as non-carbonate hardness.
- Can be removed through zeolite, Lime-soda, ion-exchange processes.

Measurement of hardness of water

- Hardness of water is measured in **parts per millions** (ppm.) as **calcium carbonate (CaCO_3) equivalents**.
- Reasons for expressing hardness in CaCO_3 equivalents:
 - its molecular weight is **100** ; equivalent weight(atomic weight/ valency) is 50.
- - it is the most common insoluble impurity in water.
- Units of hardness:
 - **parts per million in CaCO_3 equivalents** (1 mg/L is 1 ppm.).
- When expressed in CaCO_3 equivalents, the formula for conversion is:

$$\frac{\text{mass of hardness causing substance}}{\text{Mol. wt of hardness causing substance}} \times 100$$

Example: if 146 mg/L of MgSO_4 is present in water, calculate the total hardness of the water. (atomic weight of Mg = 24, Ca = 40, O = 16 and S = 32)

Examples of hardness calculations

A sample hard water contains,

8.1 mg/L $\text{Ca}(\text{HCO}_3)_2$; 7.5 mg/L $\text{Mg}(\text{HCO}_3)_2$; 13.6 mg/L CaSO_4 ;
12.0 mg/L MgSO_4 and 2.0 mg/L MgCl_2 .

To calculate the hardness and express in CaCO_3 equivalents:

Constituent	Multiplication factor	CaCO_3 equivalents
$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/L}$	$100/162$	$8.1 \times 100/162 = 5.0 \text{ mg/L}$
$\text{Mg}(\text{HCO}_3)_2 = 7.5 \text{ mg/L}$	$100/146$	$7.5 \times 100/146 = 5.14 \text{ mg/L}$
$\text{CaSO}_4 = 13.6 \text{ mg/L}$	$100/136$	$13.6 \times 100/136 = 5.0 \text{ mg/L}$
$\text{MgSO}_4 = 12.0 \text{ mg/L}$	$100/120$	$12.0 \times 100/120 = 10.0 \text{ mg/L}$
$\text{MgCl}_2 = 2.0 \text{ mg/L}$	$100/95$	$2.0 \times 100/95 = 2.11 \text{ mg/L}$

**Q1. Calculate the temporary hardness and permanent hardness of a sample water containing $Mg(HCO_3)_2 = 7.3$ mg/L; $Ca(HCO_3)_2 = 16.2$ mg/L; $MgCl_2 = 9.5$ mg/L; $CaSO_4 = 13.6$ mg/L
(atomic weight of Mg = 24, Ca = 40, Cl = 35.45 and S = 32)**

**Q1. Calculate the temporary hardness and permanent hardness of a sample water containing $Mg(HCO_3)_2 = 7.3 \text{ mg/L}$; $Ca(HCO_3)_2 = 16.2 \text{ mg/L}$; $MgCl_2 = 9.5 \text{ mg/L}$; $CaSO_4 = 13.6 \text{ mg/L}$
(atomic weight of Mg = 24, Ca = 40, Cl = 35.45 and S = 32)**

Solution: Conversion into $CaCO_3$ equivalent

Constituent	Molecular Weight	$CaCO_3$ equivalent
$Mg(HCO_3)_2 = 7.3 \text{ mg/L}$	146	5 mg/L
$Ca(HCO_3)_2 = 16.2 \text{ mg/L}$	162	10 mg/L
$MgCl_2 = 9.5 \text{ mg/L}$	95	10 mg/L
$CaSO_4 = 13.6 \text{ mg/L}$	136	10 mg/L

- ✓ Temporary hardness is due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$
 $= (5 + 10) \text{ mg/L} = \underline{15 \text{ mg/L or } 15 \text{ ppm}}$
- ✓ Permanent hardness, due to $MgCl_2$ and $CaSO_4$
 $= (10 + 10) \text{ mg/L} = \underline{20 \text{ mg/L or } 20 \text{ ppm}}$
- ✓ Total hardness = Temporary hardness + Permanent hardness
 $= \underline{35 \text{ mg/L or } 35 \text{ ppm}}$

- Calculate the temporary hardness and total hardness of a sample water containing $Mg(HCO_3)_2 = 73 \text{ mg/L}$; $Ca(HCO_3)_2 = 162 \text{ mg/L}$; $MgCl_2 = 95 \text{ mg/L}$; $CaSO_4 = 136 \text{ mg/L}$ (atomic weight of Mg = 24, Ca = 40, Cl = 35.45 and S = 32)
- A sample hard water contains, 8.1 mg/L $Ca(HCO_3)_2$; 7.5 mg/L $Mg(HCO_3)_2$; 13.6 mg/L $CaSO_4$; 12.0 mg/L $MgSO_4$ and 2.0 mg/L $MgCl_2$. Calculate the hardness and express in $CaCO_3$ equivalents
- How many grams of $FeSO_4$ dissolved per litter gives 210.5 ppm of hardness? (Atomic weights: Fe = 56, S = 32, O = 16, Ca = 40, C = 12)

- Calculate the temporary hardness and total hardness of a sample water containing $Mg(HCO_3)_2 = 73 \text{ mg/L}$; $Ca(HCO_3)_2 = 162 \text{ mg/L}$; $MgCl_2 = 95 \text{ mg/L}$; $CaSO_4 = 136 \text{ mg/L}$ (atomic weight of Mg = 24, Ca = 40, Cl = 35.45 and S = 32)
- A sample hard water contains, 8.1 mg/L $Ca(HCO_3)_2$; 7.5 mg/L $Mg(HCO_3)_2$; 13.6 mg/L $CaSO_4$; 12.0 mg/L $MgSO_4$ and 2.0 mg/L $MgCl_2$. Calculate the hardness and express in $CaCO_3$ equivalents
- How many grams of $FeSO_4$ dissolved per liter gives 210.5 ppm of hardness? (Atomic weights: Fe = 56, S = 32, O = 16, Ca = 40, C = 12)

Solution:

$FeSO_4$ (56 + 32 + 64 = 152g)	$CaCO_3$ 100g
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100 ppm of hardness is given by 152 ppm of $FeSO_4$

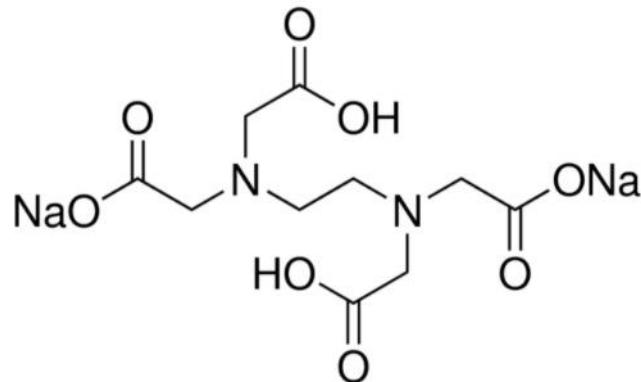
To give 210.5 ppm of hardness, $\frac{152 \times 210.5}{100} = 319.9 \text{ ppm of } FeSO_4$
 $= 319.9 \text{ mg/L or } 0.319 \text{ g/L of } FeSO_4$ is needed.

Estimation of water hardness

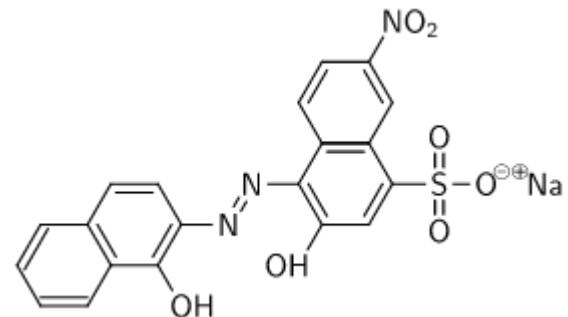
EDTA method:

- Ethylene diamine tetraacetic acid disodium salt (EDTA disodium salt) is used as a strong complexing agent with Ca^{2+} and Mg^{2+} in hard water.

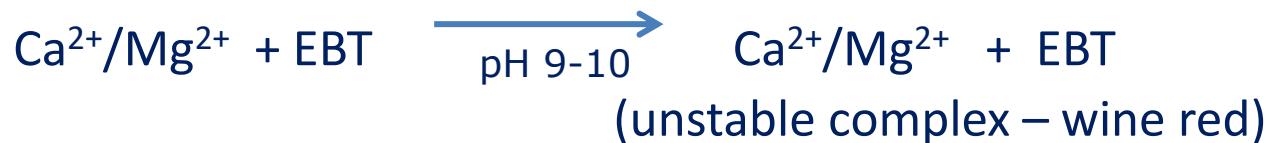
The structure of EDTA disodium salt is:



EBT indicator



- Initially, Ca^{2+} and Mg^{2+} are treated with Eriochrome Black T (EBT) indicator using ammonia buffer (to maintain pH between 9-10) to get an unstable complex of Ca^{2+} and Mg^{2+} formed with EBT.

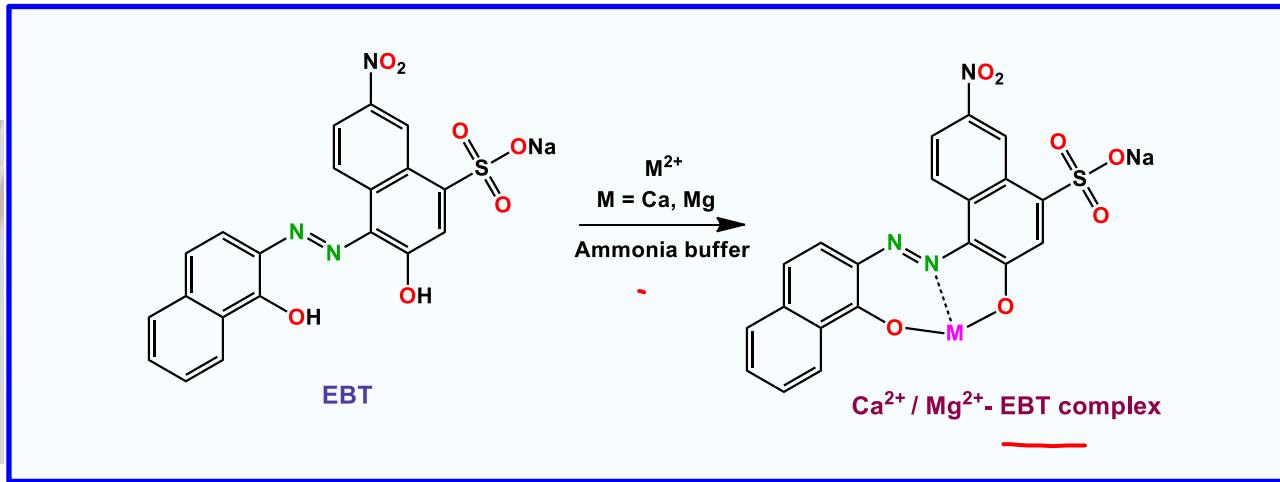


Wine red

Estimation of water hardness

EDTA method:

- Ethylene diamine tetraacetic acid disodium salt (EDTA disodium salt) is used as a strong complexing agent with Ca^{2+} and Mg^{2+} in hard water.



steel blue

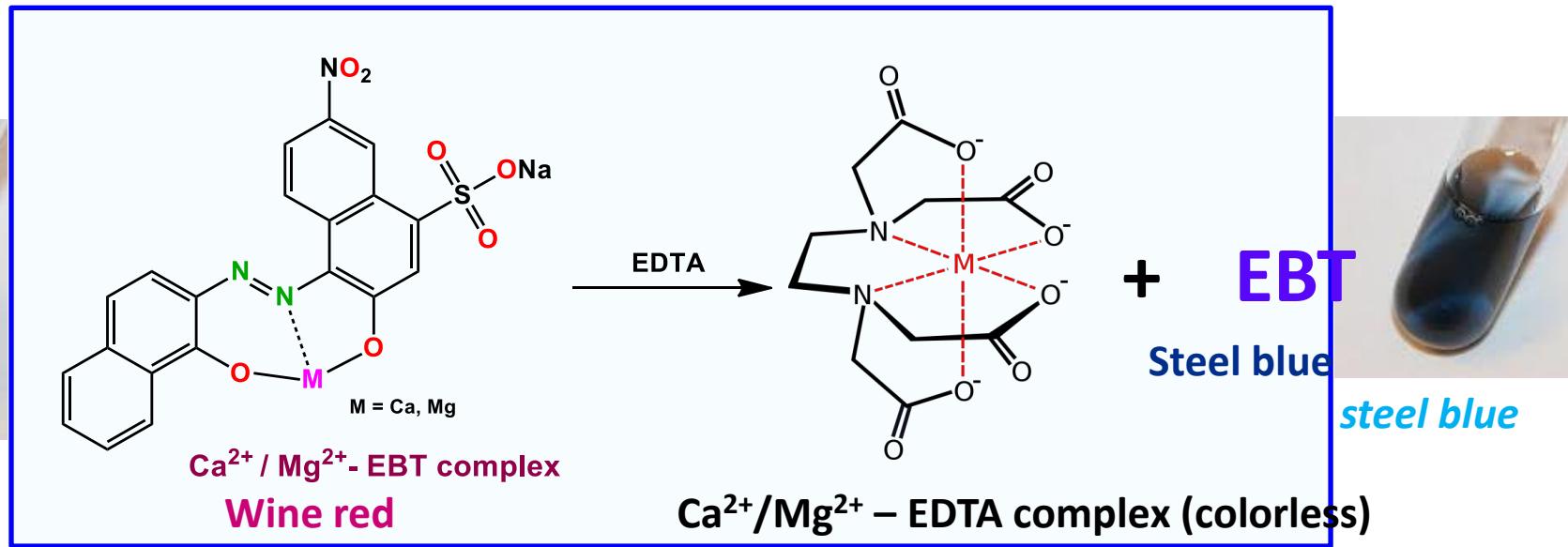
wine red

- EBT is blue in a buffered solution at pH 10,
- Turns red when Ca^{2+} or Mg^{2+} ions were added

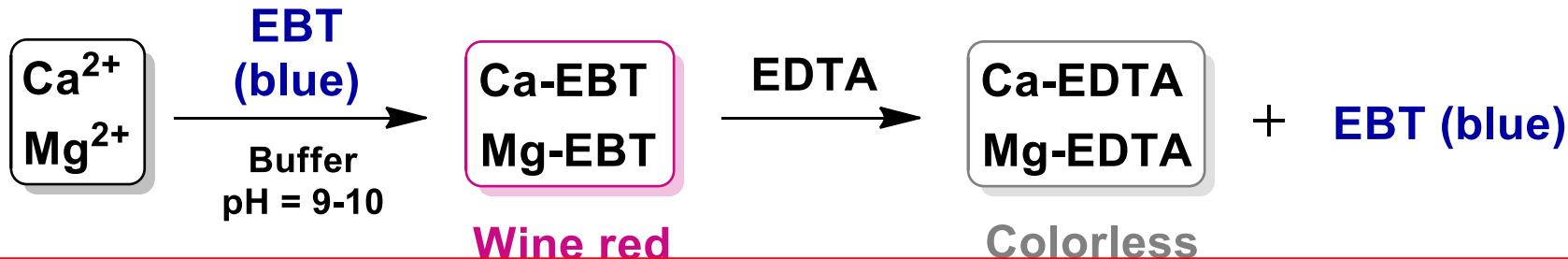
Estimation of water hardness

EDTA method:

- On addition of EDTA, EBT gets replaced by EDTA since EDTA forms a stronger complex with the metal ions



Overall process



Procedure

- o First EDTA Solution is standardized using standard hard water (1 mg/mL of CaCO_3 equivalents is prepared as standard hard water).
- o For this, first known aliquot of Standard hard water is taken, and 50 mL of ammonia buffer is added to bring the pH between 9-10.
- o Then a few drops of EBT solution is added to form the unstable complex giving wine red colour.
- o This solution is titrated with the EDTA solution till the solution turns to steel blue indicating the formation of stable EDTA-Metal ion complex.
- o This volume of EDTA is noted as V_1 .
- o The above procedure is repeated with sample hard water of unknown hardness.
- o Volume of EDTA is noted as V_2 .

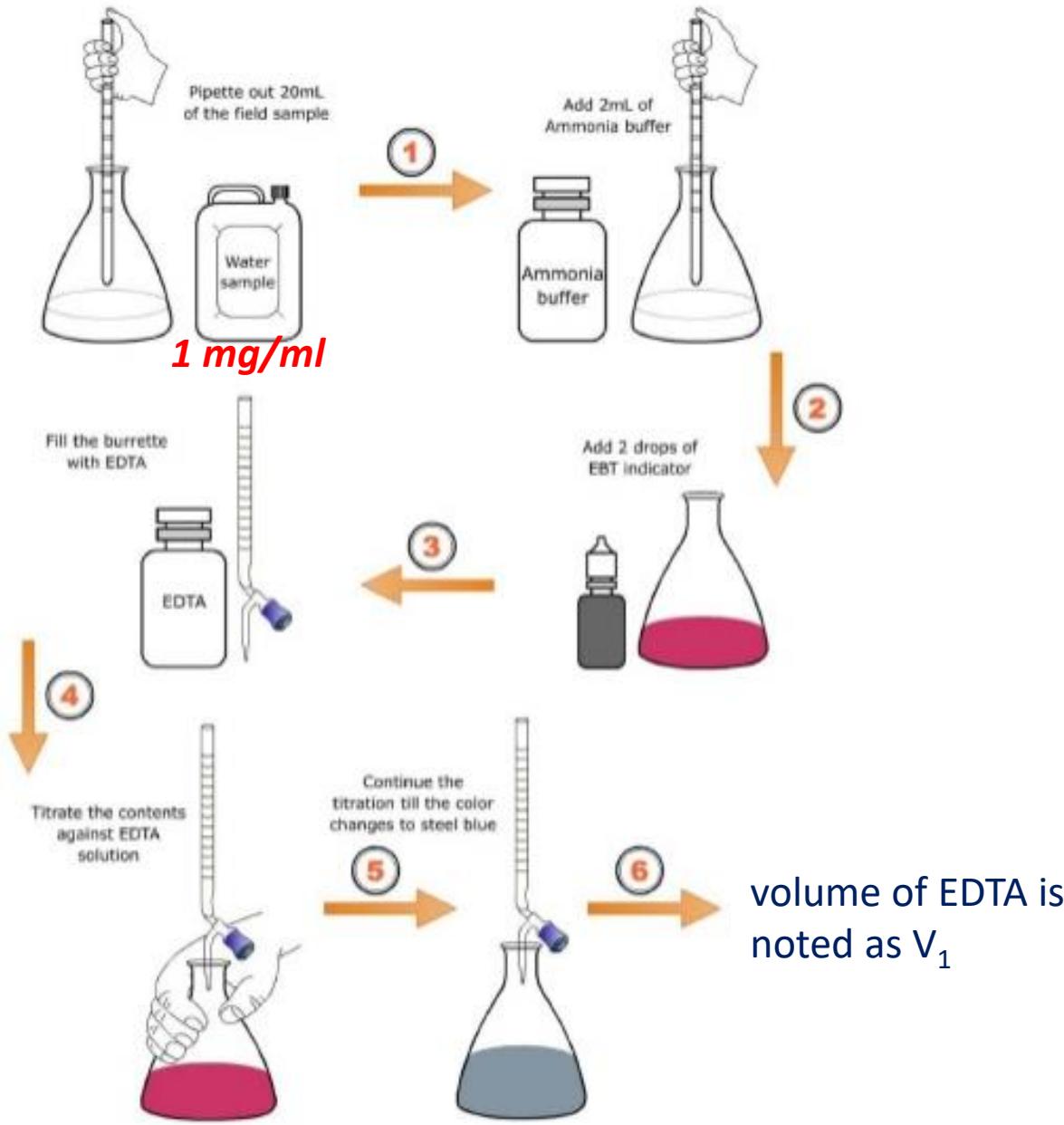
Procedure

V_1 mL of EDTA is consumed by 50 mL of std. hard water

V_1 mL of EDTA = 50 mg of CaCO_3

1 mL of EDTA = $50/V_1$ mg of CaCO_3

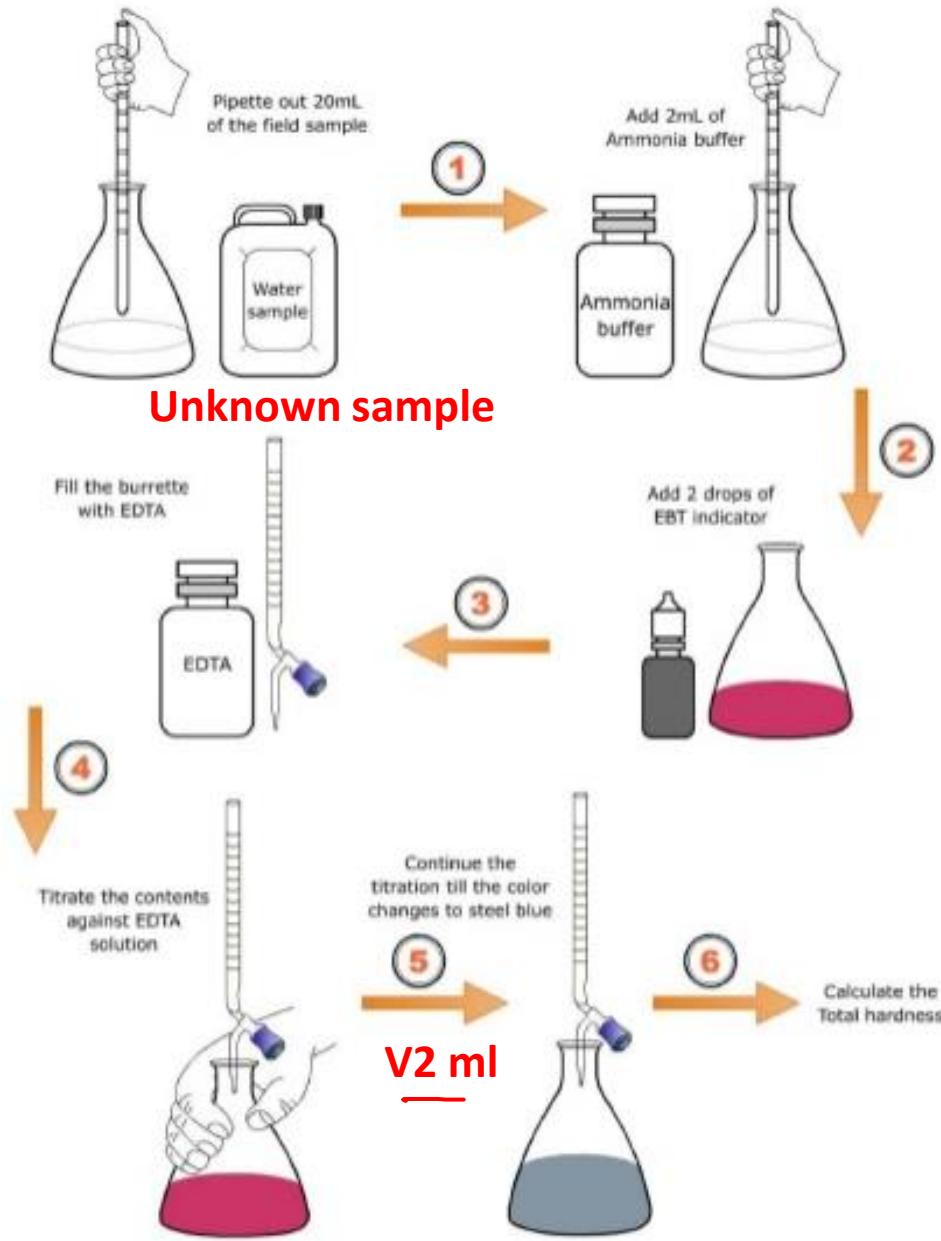
EDTA Solution is standardized



Procedure

EDTA consumed by sample
hard water = V_2 mL.
 V_2 mL of EDTA = $50/V_1 \times V_2$
mg of CaCO_3
Hence, 50 mL of sample
hard water contains $50/V_1$
 $\times V_2$ mg of CaCO_3

Unknown sample



Calculations

a) Total hardness:

V_1 mL of EDTA is consumed by 50 mL of std. hard water

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

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

EDTA consumed by sample hard water = V_2 mL

$$\text{So, } V_2 \text{ mL of EDTA} = 50/V_1 \times V_2 \text{ mg of CaCO}_3$$

Hence, 50 mL of sample hard water contains $50/V_1 \times V_2$ mg of CaCO₃

Therefore, 1000mL of sample hard water = $50/V_1 \times V_2/50 \times 1000$ mg/L

i.e. Total hardness of sample hard water = $V_2/V_1 \times 1000$ mg of CaCO₃
(ppm.)

Procedure(permanent hardness)

- o First EDTA Solution is standardized using standard hard water (1 mg/mL of CaCO_3 equivalents is prepared as standard hard water).
- o For this, first known aliquot of Standard hard water is taken, and 50 mL of ammonia buffer is added to bring the pH between 9-10.
- o Then a few drops of EBT solution is added to form the unstable complex giving wine red colour.
- o This solution is titrated with the EDTA solution till the solution turns to steel blue indicating the formation of stable EDTA-Metal ion complex.
- o This volume of EDTA is noted as V_1 .
- o The above procedure is repeated with sample hard water of unknown hardness.
- o Volume of EDTA is noted as V_2 .
- o **Then sample hard water of 250 mL is taken and evaporated to a volume of 50mL when the temporary hard salts settle down.**
- o **The solution is filtered and washed thoroughly and made up again to 250mL.**
- o **From this solution, 50 mL is pipetted out and titrated in similar manner as done with standard hard water.**
- o **Volume of EDTA is noted as V_3 .**

Calculations

Permanent hardness:

50 mL of sample hard water after removing temporary hardness consumed V_3 mL of EDTA.

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

Therefore, $V_3 \text{ mL of EDTA} = 50/V_1 \times V_3 \text{ mg of CaCO}_3 \text{ equiv.}$

50 mL of sample hard water after boiling contained $50/V_1 \times V_3$ mg of CaCO₃ equiv.

Therefore, 1000 mL of sample hard water contains

$$= 50/V_1 \times V_3/50 \times 1000 \text{ mg/L CaCO}_3 \text{ equiv.}$$

Permanent hardness $= V_3/V_1 \times 1000 \text{ mg/L CaCO}_3 \text{ equiv.}$

Temporary hardness:

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

Temporary hardness calculation

Temporary hardness:

Temporary hardness = Total hardness – permanent hardness

$$\frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000$$

$$= 1000 \times \frac{V_2 - V_3}{V_1}$$

1) Calculate Total, Temporary and Permanent hardness of the given hard water sample with following analysis report:-

- [i] 50 mL of standard hard water sample consume 42 mL of EDTA solution.**
- [ii] 50 mL of hard water sample consume 19.9 mL of EDTA solution before boiling.**
- [iii] 50 mL of hard water sample consume 8.9 mL of EDTA solution after boiling.**

Standard hard water is prepared by dissolving 1.5 mg of CaCO_3 per ml.

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[i] 50 mL of standard hard water sample consume 42 mL of EDTA solution.

[ii] 50 mL of hard water sample consume 19.9 mL of EDTA solution before boiling.

[iii] 50 mL of hard water sample consume 8.9 mL of EDTA solution after boiling.

Standard hard water is prepared by dissolving 1.5 mg of CaCO_3 per ml.

1mL of standard hard water contains 1.5 mg of CaCO_3

[i] total hardness: 708.44 ppm

[ii] permanent hardness: 316.8 ppm

[iii]Temporary hardness: 391.6 ppm

2) 0.5 g of CaCO_3 was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample requires 15 ml EDTA and after boiling and filtering requires 10 ml of EDTA solution. Calculate the total Temporary and Permanent hardness .

3) In an EDTA titration, 50 ml of standard hard water sample(1mg CaCO₃ in 1ml) consumed 25 ml of EDTA, 50 ml of hard water sample consumed 35 ml of EDTA and the 50ml sample hard water (after boiling, cooling and filtering) required 10ml EDTA. Calculate the permanent and temporary hardness of the given water sample.

4) 1.0 gm of CaCO_3 was dissolved in HCl and the solution made up to 1000 ml with distilled water. 50 ml of the solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 28 ml of EDTA and after boiling and filtering required 15 ml of EDTA solution. Calculate the hardness of water.

2) 0.5 g of CaCO_3 was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample requires 15 ml EDTA and after boiling and filtering requires 10 ml of EDTA solution calculate the hardness.

- [i] total hardness: 312.5 ppm
- [ii] permanent hardness: 208.3 ppm
- [iii]Temporary hardness: 104.2 ppm

3) In an EDTA titration, 50 ml of standard hard water sample(1mg CaCO₃ in 1ml) consumed 25 ml of EDTA, 50 ml of hard water sample consumed 35 ml of EDTA and the 50ml sample hard water (after boiling, cooling and filtering) required 10ml EDTA. Calculate the permanent and temporary hardness of the given water sample.

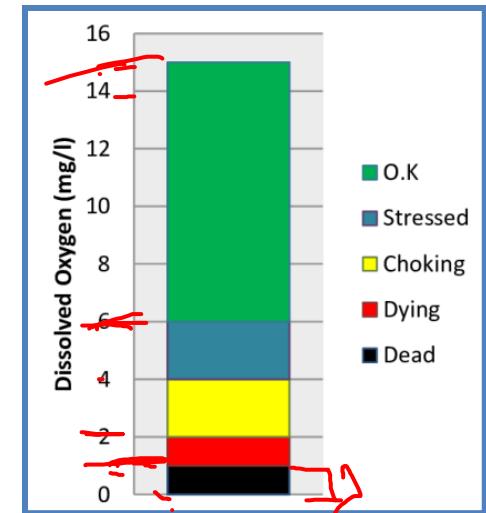
- [i] total hardness: 1400 ppm
- [ii] permanent hardness: 400 ppm
- [iii]Temporary hardness: 1000 ppm

Dissolved Oxygen

Dissolved oxygen (DO) is the amount of oxygen dissolved in a given quantity of water at a particular temperature and atmospheric pressure.

- **DO depends on**

- Aeration,
- Photosynthetic activity of the water,
- Respiration of animals and plants
- Speed of water flow
- Roughness of surface over which water flows
- Temperature of the water body



- **Oxygen Demanding Wastes**

- **Chemical Oxygen Demand (COD)**

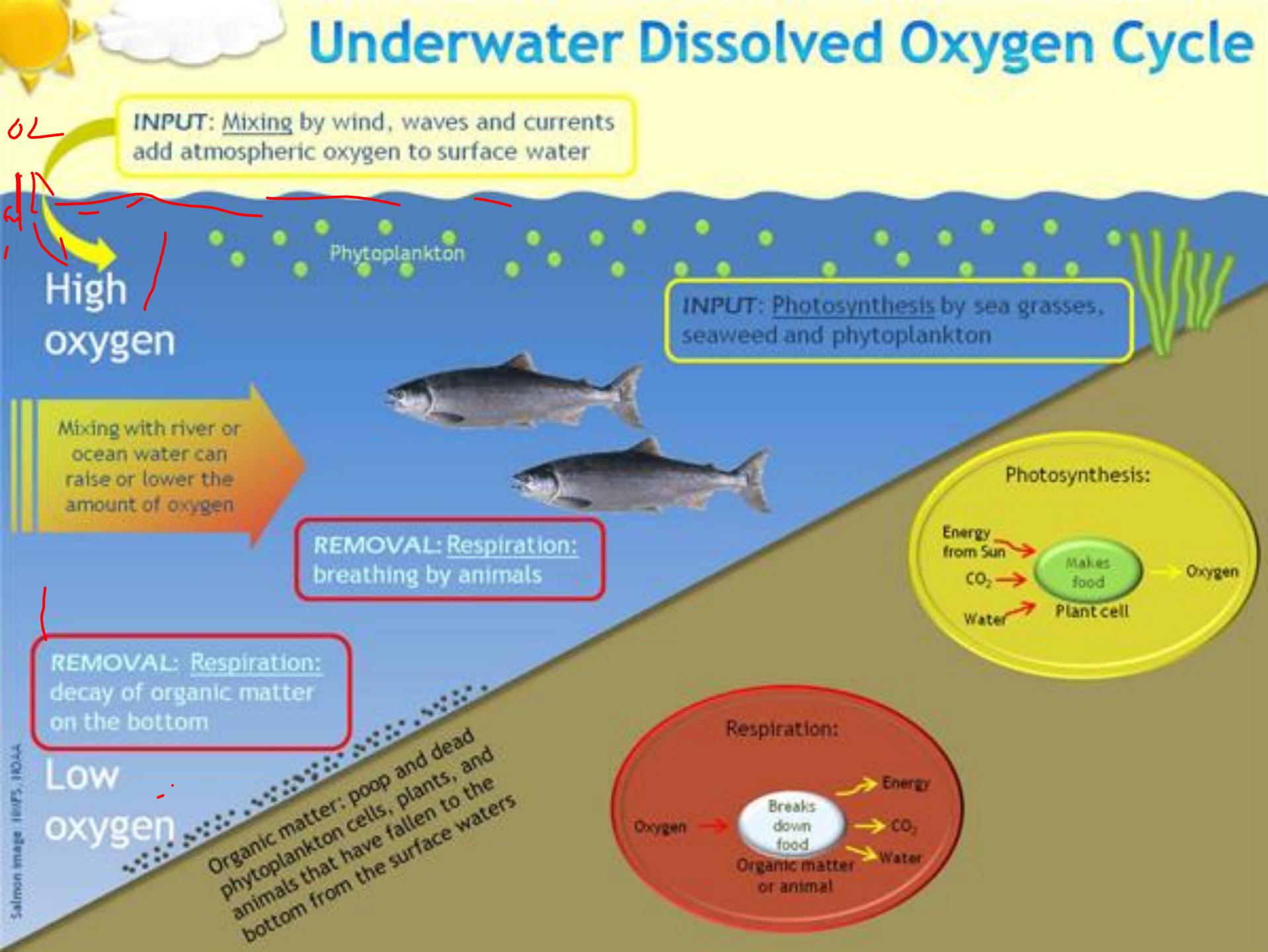
- Chemicals/Organic wastes present in water consume the DO

- **Biological Oxygen Demand (BOD)**

- Organic wastes reaching water consume oxygen from water bodies for their decomposition by bacteria through biochemical oxidation

- **These are useful measures to check water quality**

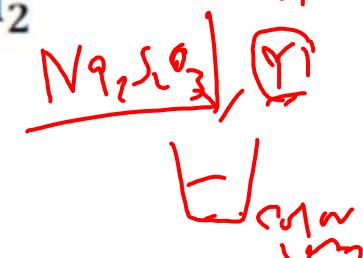
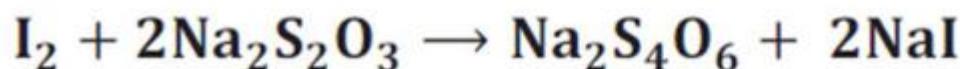
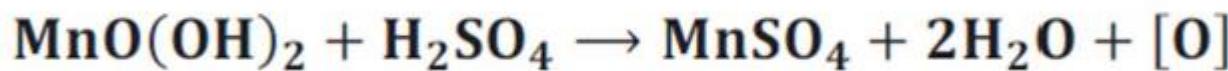
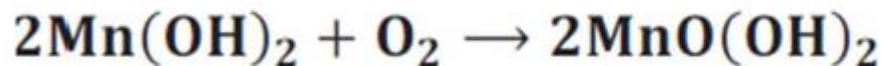
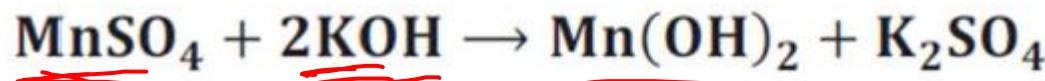
Underwater Dissolved Oxygen Cycle



Estimation of DO by Winkler's method

Theory of Winkler's Method:

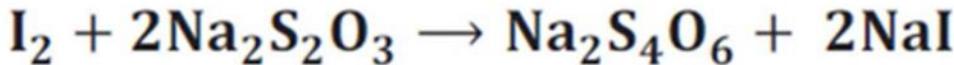
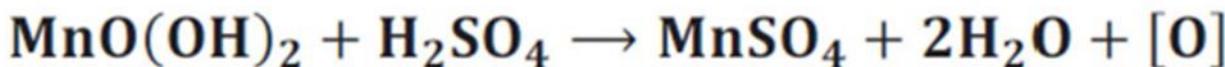
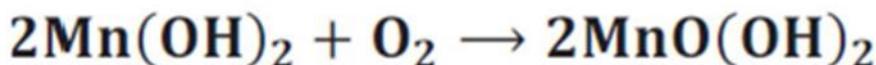
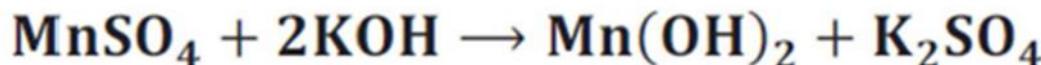
- Oxygen in the water sample oxidizes **iodide ion (I^-) to iodine (I_2)** quantitatively.
- The amount of iodine generated is then determined by titration with a standard thiosulfate ($S_2O_3^{2-}$) solution.
- The endpoint is determined by using starch as a visual indicator.
- The amount of oxygen can then be computed from the titre values



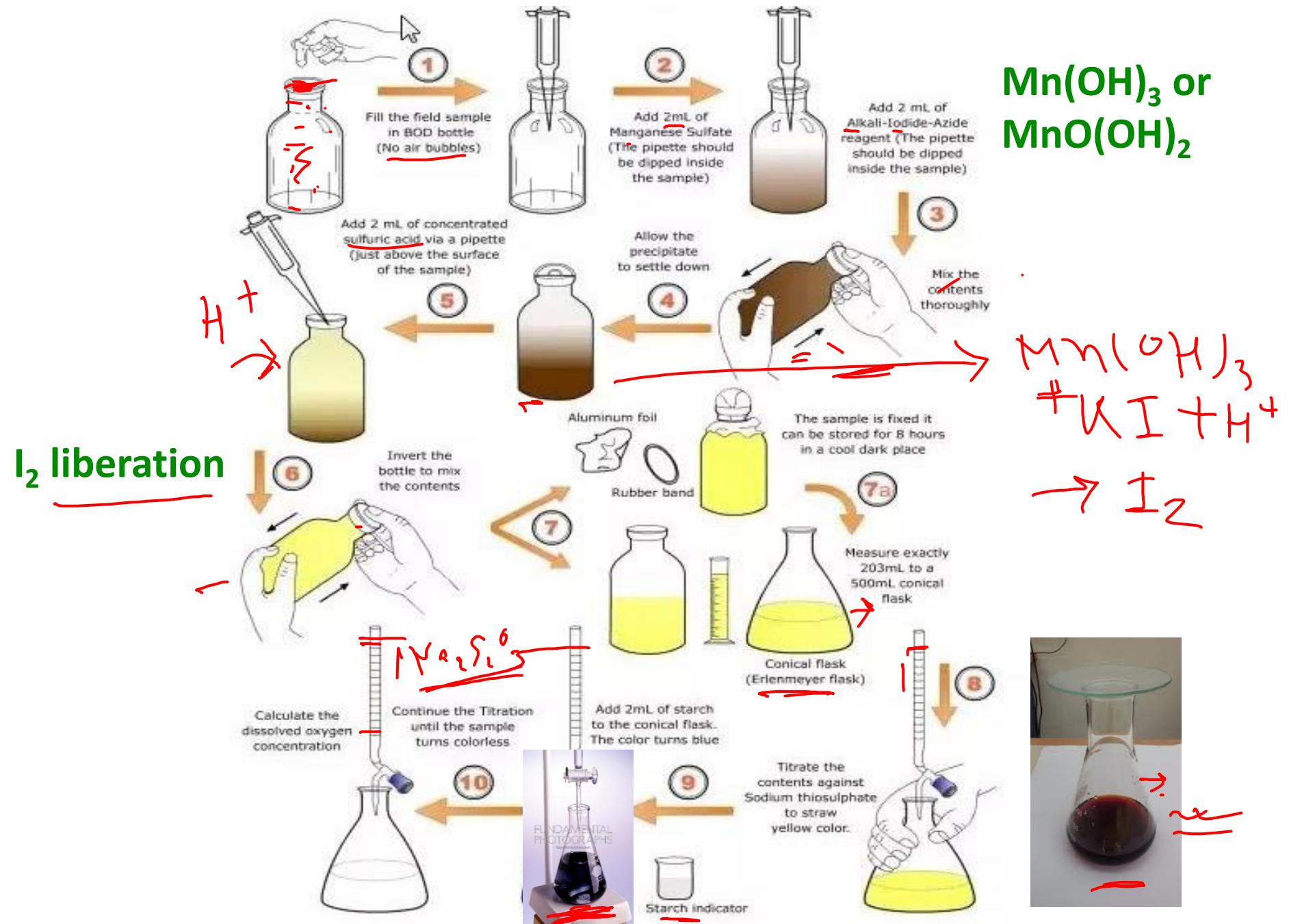
Reactions Involved



Sodium thiosulfate Sodium tetrathionate



■ Estimation of DO

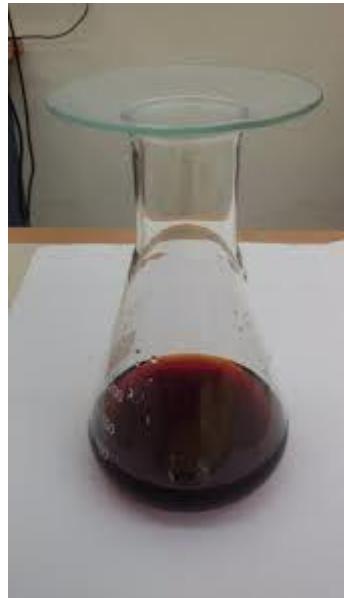


Procedure:

Titration 1: Standardization of Sodium Thiosulphate

Rinse and fill the burette with given sodium thiosulphate solution (Bottle B). Pipette out 20 mL of 0.01N K₂Cr₂O₇ solution (Bottle A) into a clean conical flask. To this, 5 ml (1/2 T.T.) of 10% KI followed by 5 mL dil. H₂SO₄ (1/2 T.T.) and titrate against sodium thiosulphate solution. When the solution becomes straw yellow color, add starch indicator and continue the titration. End point is the disappearance of bluish brown color. Repeat the titration to get concordant value

- Standardization of $\text{Na}_2\text{S}_2\text{O}_3$
- The secondary standard solution of sodium thiosulphate is standardized by titrating with a primary standard potassium dichromate using starch as indicator
- Color change occurs from straw yellow to blue to colorless



Starch
→



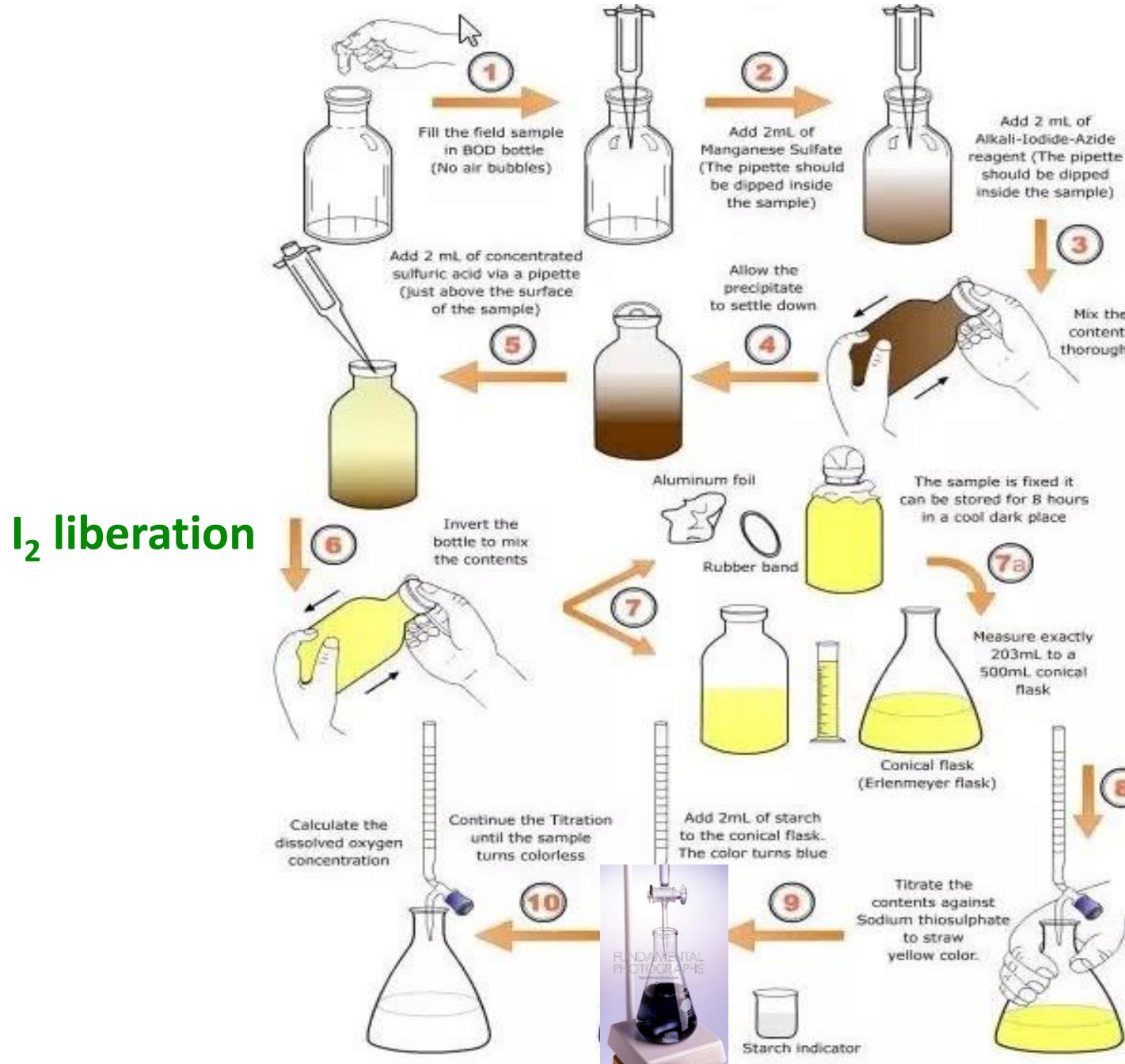
$\text{Na}_2\text{S}_2\text{O}_3$
→ Colorless mixture

Titration 2: Estimation of Dissolved Oxygen

Using a measuring cylinder, add 100 mL of sample water in a conical flask. Further, add 2 mL of MnSO_4 and 2 mL of alkali KI solution and shake well for the rough mixing of the reagents. Set aside the flask for few minutes to allow the precipitate to settle down, and then add 2 mL of conc. H_2SO_4 for complete dissolution of the precipitate. Then, titrate against std. sodium thiosulphate solution. When the solution turn into light yellow, add starch indicator. End point is the disappearance of bluish brown colour. Repeat the titration to get the concordant value. Calculate the strength of dissolved oxygen from the titer value. Based on that, calculate the amount of DO in the given water sample.

- The principle involved in this methods of determination of DO is to bring about the oxidation of **potassium iodide (KI)** to **iodine** with dissolved oxygen present in water sample after adding MnSO_4 , KI and KOH.
- The reaction with manganese(II) hydroxide which is converted rapidly and quantitatively to manganese(III) hydroxide. Here **MnSO_4 acts oxygen carrier** to enable the dissolved oxygen in molecular form to take part into the reaction.
- On acidification, the manganese reverts back to the divalent state and an equivalent amount of iodine is liberated form the KI present.
- The liberated I_2 is titrated against standard sodium thiosulfate (hypo) solution, using starch as indicator.

■ Estimation of DO



$\text{Mn}(\text{OH})_3$ or
 $\text{MnO}(\text{OH})_2$



Total Dissolved Solids (TDS)

Total dissolved solids (TDS) is the amount of particles dissolved in water

- They come from
 - a) Organic sources (leaves)
 - b) Silt
 - c) Industrial wastage and sewage as well as runoff from urban sources, fertilizers and pesticides.
 - d) Inorganic materials such as rocks and air that may contain calcium bicarbonate, nitrogen, iron, sulphur and other minerals.
- A constant level of minerals, eg. Phosphorous, nitrogen and sulphur, is necessary for aquatic life.
- Concentration of dissolved solids should not be too high or too low which can affect the growth and leads to death of many aquatic organisms.
- High concentration of dissolved solids reduces the clarity of water and can decrease the photosynthesis and raises the water temperature.
- It can be determined taking a known amount (say 100 mL) of water and by evaporating the contents carefully to dryness.
- The residue (W/g) left after evaporation of the filtered sample shows the total dissolved solids present in that articular water sample.

Total Dissolved Solids

$$\text{TDS} = (W/100) \times 10^6 \text{ mg/L or ppm}$$

- Recommended TDS for drinking water is 25-250 mg/L
- At any cost drinking water TDS should not exceed 500 mg/L
- TDS for distilled water will be 0.5-1.5 mg/L
- TDS ranges from 100-20,000 mg/L in river water and will be generally higher in ground water
- Sea water will have 3500 mg/L of TDS
- Lakes and streams will have a TDS of 20-250 mg/L

- Concentration of dissolved solids should not be too high or too low which can affect the growth and leads to death of many aquatic organisms.
- High concentration of dissolved solids reduces the clarity of water and can decrease the photosynthesis and raises the water temperature.

Estimation of TDS

- By gravimetric method:* Involve evaporating water sample and measuring the mass of residues left.



✓ *By conductometric method:* Ions from the dissolved solids makes water to conducting electric current, which can be measured using a conventional conductivity meter or TDS meter ✓



Modern methods of water analysis

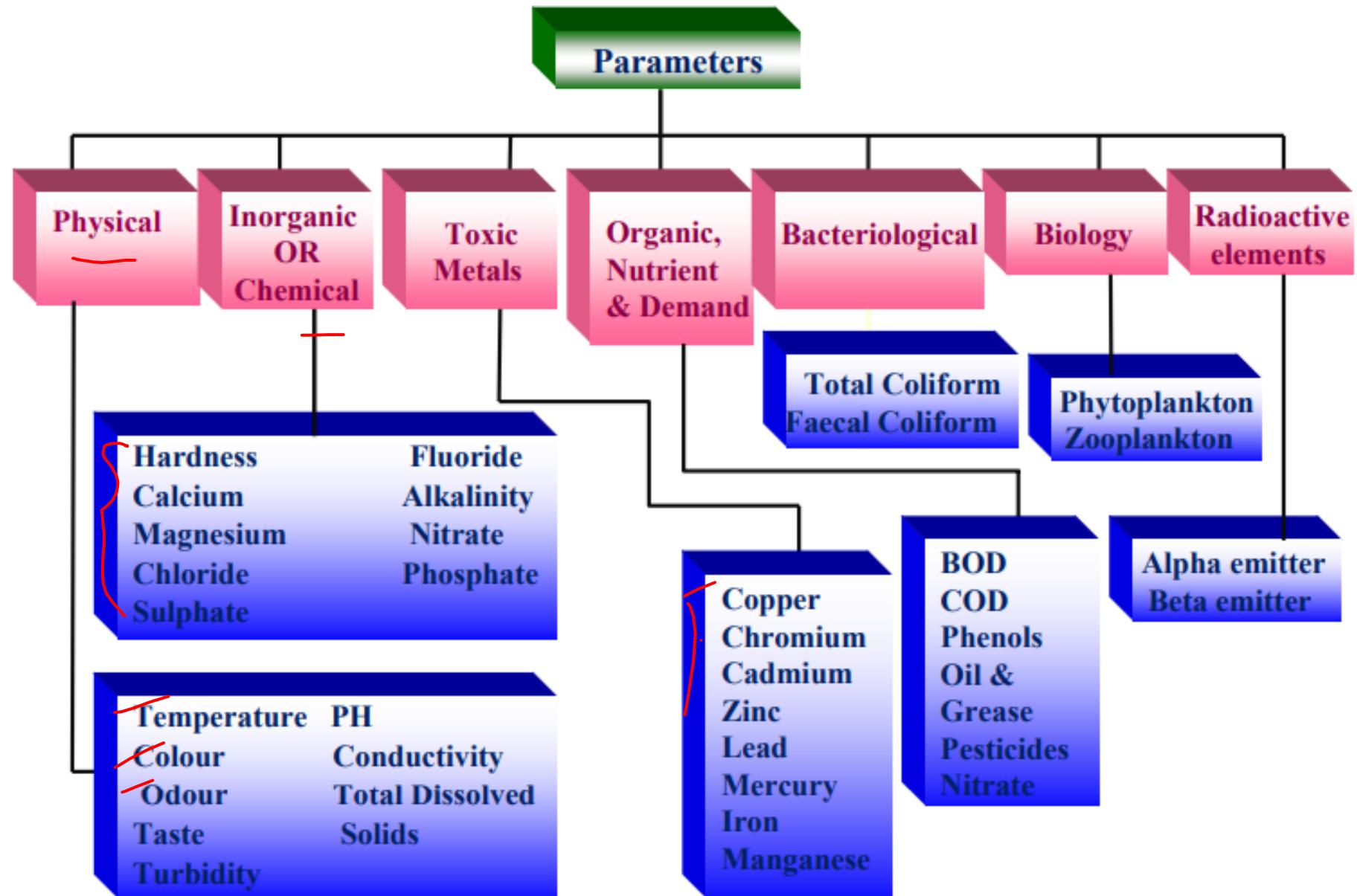
- **Importance of Water Analysis**

Water analysis is essential to ensure its quality or to detect pollutants that should be removed by water treatment. However, water quality does not mean making the water suitable for human consumption; it depends on its end use. For example, completely different quality standards are applied in case of industrial water compared to those applied to drink water, i.e., drinking water must be fit for human consumption, while industrial water should be free from any contaminants that may corrode or damage equipment.

- **Limitations of Traditional Methods of Water Analysis**

The traditional analysis includes **chemical analysis, colorimetry, spectrometry, chromatography, and atomic absorption**. Although these techniques differ in sensitivity and accuracy, most of them are highly accurate. Nevertheless, they require sampling, expensive devices, and manpower; besides, they are time-consuming and difficult to conduct onsite.

Water Quality Assessment : Potable & Industrial Uses



Problems of hard water for domestic use

a) Washing:

- Hard water, when used for washing purposes, does not lather freely with soap.
- It produces sticky precipitates of calcium and magnesium soaps.
- Similar problem exists in bathing.

b) Cooking:

- Due to the presence of dissolved hardness producing salts the boiling point of water is elevated.
- Consequently more fuel is and time are required for cooking.

c) Drinking:

- Hard water causes bad effect on our digestive system.
- The possibility of forming calcium oxalate crystals in urinary tracks is increased (Kidney stones).

Disadvantages of hard water in industries

Paper Industry:

The presence of calcium and magnesium has impact on the properties and quality of paper and their products

Textile industry :

Hard water cause much of the soap to go as waste.

During dyeing process, calcium and magnesium salts present in water make the quality of the shades very poor.

Sugar industry :

If nitrates, sulphates of calcium and magnesium are present, they cause hindrance to crystallization of sugar

Concrete making :

Water containing chlorides and sulphates, if used for concrete making, affects the hydration of the cement and the final strength of the hardened concrete.

In steam generation in boilers:

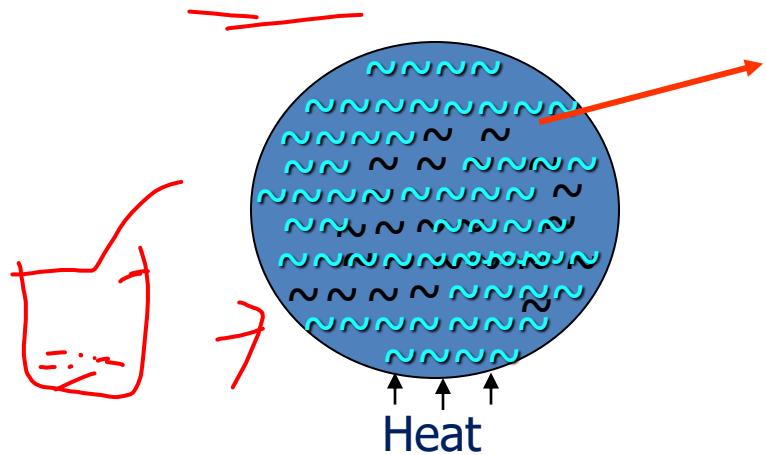
If the hard water is fed directly to the boilers, which led to the many problems such as

Formation of scales which corrodes the boiler, wastage of fuel etc.

Disadvantages of hard water

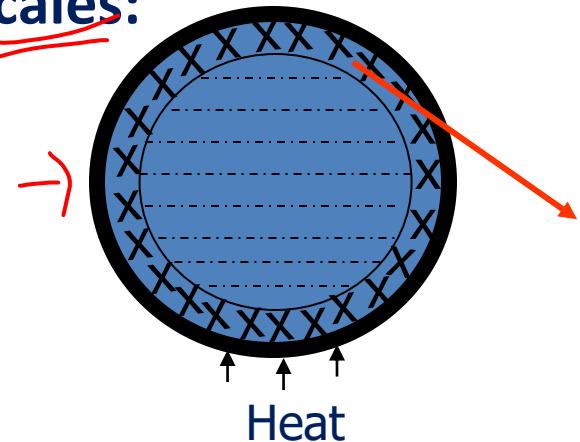
1. Scale and Sludge formation:

a) Sludges:



- o Soft, loose, slimy precipitates are sludge
- o Can be easily scrapped off with a wire brush
- o Forms in comparatively colder portions of the boiler such as bends etc.
- o Formed because of MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4
 Mg(OH)_2 (more soluble in hot water)

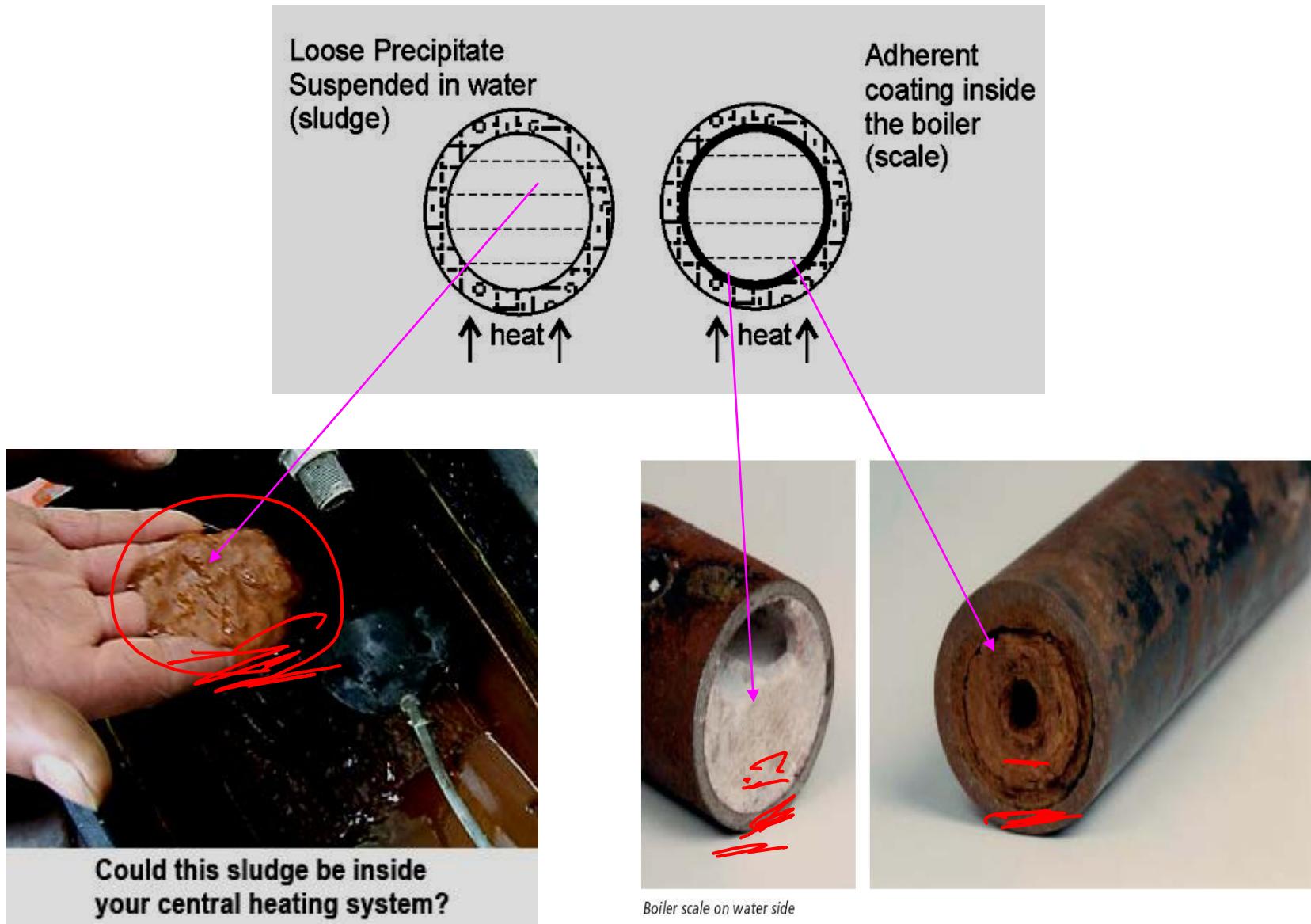
b) Scales:



- o Dissolved salts deposit because of continuous evaporation of water concentration of salts increases
- o These are hard and stick strongly to the walls
- o Difficult to be removed even with a hammer and chisel.
- o Formed because of CaCO_3 , CaSO_4 , CaSiO_3 , MgSiO_3



Examples of Sludge and Scale



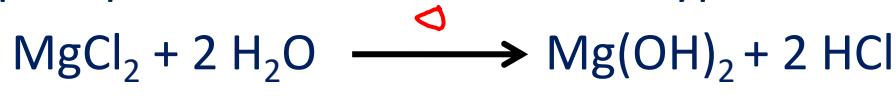
Scales

- Scales are the main source of boiler troubles.

Scale are mainly formed by decomposition of calcium bicarbonate



- Dissolved magnesium salts undergo hydrolysis forming magnesium hydroxide precipitate which forms a soft type of scale



- Presence of silica in small quantities deposits as calcium silicate (CaSiO_3) or magnesium silicate (MgSiO_3).

These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove.

- Scales reduce the thermal conductivity and if there is a crack on the scale, it may lead to differential heating and increases the possibility of boiler explosion.

Disadvantages of hard water

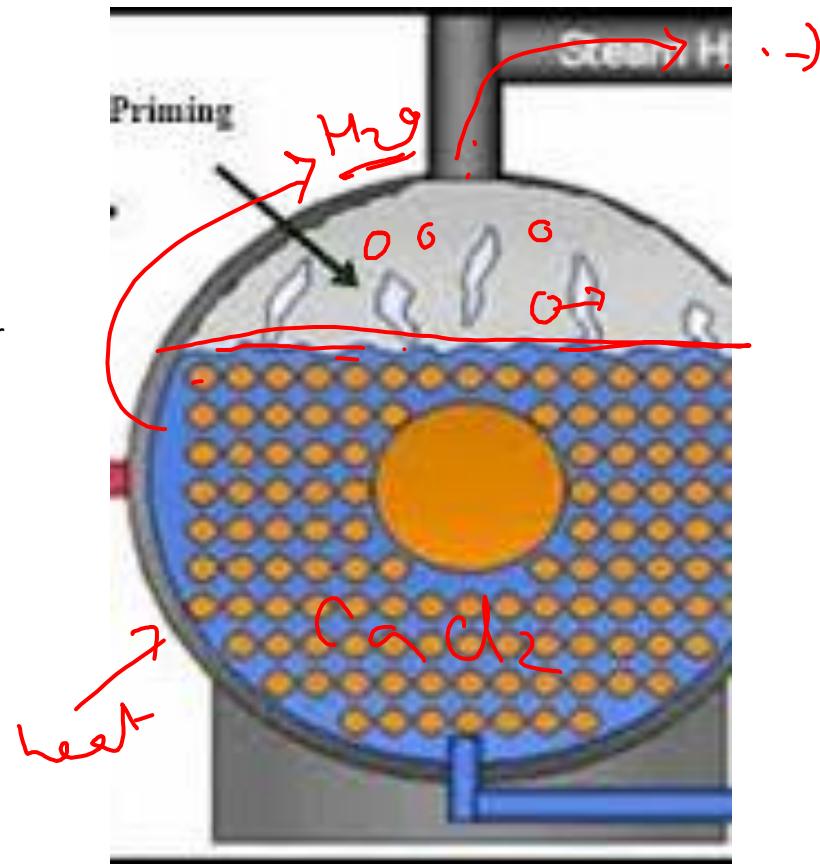
2. Priming and Foaming:

a) Foaming:

- o Foaming is the production of persistent foam or bubbles in boilers which do not break easily.
- o This is because of presence of oils which reduce the surface tension of water.
- o Can be avoided by adding anti-foaming agents like caster oil or removing oil from the boiler feed water by adding sodium aluminate.

b) Priming:

- o Along with steam, some particles of water are carried (wet steam) which is called priming.
- o This is because of large amounts of dissolved salts, high steam velocities, sudden boiling, improper boiler design, sudden increase in steam production rate.
- o Priming can be avoided by maintaining low water level in boilers, avoiding rapid steam generation, efficient softening, installing mechanical steam purifiers.



Water Softening methods

- The process of removing the hardness producing substance from the water is called softening of water
- In Industry three main methods are employed for softening of water
 - ✓ Lime soda process: lime Ca(OH)_2 and soda Na_2CO_3 is added; (residual hardness: 15 to 60 ppm)
 - ✓ Zeolite (permutit) process: Hard water is filtered through a natural sand called the zeolite (residual hardness: up to 10 ppm)
 - ✓ Ion-exchange and Mixed bed ion-exchange process:
 - Cation exchange resins (RH^+)
 - Anion exchange resins ($\text{R}'\text{OH}^-$)
 - Mixed bed ion-exchange

Basic principles of Lime-soda process

- In this process, all the soluble hardness-causing impurities are converted into insoluble precipitates which may be removed by setting and filtration
- Lime [Ca(OH)₂] and soda [Na₂CO₃] are the reagents used to precipitate the dissolved salts of Ca²⁺ and Mg²⁺ as CaCO₃ and Mg(OH)₂.

Lime removes the temporary hardness

Reaction of Ca(HCO₃)₂ :



Reaction of Mg(HCO₃)₂ :



Lime cannot remove the calcium permanent hardness which should be removed by soda

Basic principles of Lime-soda process

a. Reaction of permanent calcium:



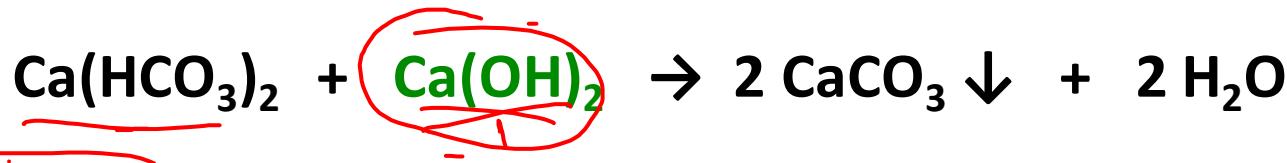
b. Reactions of permanent magnesium:



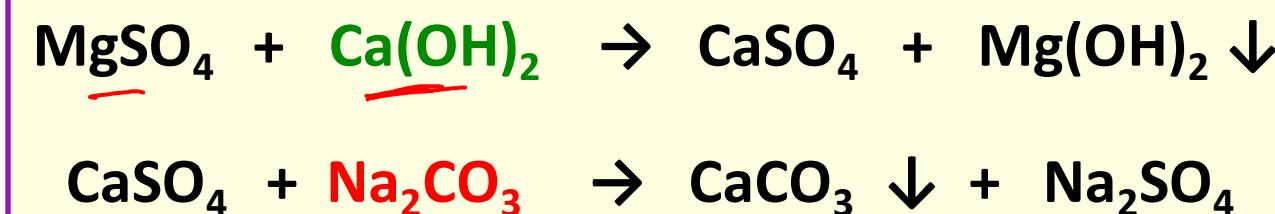
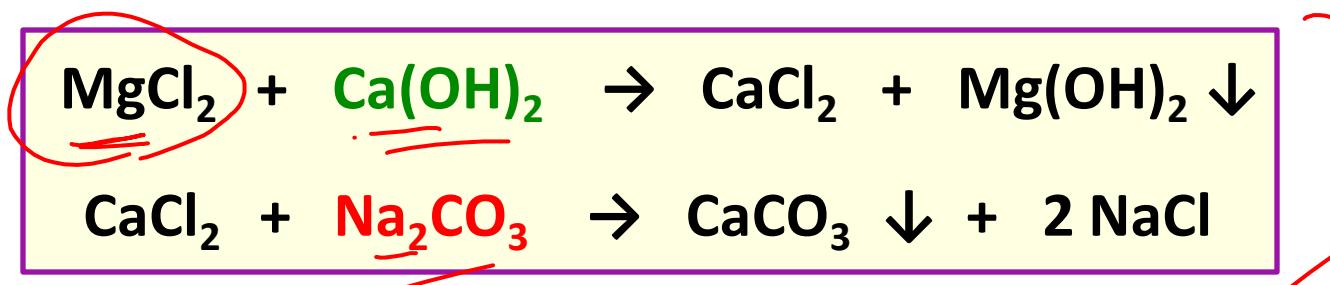
Lime cannot remove the calcium permanent hardness which should be removed by soda

Lime Soda Process - Reactions of Lime and Soda

- Lime removes the temporary hardness:



- Soda and Lime removes the magnesium permanent hardness:



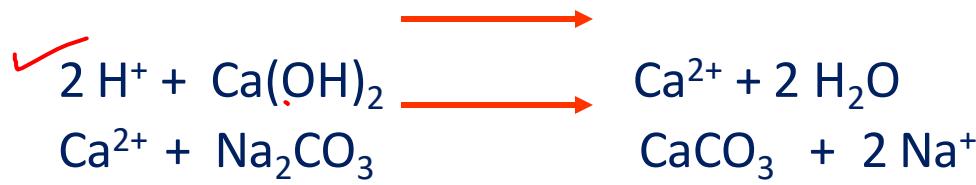
■ Soda removes all calcium permanent hardness:



- Reaction of CO₂:

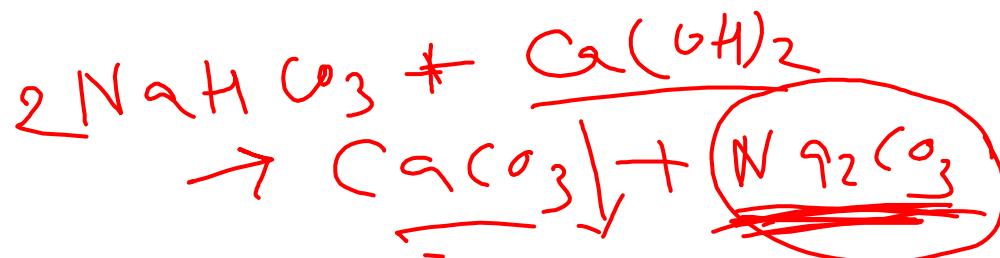


- Reaction of H⁺:

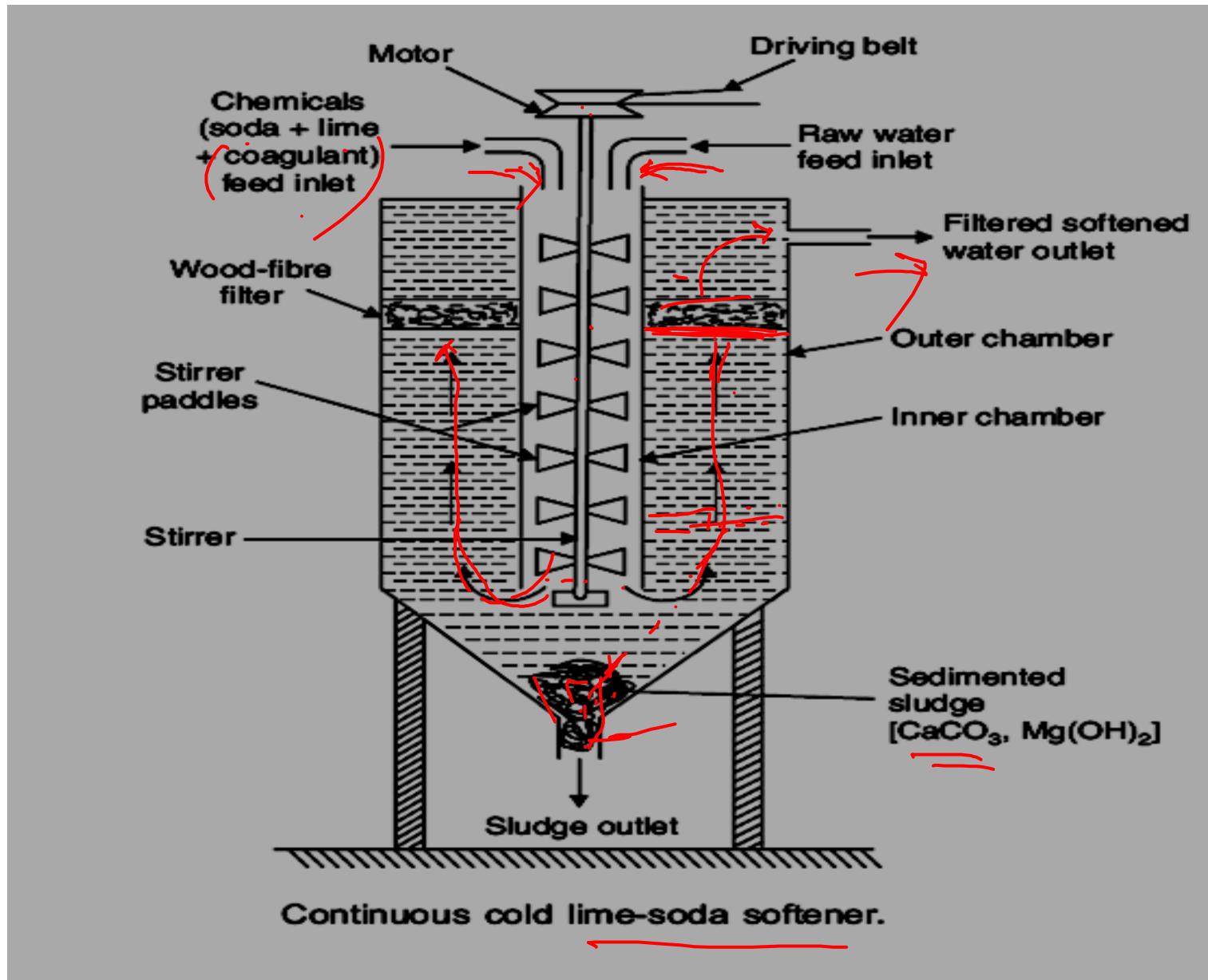


(E - S)

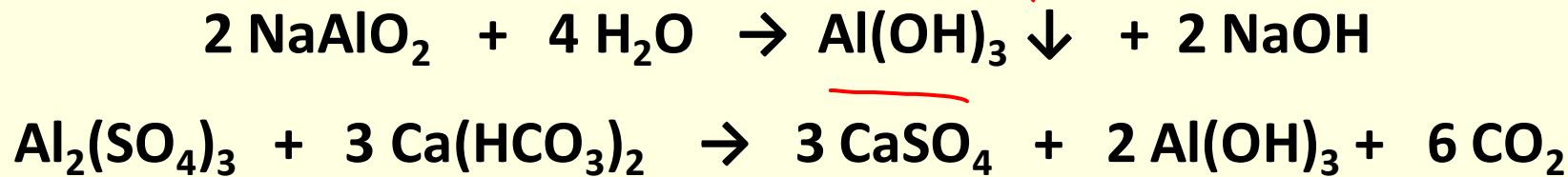
Reaction of HCO₃⁻ (Example: NaHCO₃)



Working of Cold Lime –Soda Process



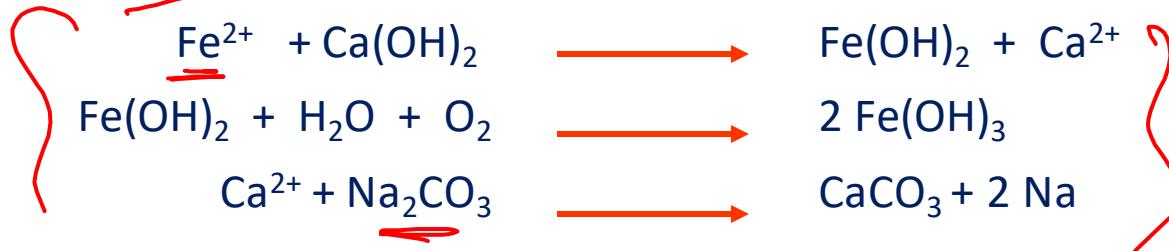
- Operated at room temperature.
- Calculated amount of lime & soda mixed with water at room temperature with stirring.
- Precipitate formed are finely formed hence do not settle down easily.
- It is essential to add small amount of **coagulant** [aluminium sulphate, sodium aluminate, Alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)]
- Coagulant hydrolyse to form gelatinous precipitates and entraps the fine precipitate



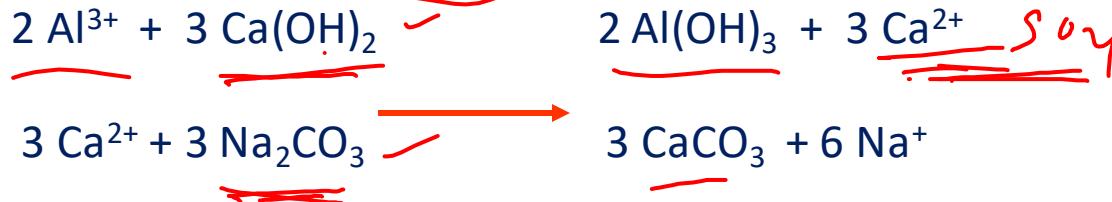
- The softened water passes through a filtering media (wood fibre) for complete removal of sludge
- It provides water with a residual hardness of 50 to 60 ppm.

Reactions of coagulants:

a) Reaction of FeSO_4 :



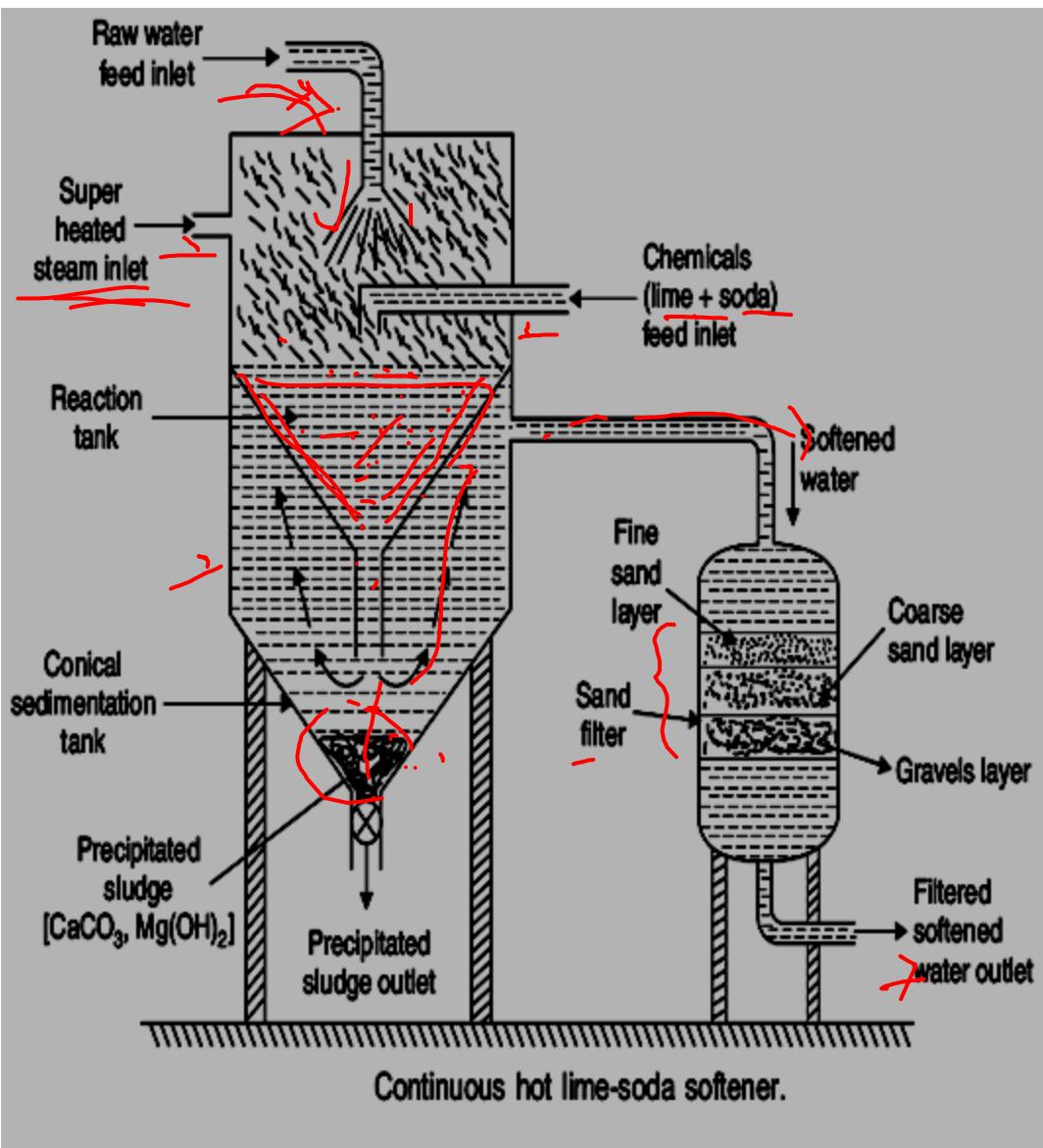
b) Reactions of Aluminium Sulphate ($\text{Al}_2(\text{SO}_4)_3$):



c) Reactions of Sodium Aluminate (NaAlO_2):



Hot Lime –Soda Process



Hot lime-soda process consists of three parts:

- Reaction tank to mix all ingredients
- Conical sedimentation vessel where the sludge settles down
- Sand filter where sludge is completely removed

Advantages of hot lime-soda process:

- The precipitation reactions are almost complete.
- Reactions takes place faster.
- Sludge settles down rapidly; No coagulant is needed.
- Dissolved gases (which may cause corrosion) are removed.
- Viscosity of soft water is lower, hence filtered easily.
- Residual hardness is low compared to cold lime-soda process.

Difference Between Soft and Hot lime soda Process

Cold lime-soda process	Hot lime-soda process
Done at room temp, 25 to 30°C.	Elevated temperature, 94 to 100°C
Slow Process	Rapid process
Use of Coagulants is must	Coagulants are not required
Filtration is not easy	Filtration is easy since the viscosity is low at high temperature
Residual hardness is around 60ppm	Residual hardness is 15-30ppm
Dissolved gases are not removed	Dissolved gases like O ₂ and CO ₂ removed to some extent
Low softening capacity	High softening capacity

Advantages & disadvantages of lime-soda process:

Advantages of Lime – soda process:

- Economical
- Process improves the corrosion resistance of water.
- Mineral content of water is reduced
- The pH of water raises thus reducing content of pathogenic bacteria.
- No skilled labour is required

Disadvantages of Lime – soda process:

- Huge amount of sludge is formed and its disposal is difficult.
- Due to residual hardness, water is not suitable for high pressure boilers.

Lime $[\text{Ca}(\text{OH})_2]$ required for softening

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

100 parts by mass of $\text{CaCO}_3 \equiv 74$ parts of $\text{Ca}(\text{OH})_2$

1 part of $\text{CaCO}_3 \equiv 74/100$ of Lime

Soda $[\text{Na}_2\text{CO}_3]$ required for softening

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

100 parts by mass of $\text{CaCO}_3 \equiv 106$ parts of $\text{Ca}(\text{OH})_2$



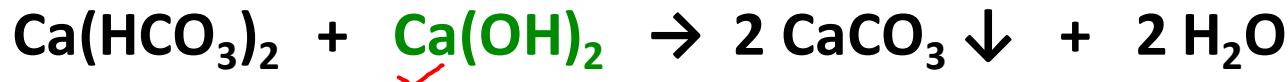
1 part of $\text{CaCO}_3 \equiv 106/100$ of Lime

- All components in CaCO_3 equivalent
- V = volume of water
- Final result in mg >> kg



Lime Soda Process - Reactions of Lime and Soda

- Lime removes the temporary hardness:



- Soda and Lime removes the magnesium permanent hardness:



- Soda removes all calcium permanent hardness:



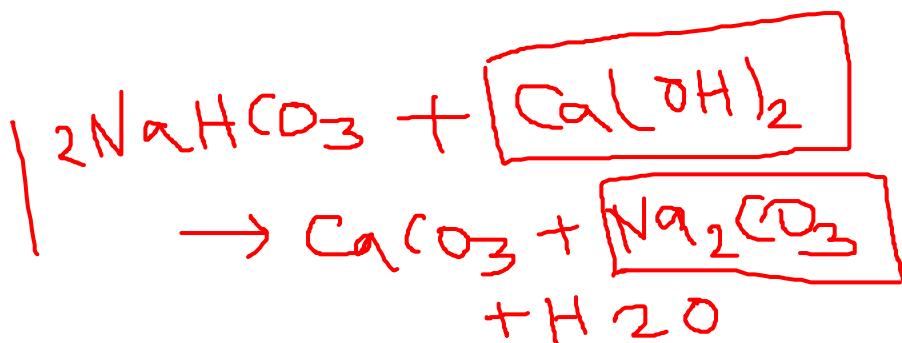
- Reaction of CO₂:



- Reaction of H⁺:



- Reaction of HCO₃⁻ (Example: NaHCO₃)



Example

1. Calculate the amount of lime and soda required for softening 50,000 liters of hard water containing $\text{Ca}(\text{HCO}_3)_2 = 81 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 73 \text{ ppm}$, $\text{CaCl}_2 = 222 \text{ ppm}$, $\text{MgSO}_4 = 180 \text{ ppm}$, $\text{Na}_2\text{SO}_4 = 15 \text{ ppm}$, $\text{NaCl} = 165 \text{ ppm}$, and $\text{Fe}_2\text{O}_3 = 25 \text{ ppm}$.

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Sol: No hardness is caused by Na_2SO_4 , NaCl , and Fe_2O_3 (insoluble solid), so they should not be included in the calculations.

Conversion to CaCO_3 equivalents

Constituent	ppm	Multiplication factor (M.Wt. of CaCO_3 / M.Wt. of Constituent)	CaCO_3 equivalents
$\text{Ca}(\text{HCO}_3)_2$	81	$100/162$	$81 \times 100/162 = 50$ ppm
$\text{Mg}(\text{HCO}_3)_2$	73	$100/146$	$73 \times 100/146 = 50$ ppm
CaCl_2	222	$100/111$	$222 \times 100/111 = 200$ ppm
MgSO_4	180	$100/120$	$180 \times 100/120 = 150$ ppm

$$\text{eq. CaCO}_3 = \frac{\text{mass}}{\text{M.Wt.}} \times 100 = \frac{\text{amount}}{\text{mass}} \times \left(\frac{100}{\text{M.Wt.}} \right)$$

Lime required for softening 50,000 L of Water

$$= \frac{74}{100} \times [\text{Ca}(\text{HCO}_3)_2 + 2 \times \text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq}] \times \text{Vol. of Water}$$

$$= \frac{74}{100} \times [50 + 2 \times 50 + 180] \times 50,000$$

$$= \frac{74}{100} \times [330] \times 50,000 = 12,21 \text{ kg}$$

$$= \left(33 \times \frac{74}{100} \right) \text{ m}^3 \text{ L}$$

$$= \frac{106}{100} \times [\text{CaCl}_2 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq}] \times \text{Vol. of Water}$$

$$= \frac{106}{100} \times [200 + 150] \times 50,000$$

$$= 33 \times \frac{74}{100} \times 50,000$$

$$= 18.55 \text{ kg}$$

Soda required for softening 50,000 L of Water

$$= \frac{106}{100} \times [350] \times 50,000 = 18.55 \text{ kg}$$

1. Calculate the amount of lime and soda required to soften 50000 L of the water sample containing $Mg(HCO_3)_2 = 15.6$ mg/L; $Ca(HCO_3)_2 = 34.4$ mg/L; $MgSO_4 = 60$ mg/L; $CaCl_2 = 25$ mg/L; $MgCl_2 = 35$ mg/L; $SiO_2 = 25$ mg/L; $NaCl = 20$ mg/L. [Ca = 40; Mg = 24; H = 1; C = 12; O = 16; Cl = 35.5, S = 32]
2. Calculate the amount of lime (88.3% pure) and soda (99.2% pure) for treatment of 24,000 liters of water, whose analysis is as follows: $Ca(HCO_3)_2 = 18.5$ ppm; $Mg(HCO_3)_2 = 1.42$ ppm; $MgSO_4 = 1.90$ ppm; $CaSO_4 = 1.34$ ppm; $CaCl_2 = 1.75$ ppm. Also calculate the carbonate and non-carbonate hardness of the water sample.

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$$\begin{aligned} \text{Lime} &= 4.789 \text{ kg} \\ \text{Soda} &= 5.796 \text{ kg} \end{aligned}$$

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$$\begin{array}{lll} \text{Lime} = 0.3 \text{ kg} & \text{non-carbonate hardness} & = 12.39 \text{ ppm} \\ \text{Soda} = 0.106 \text{ kg} & \text{carbonate hardness} & = 4.141 \end{array}$$

3. A sample water on analysis has been found to contain the following impurities in ppm: $\text{Ca}(\text{HCO}_3)_2 = 48.6$; $\text{Mg}(\text{HCO}_3)_2 = 29.2$; $\text{MgCl}_2 = 3.8$; $\text{CaCl}_2 = 33.3$; $\text{CaSO}_4 = 54.4$; $\text{NaCl} = 659$. Calculate the quantity of lime and soda required for softening one million liters of water {Atomic weight: Ca = 40; Mg = 24; H = 1; C = 12; O = 16; Cl = 35.5, S = 32}

4. Calculate the amount of lime (85%) and soda (90%) required for softening 50,000 litres of hard water containing following impurities (mg/L): $\text{CaSO}_4 = 40$, $\text{MgCl}_2 = 46$, $\text{Mg}(\text{HCO}_3)_2 = 82$, $\text{Ca}(\text{HCO}_3)_2 = 35$, $\text{KCl} = 10$

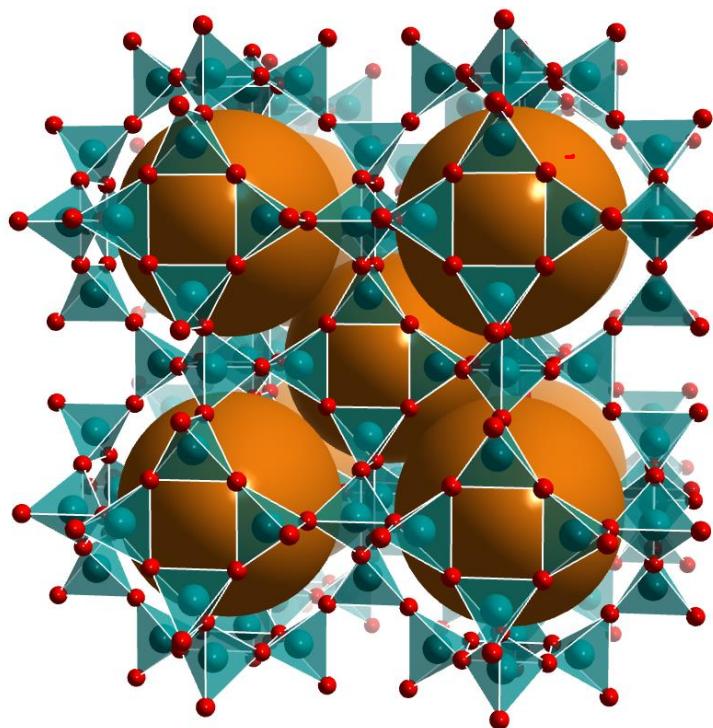
5. Explain with chemical equations and calculate the amount of lime and soda needed for softening 1,00,000 liters of water containing the following: HCl = 7.3 mg/L; Al₂(SO₄)₃ = 34.2 mg/L; MgCl₂ = 9.5 mg/L; NaCl = 29.25 mg/L. Purity of Lime is 90% and purity of soda is 98%. 10% of Lime and Soda are to be used in excess in order to complete the reaction quickly.

Water Softening methods

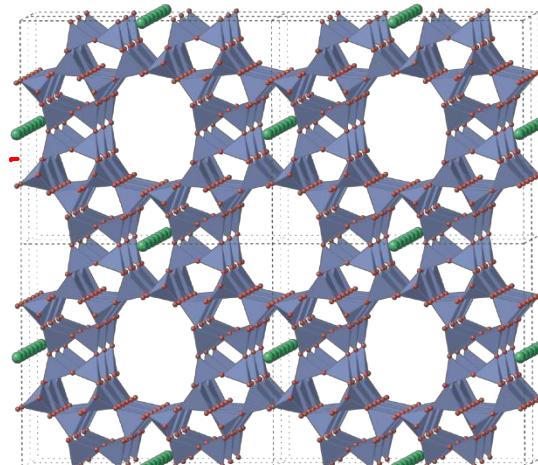
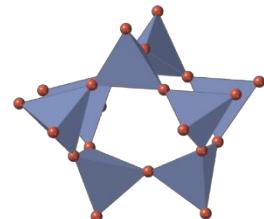
- The process of removing the hardness producing substance from the water is called softening of water
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 - Lime soda process: lime $\underline{\text{Ca(OH)}_2}$ and soda $\underline{\text{Na}_2\text{CO}_3}$ is added; (residual hardness: 15 to 60 ppm)
 - ✓ Zeolite (permutit) process: Hard water is filtered through a natural sand called the zeolite (residual hardness: up to 10 ppm)
 - Ion-exchange and Mixed bed ion-exchange process:
 - Cation exchange resins (RH^+)
 - Anion exchange resins ($\text{R}'\text{OH}^-$)
 - Mixed bed ion-exchange

Permutit or Zeolite Process

- Zeolite is hydrated sodium aluminium silicate having a general formula,
 $\text{Na}_2\text{OAl}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$. ($x=2$ to 10 and $y=2$ to 6)
- It exchanges Na^+ ions for Ca^{2+} and Mg^{2+} ions.
- Common Zeolite is $\text{Na}_2\text{OAl}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ known as natrolith.
- Other gluconites, green sand (iron potassium phyllosilicate with characteristic green colour, a mineral containing Glauconite)etc. are used for water softening.
- Artificial zeolite used for water softening is Permutit.
- These are porous, glassy particles having higher softening capacity compared to green sand.
- They are prepared by heating china clay (hydrated aluminium silicate), feldspar ($\text{KAlSi}_3\text{O}_8 - \text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$) are a group of rock-forming tectosilicate minerals which make up as much as 60% of the earth's crust) and soda ash (Na_2CO_3)



secondary building unit (cage)



Mordenite (MOR framework)

↓ Na^{+}

Types of zeolite

■ Natural Zeolites:

Mineral	Chemical formula	Crystallographic Systems	Porosity %	CEC*
Analcim	16 [Na (Al Si ₂ O ₆)H ₂ O]	Cubic	18	4.54
Chabazit	2[(Ca, Na ₂) (Al ₂ Si ₄ O ₁₂) 6H ₂ O]	Trigonal	47	3.81
Clinoptilolit	2(Na ₂ K ₂ Ca) ₃ Al ₆ Si ₃₀ O ₇₂ 21H ₂ O	Monoclinic	39	2.54
Erionit	(Na, Ca _{0.5} K) ₉ (Al ₉ Si ₂₇ O ₇₂) 27H ₂ O	Hexagonal	35	3.12
Heulandit	Ca ₄ (Al ₈ Si ₂₈ O ₇₂) 24H ₂ O	Monoclinic	39	2.91
Mordenit	(Na ₂ Ca) ₄ (Al ₈ Si ₄₀ O ₉₆) 28H ₂ O	Rhombus	28	2.29
Phillipsit	(Na, K) ₁₀ (Al ₁₀ Si ₂₂ O ₆₂) 20H ₂ O	Rhombus	31	3.87

*CEC – cationic exchange capacity

- Natrolite: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- Laumontite: $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
- Harmotome: $(\text{BaO} \cdot \text{K}_2\text{O}) \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$
- They are capable of exchanging its Na ions.

These are less porous, amorphous and durable

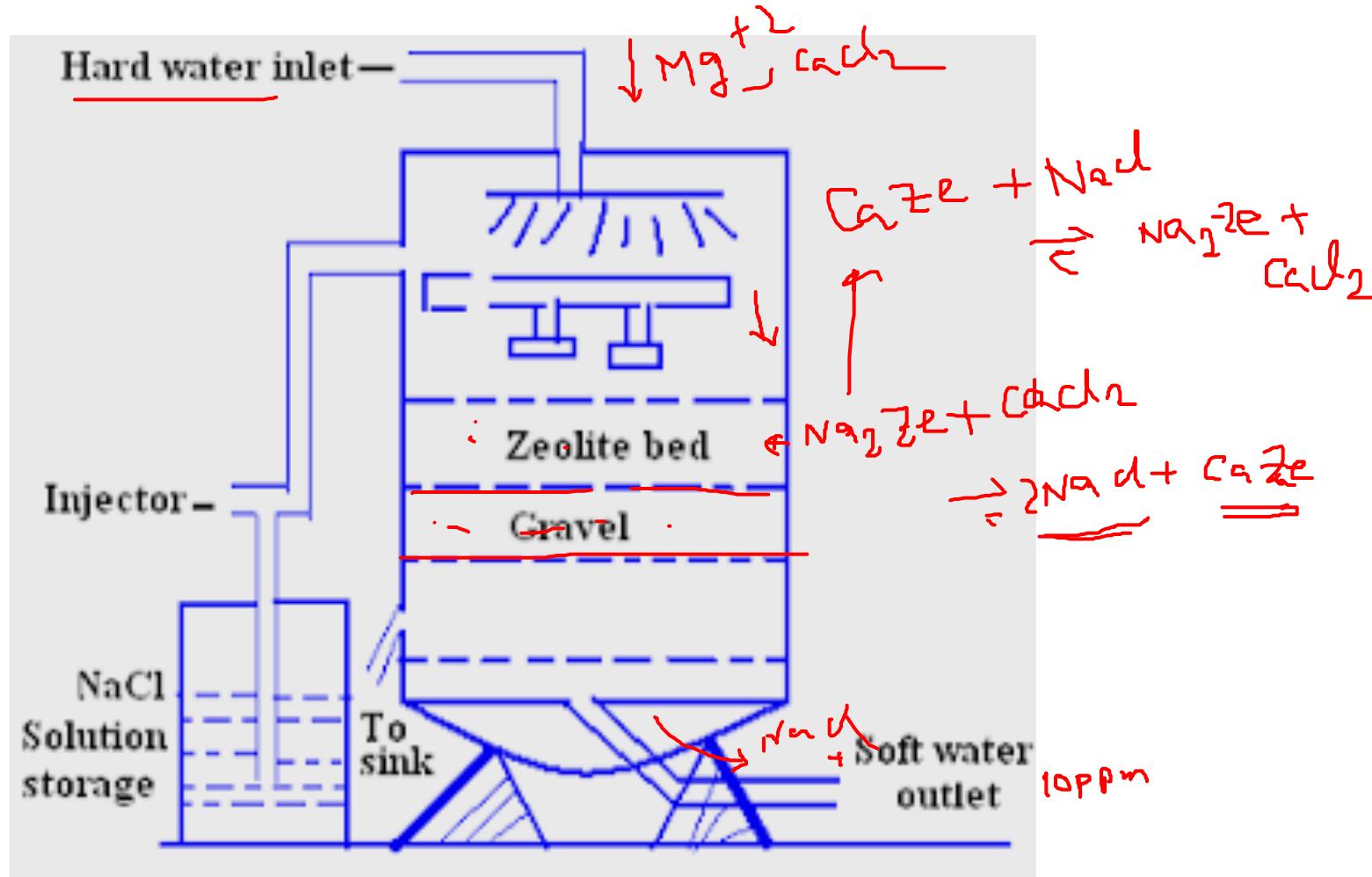
Zeolite process

- For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. Zeolite holds sodium ions loosely and can be represented as Na₂Ze. Where Ze = insoluble radical frame work.
- The hardness causing ions(Ca²⁺, Mg²⁺) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts. During this process, the water becomes free from Ca²⁺ and Mg²⁺ ions.

o Method of softening:

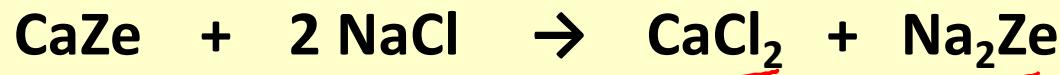


Zeolite Process Diagram



■ Regeneration:

- After some time, the zeolite is completely converted into calcium and magnesium zeolite and it ceases to soften water, i.e., it gets exhausted.
- At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated (10%) brine (NaCl) solution.
- The washing (containing CaCl_2 and MgCl_2) are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.



(Brine solution)

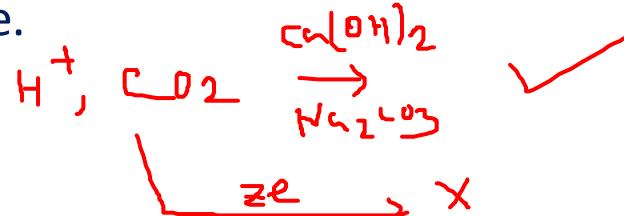
Zeolites

Advantages:

- o Residual hardness of water is about 10 ppm only
- o Equipment is small and easy to handle
- o Time required for softening of water is small
- o No sludge formation and the process is clean
- o Zeolite can be regenerated easily using brine solution
- o Any type of hardness can be removed without any modifications to the process

Disadvantages:

- o Coloured water or water containing suspended impurities cannot be used without filtration
- o Water containing acidic pH cannot be used for softening since acid will destroy zeolite.



Ion-Exchange Process

- o Ion-exchange resins are cross linked long chain polymers with microporous structure.
- o Cation exchange resins will exchange cations with H^+ .
- o Anion exchange resins will exchange anions with OH^- .
- o Functional groups present are responsible for ion-exchange properties.
- o Acidic functional groups ($-COOH$, $-SO_3H$ etc.) exchange H^+ for cations &
- o Basic functional groups ($-NH_2$, $=NH$ etc.) exchange OH^- for anions.

Ion Exchange Resin

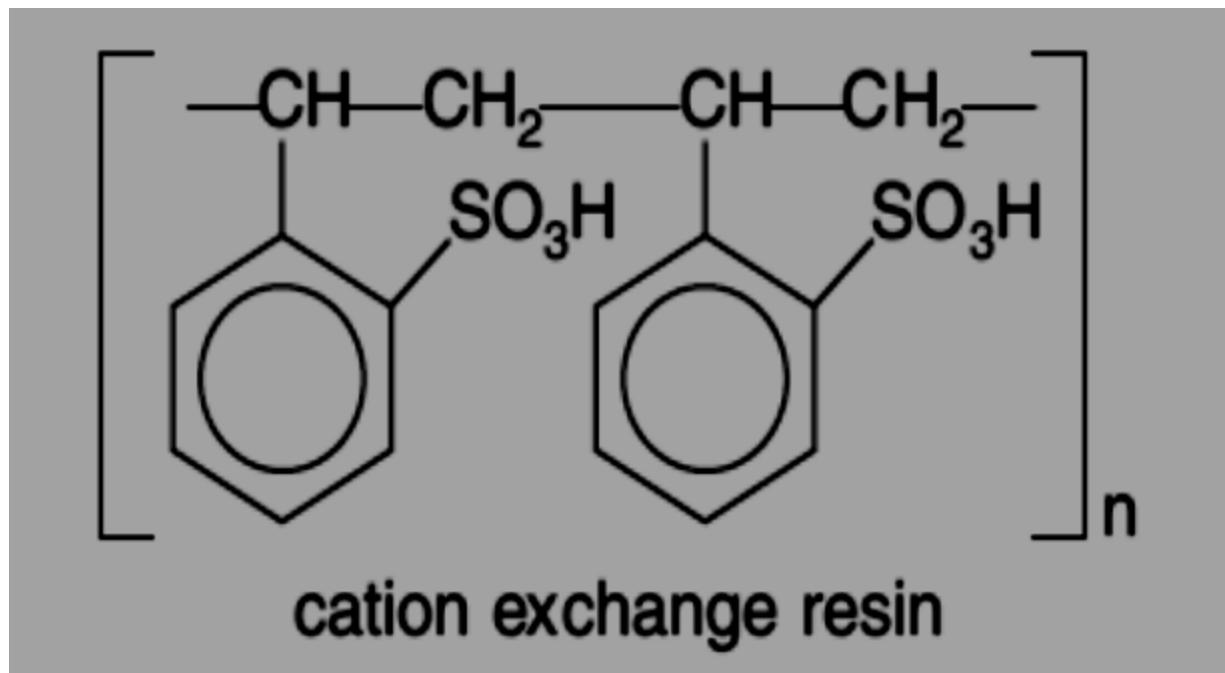
- Resins are natural or synthetic organic compound consisting of a noncrystalline or viscous liquid substance
- For water treatment purpose we use synthetic ion exchange resins
- Ion-exchange resins are insoluble, cross-linked, long chain polymers with micro-porous structure
- These microporous beads are insoluble in water and organic solvents.
- The most widely used base-materials are polystyrene and polyacrylate
- the functional groups attached to the polymer are responsible for the ion-exchanging properties



Ion-Exchange Process

A. Cation-exchange Resins(RH^+):

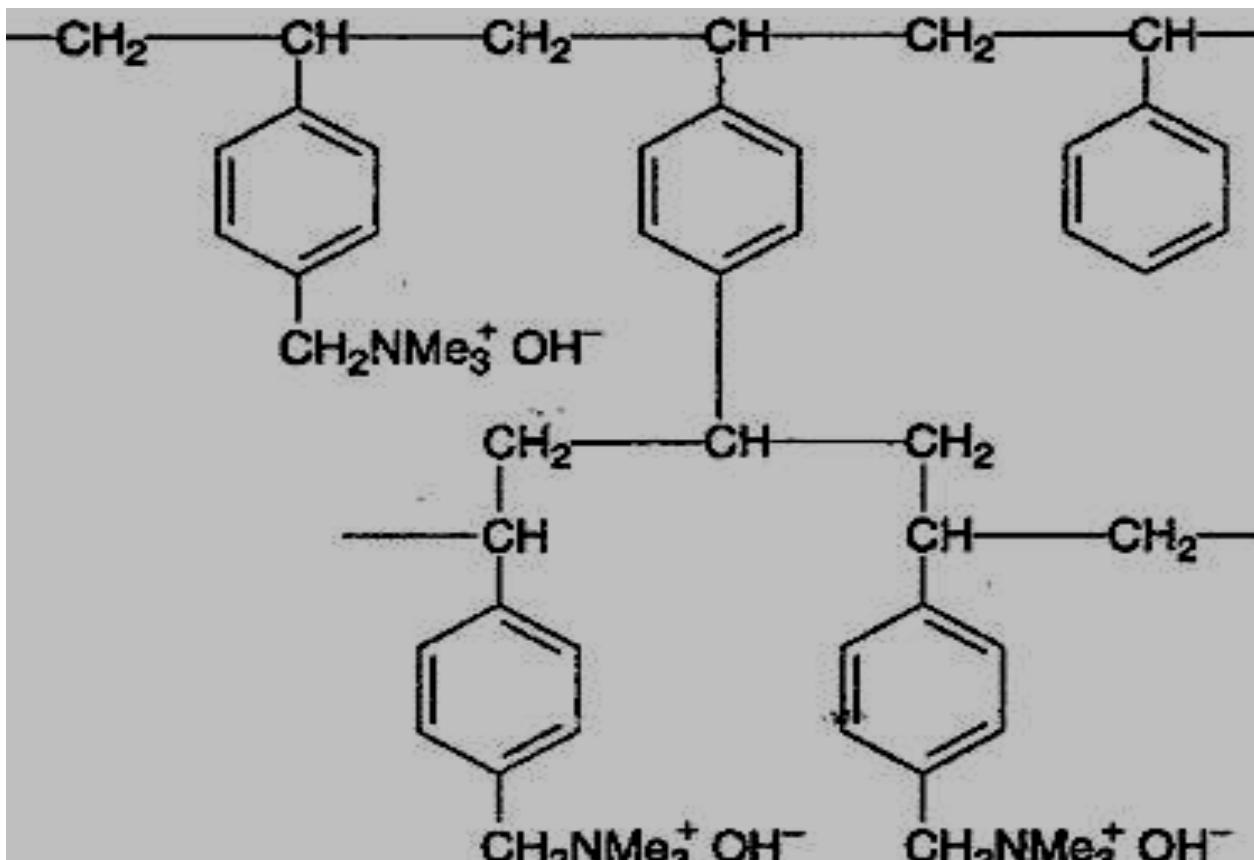
- Styrene divinyl benzene copolymers
- When sulphonated, capable of exchange H^+



Ion Exchange Process

B. Anion-exchange resins ($R'OH$):

- Styrene divinyl benzene copolymers or amine formaldehyde copolymers with NH_2 , QN^+ , QP^+ , QS^+ , groups.
- On alkali treatment, capable of exchange of OH^-



Anion Exchange resin

Ion Exchange Process

The Process of Ion-exchange is:



Finally,

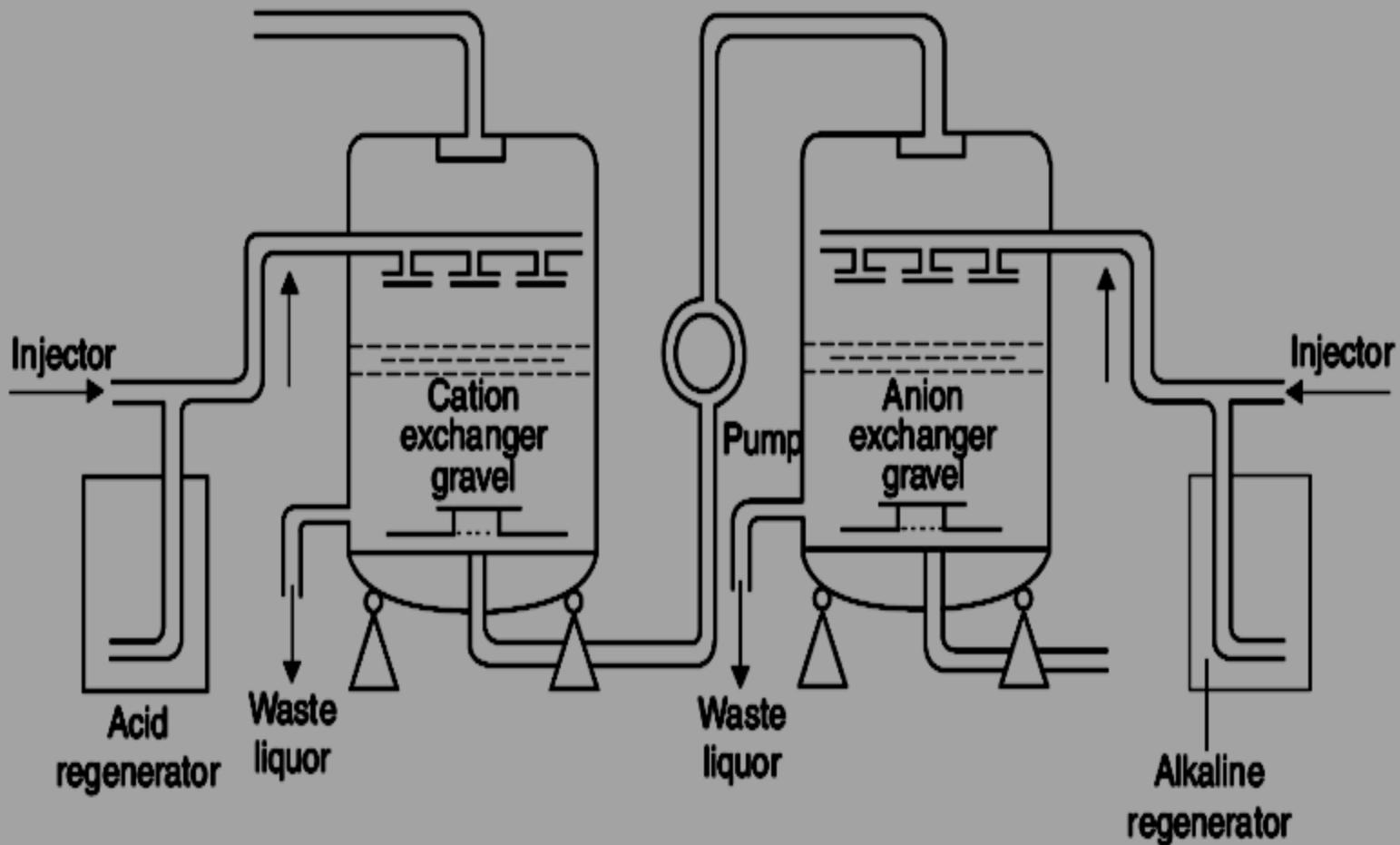


Regeneration of exhausted resins:

Saturated resins are regenerated by treating with strong mineral acid or alkali respectively

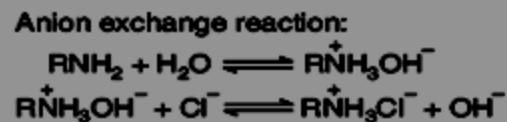
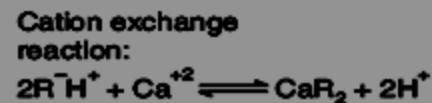
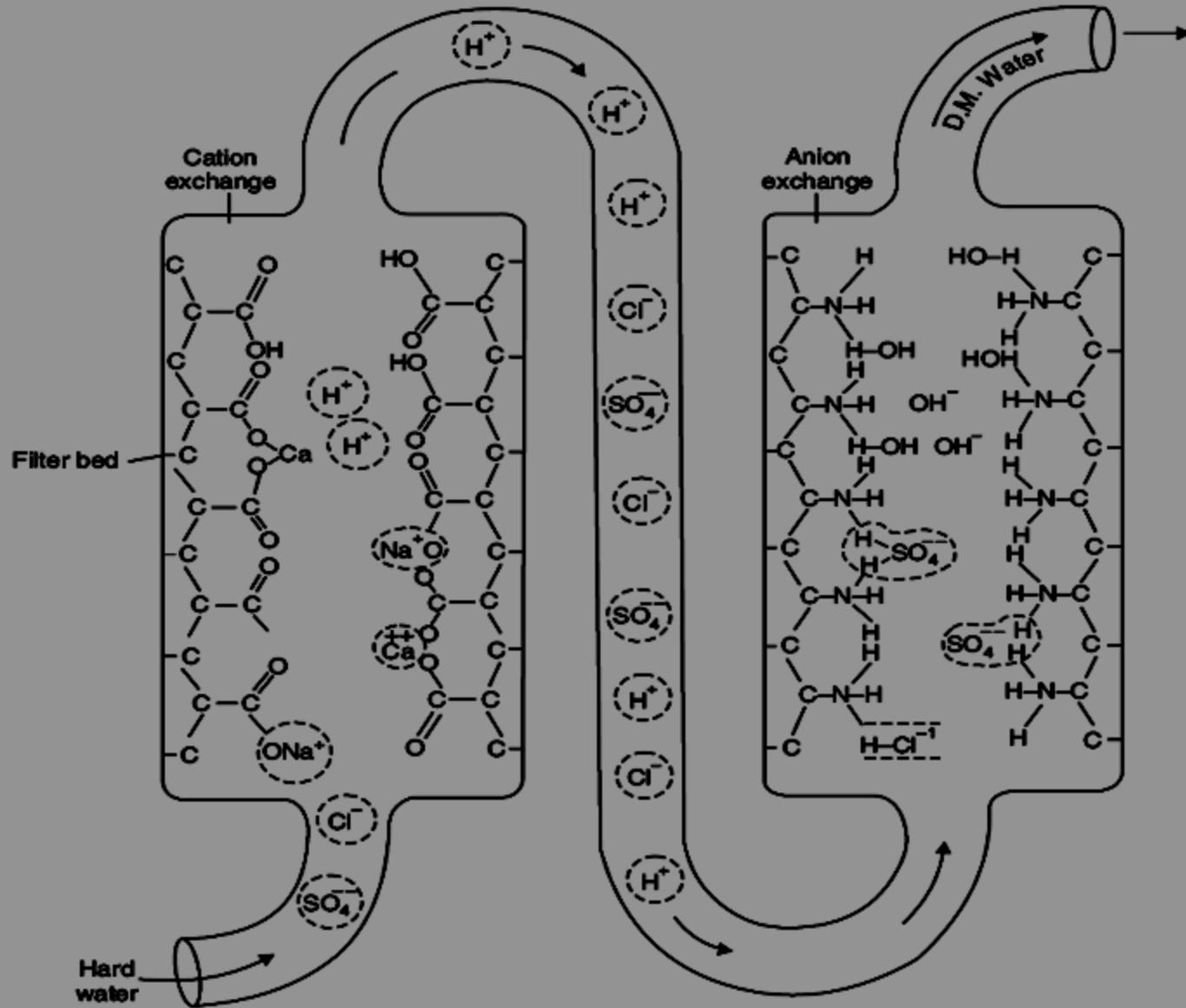


Ion-exchange process



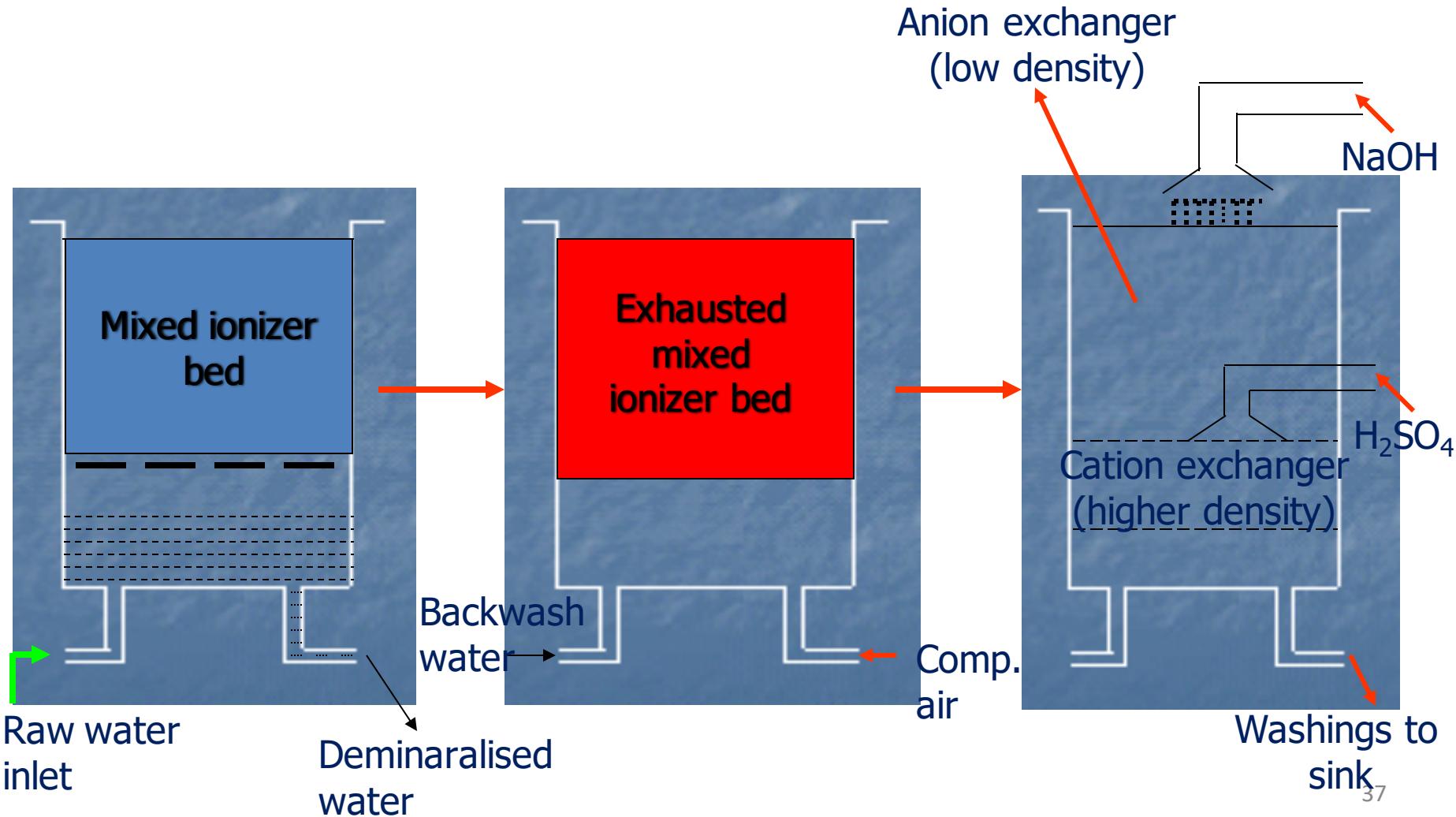
Demineralisation of water.

Note: Hard water should be first passed through the cation exchanger and then Anion exchanger to avoid the hydroxide precipitates of Al^{3+} and Mg^{2+} ions getting formed.

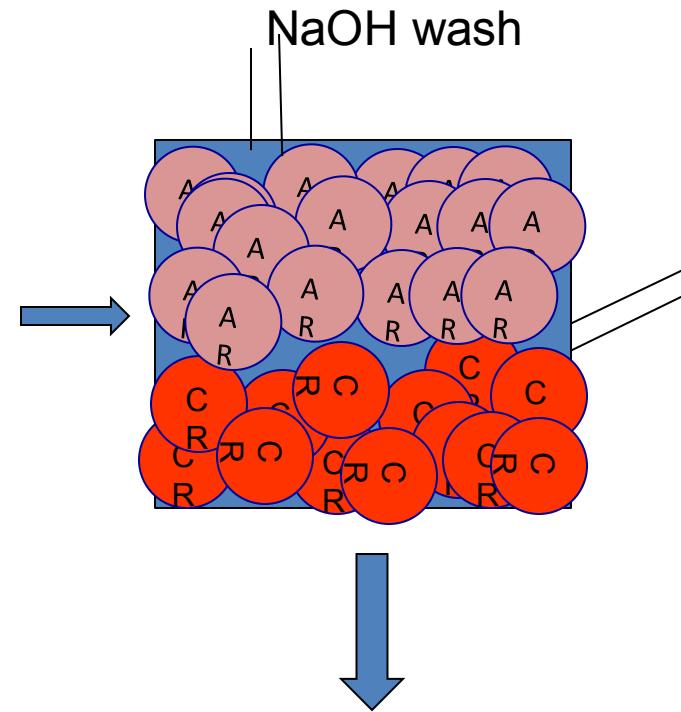
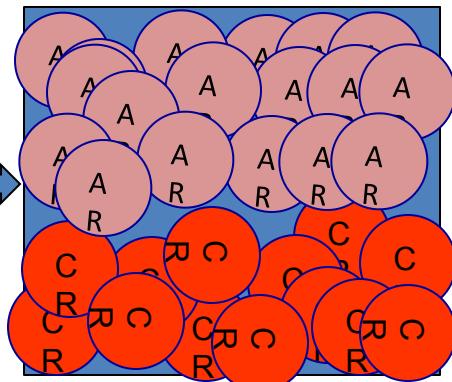
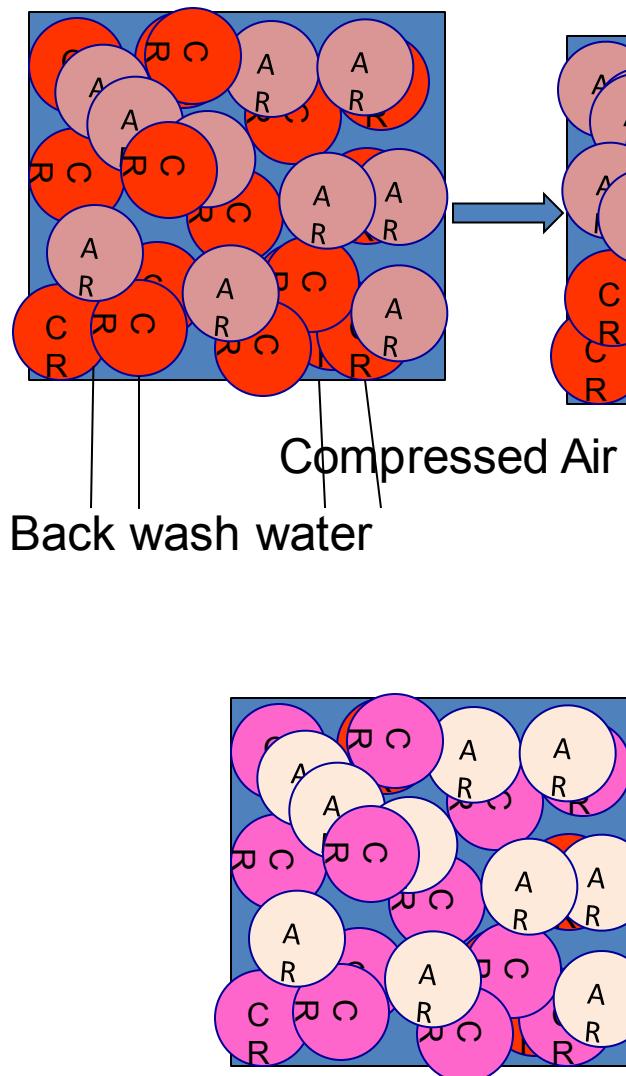


Mixed bed ion-exchanger

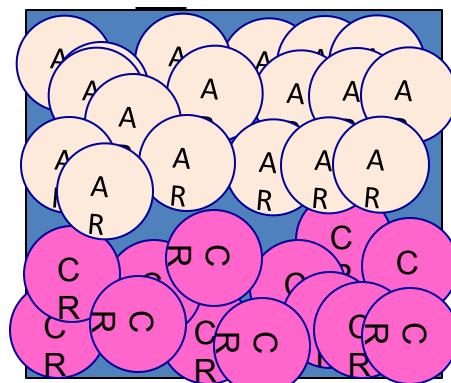
- Contains intimate mixture of cation and anion exchangers
- Water is in contact for a no. of times with the two exchangers alternatively



Mix bed to be regenerated



Forcing with
Compressed air
for mixing



After wash it is regenerated

Regenerated Mix bed read for use

- The mixed bed deionizer consist of cation and anion exchange resins mixed together in a single pressure vessel.
- When water is passed through mixed bed it comes in contact, a number of times, with the two kinds of exchanges alternatively. As a result the net effect of mixed bed exchanger is equivalent to passing water through a series of several cation and anion exchangers.
- The quality of water obtained from mixed bed is appreciably higher than the water produced from two bed plants.
- Mixed bed exchange produce water with hardness less than 1 ppm

Regeneration:

The mixed bed is back washed by forcing water in the upward direction. This separate the cation and anion exchanges from the mixed bed. Being lighter the cation resin occupies upper part and the denser one at the bottom. Now they layers will be washed with NaOH and H₂SO₄ respectively to regenerate anion and cation exchange resins. After regeneration again they are mixed by forcing compressed air.

Generally soften water (eg RO, etc) will be further purified by this method

Advantages & Disadvantages of ion-exchange process

o **Advantages:**

- Can be used for highly acid and highly alkaline water
- Residual hardness of water is as low as 2 ppm.
- Very good for treating water for high pressure boilers

o **Disadvantages:**

- Expensive equipment and chemicals
- Turbidity of water should be < 10 ppm. Otherwise output will reduce; turbidity needs to be coagulated before treatment.
- Needs skilled labour

Water for domestic use

■ Drinking or potable water

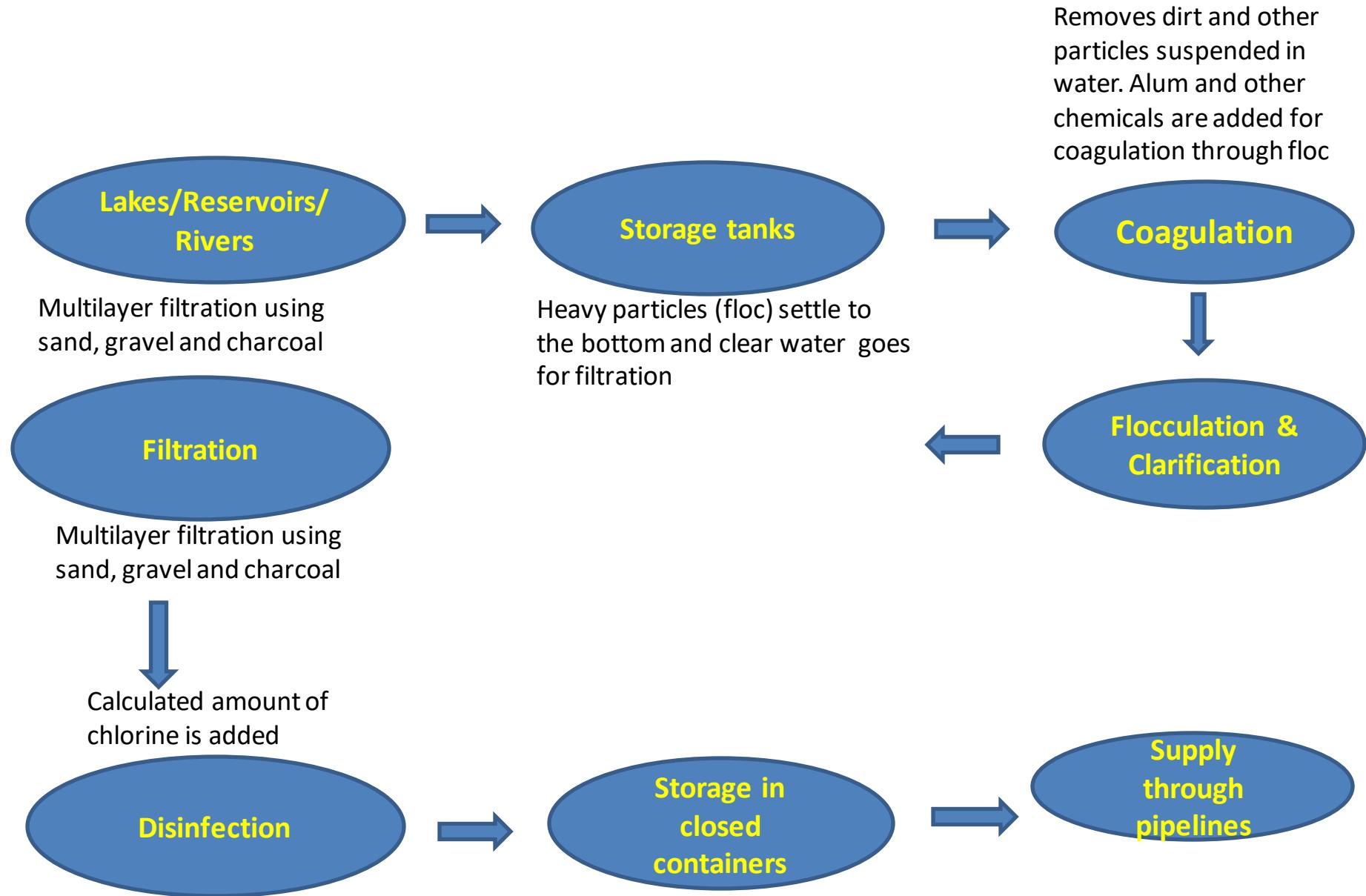
Drinking or potable water should be safe to drink and should satisfy the following requirements:

- ◊ Sparklingly clean and odorless.
- ◊ Pleasant in taste.
- ◊ Perfectly cool.
- ◊ Turbidity should not exceed 10 ppm.
- ◊ Free from dissolved gases like H₂S.
- ◊ Free from minerals like Pb, As, Cr and Mn salts
- ◊ Alkalinity should not be too high (pH should be around 8.0).
- ◊ Should be reasonably soft.
- ◊ Total Dissolved Solids (TDS) should be less than 500 ppm.
- ◊ Free from disease producing pathogenic micro-organisms.

Specifications of different materials in drinking water (ICMR and WHO)

S.No.	Parameter/Material	WHO Standards/ppm	ICMR/BIS Standards/ppm
1	Colour	Clear	Clear
2	Odour	Pleasant	Pleasant
3	Turbidity	2.5	2.5
4	pH	6.0 – 8.5	6.0 – 8.5
5	TDS	300	500
6	Total Hardness as CaCO ₃	200	300
7	Calcium	75	75
8	Chlorides	200	200
9	Sulphates	200	200
10	Fluoride	0.5	1.0
11	Mercury	0.006	0.001
12	Cadmium	0.003	0.01
13	Arsenic	0.01	0.02
14	Chromium as hexavalent	0.01	0.1
15	Lead	0.01	0.01
16	E.Coli	No colony Should be present in 100 mL water	No colony Should be present in 100 mL water

Water treatment for municipal supply



Steps involved in water purification

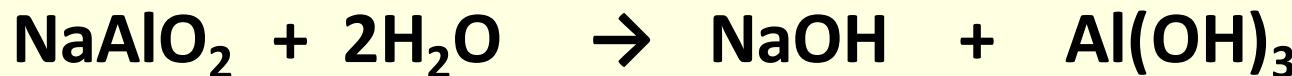
- **Removal of suspended impurities:**
 1. Screening
 2. Sedimentation with coagulation
 3. Filtration
- **Removal of micro-organisms:**
 1. By boiling the water
 2. By adding bleaching powder
 3. By chlorination
 4. Disinfection by ozone
 5. RO

Removal of suspended impurities

- **Screening:** Raw water is passed through screens having large number of holes which retain the floating particles
- **Sedimentation:** Removes suspended particles
 - Water is allowed to stand undisturbed in big tanks (about 5m deep) where most of the suspended matter settles down in the bottom due to the force of gravity.
 - The retention period of water in the tank ranges from 2-6 hours
 - Supernatant water is pumped off.
- **Sedimentation with Coagulation:** To remove colloidal and fine clay particles, coagulant is added before sedimentation
 - Coagulants form insoluble gelatinous flocculent precipitate which adsorb and entangles very fine suspended impurities and forms larger flocks which settle down in the bottom

- Alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$), Sodium Aluminate ($NaAlO_2$) and Ferrous sulphate ($FeSO_4 \cdot 7H_2O$) used as coagulant

- Sodium Aluminate ($NaAlO_2$):



Gelatinous
flocculant

pH < 7



- Copperas or Ferrous sulphate ($FeSO_4 \cdot 7H_2O$):



Gelatinous
flocculant



Above pH=8.5, if alkalinity is not present, lime should be added

■ Alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$)

- Alum reacts in water in the presence of alkalinity of water.
- If the water is not alkaline, sufficient amount of lime should be added



Removal of suspended impurities

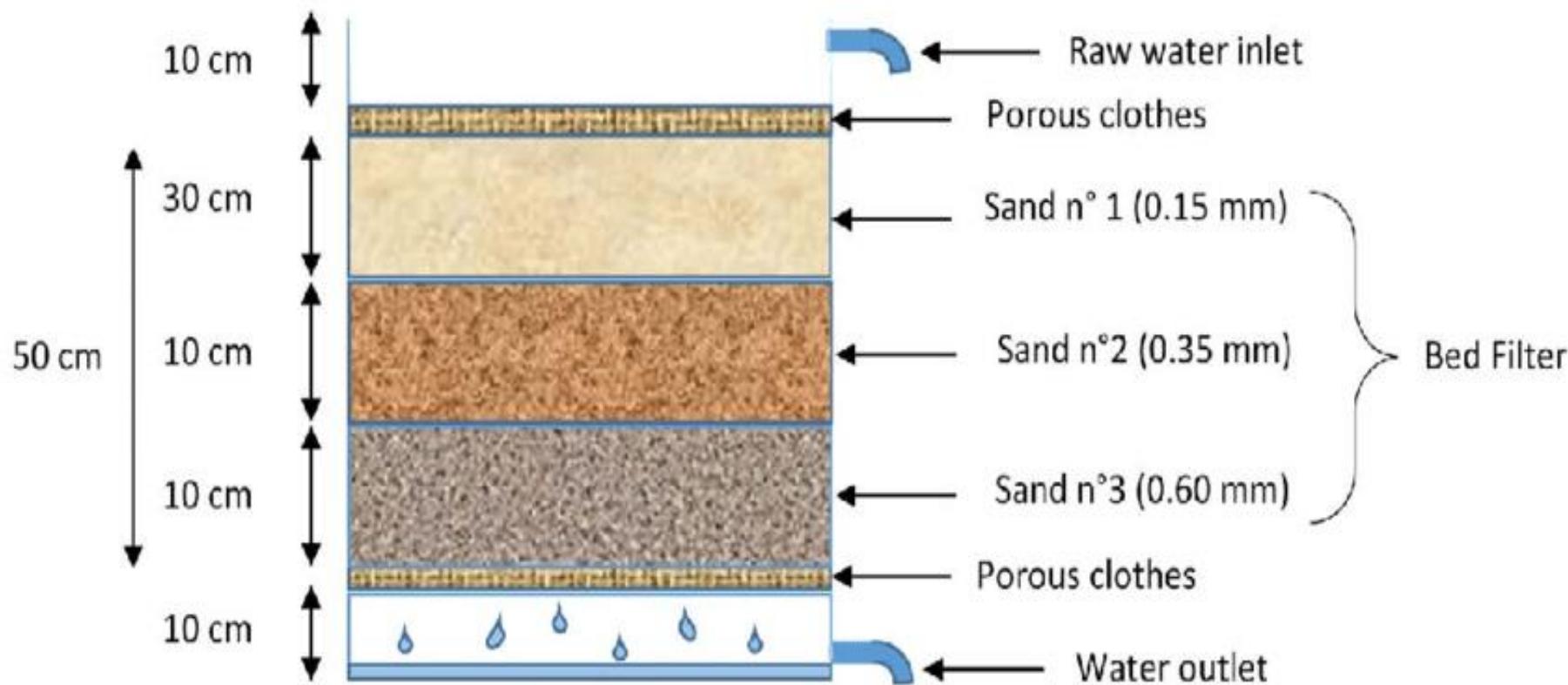
■ Sand filtration

- Filtration is the process of removing colloidal matter, and most of the microorganisms, etc by passing water through a bed of fine sand and other proper sized granular materials
- Filtration is carried out by passing water through an inlet through a bed of fine sand, coarse sand and granular materials
- The irregular pores in the sand filter hold the sediment particles thereby allowing the filtered water to pass through an underground drain
- When the flow rate of the filtered water becomes slow, the setup is stopped and about 2 to 3 cm of the top fine sand layer is scrapped off, replaced with clean sand and the filter is back to use again.

Slow sand filter

■ Working Principle

- Freshwater flows through a **sand-bed** with a thin layer populated by **microorganisms**. Hereby, the water gets purified through various biological, physical and chemical processes
- **100-300 litres per hour per m² of surface**



Disinfection (Sterilization)

Removal of bacteria is sterilization or disinfection. There are several important sterilization methods

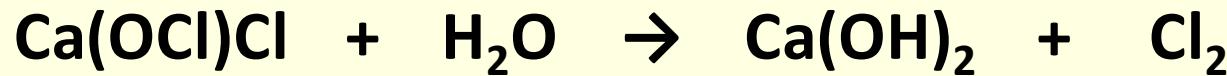
- Water contains the small percentage of pathogenic bacteria
- Drinking water must be freed from pathogenic bacteria and micro-organisms
- The process of destroying/killing the disease producing bacteria, micro-organism in drinking water is called disinfection
- The chemicals or substances – added to water for killing the bacteria – disinfectants
 - 1. By boiling
 - 2. By adding bleaching powder
 - 3. By chlorination
 - 4. By using chloramine
 - 5. By ozone
 - 6. Ultrafiltration
 - 7. Reverse Osmosis

- **By boiling water for 10-15 min.**

- kill only existing germs in water at the time of boiling
- does not provide any protection against future possible contamination
- very costly
- impossible to employ this in the **large scale systems**

Disinfection by bleaching powder treatment

- About 1kg of bleaching powder $[\text{Ca}(\text{OCl})\text{Cl}]$ per 1000 kiloliters of water is mixed
- The chemical action produces HOCl (Hypochlorous acid, a powerful germicide)

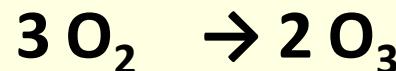


■ Disadvantages

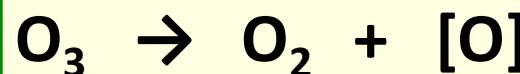
- Introduces Calcium in water, thereby making it more hard
- Bleaching powder deteriorates or decomposes within its storage time
- Excess of it gives a bad taste and smell to treated water

Disinfection by Ozone (ozonolysis)

- Ozone gas is a very good disinfecting agent.
- Produced by passing silent electric discharge through cold and dry oxygen



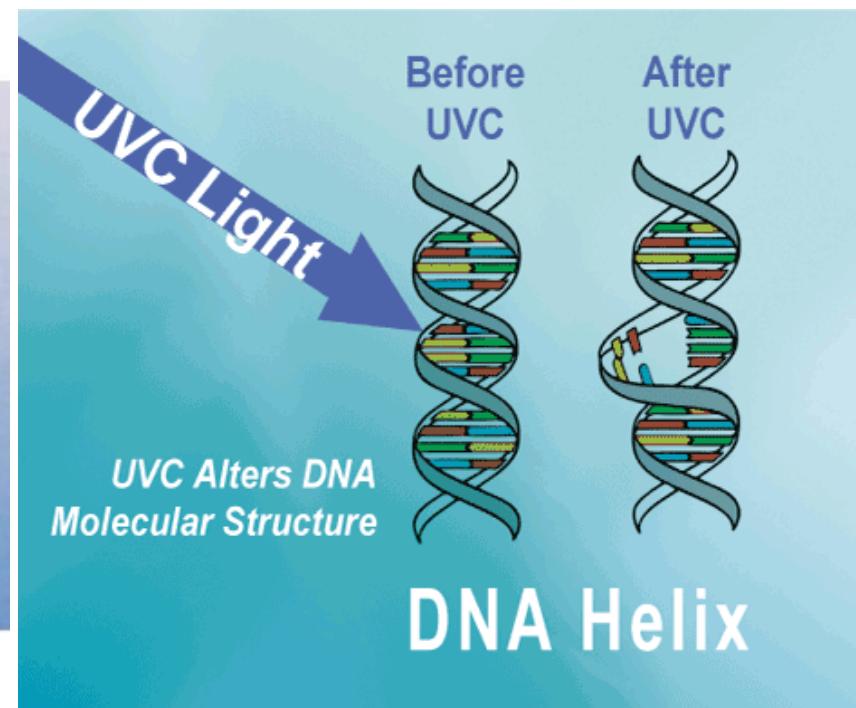
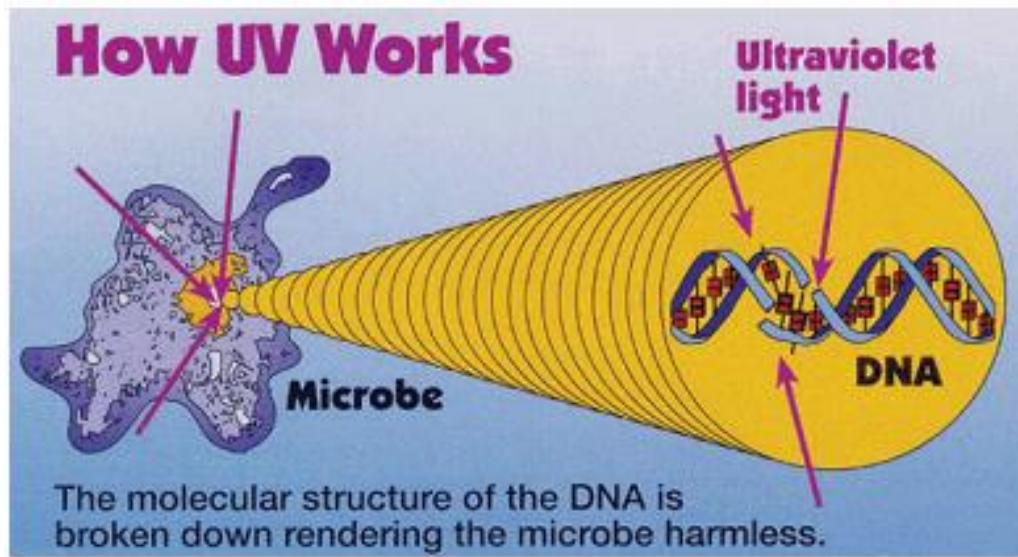
- Ozone is highly unstable and breaks down to give nascent oxygen



- Nascent oxygen is a powerful disinfecting agent and kills all the microorganisms and oxidizes the organic matter present in the water.
- Disadvantage: Expensive than chlorine, not employed for municipal water treatment.
- Advantages: simultaneous removal of color, smell and taste in water without giving any residue. Excess not harmful, since O_3 is unstable and decomposes to O_2

UV treatment

Disinfection of Drinking Water with Ultraviolet Light



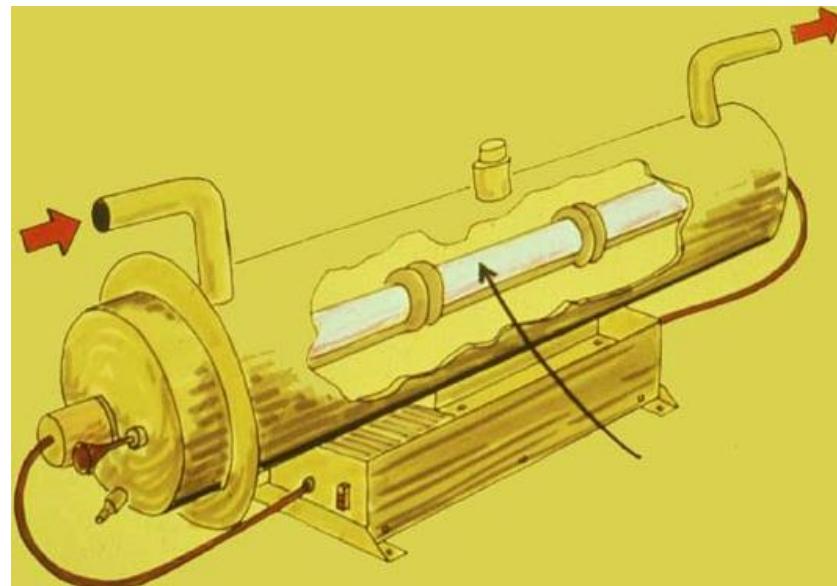
UV - Sterilizer

UV radiation

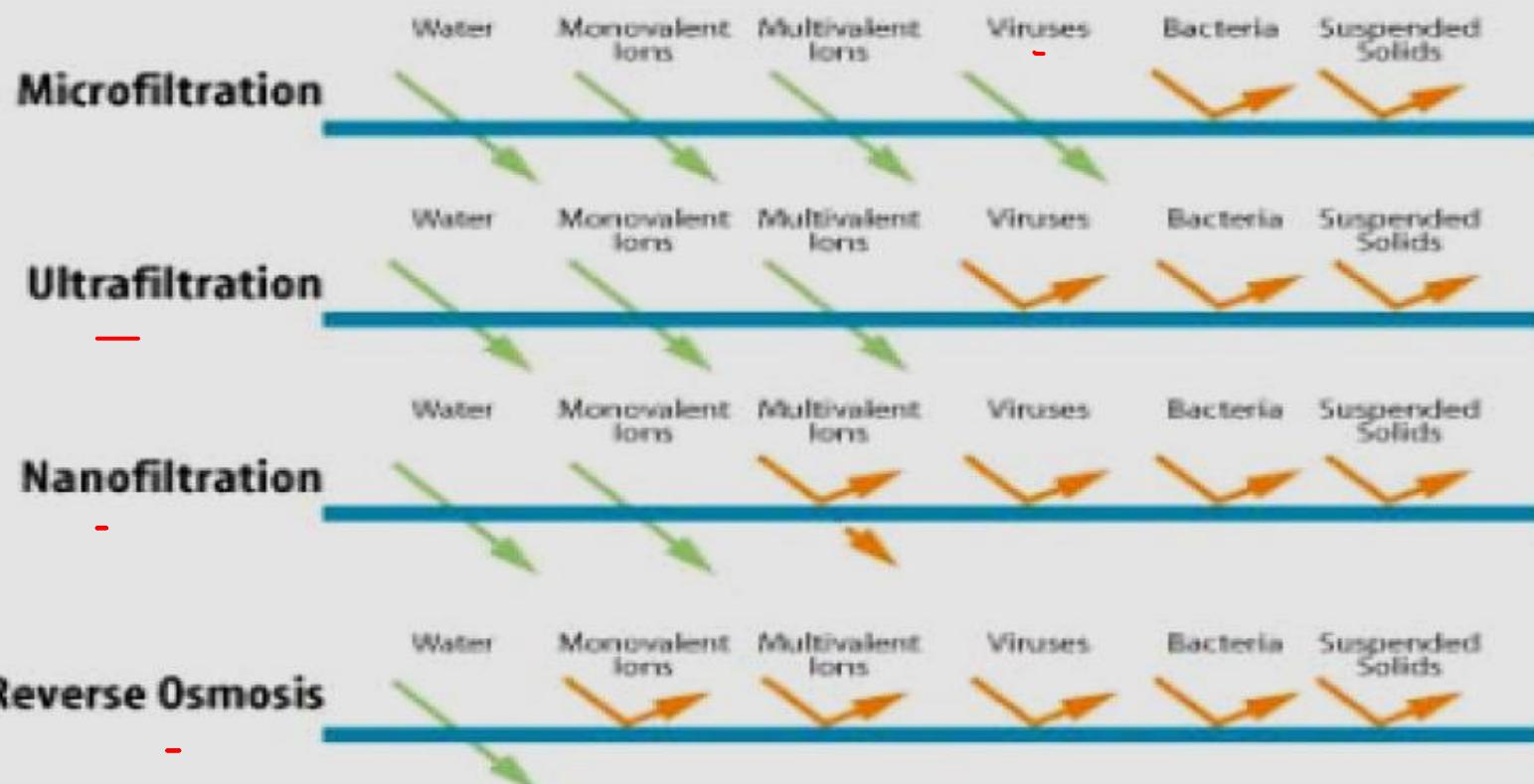
- Low pressure and medium pressure UV lamps are available
- reacts primarily with nucleic acids: pyrimidine dimers and other alterations

Primary uses:

Primary physical disinfectant



Water purification by Filtration process



Membrane Process Characteristics

Substances Removed From Water By Membrane Filtration Processes

The green arrow indicates that the particle is small enough to pass through the filter, whereas the deflected orange arrow indicates that the filter blocks the particle from passing through the filter.

Different filtration processes

A. Ultrafiltration:

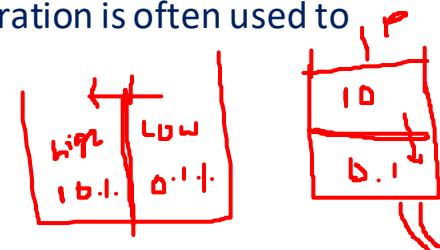
- An ultrafiltration filter has a pore size around 0.01 micron.
- A microfiltration filter has a pore size around 0.1 micron, so when water undergoes microfiltration, many microorganisms are removed, but viruses remain in the water. Ultrafiltration would remove these larger particles, and may remove some viruses.
- Neither microfiltration nor ultrafiltration can remove dissolved substances unless they are first adsorbed (with activated carbon) or coagulated (with alum or iron salts).

B. Nanofiltration

- A nanofiltration filter has a pore size around 0.001 micron.
- Nanofiltration removes most organic molecules, nearly all viruses, most of the natural organic matter and a range of salts.
- Nanofiltration removes divalent ions, which make water hard, so nanofiltration is often used to soften hard water.

C. Reverse osmosis

- Reverse osmosis filters have a pore size around 0.0001 micron.
- After water passes through a reverse osmosis filter, it is essentially pure water. In addition to removing all organic molecules and viruses, reverse osmosis also removes most minerals that are present in the water.
- Reverse osmosis removes monovalent ions, which means that it desalinates the water.



REVERSE OSMOSIS

- RO membranes give 96%-99% NaCl rejection. Greater than 95-99% of inorganic salts and charged organics will also be rejected by the membrane due to charge repulsion established at the membrane surface.
- RO membranes are made of polymers, cellulosic acetate and aromatic polyamide types.
- Applications:
 1. Potable water from sea or brackish water
 2. Ultra pure water for food processing and electronic industries
 3. Pharmaceutical grade water
 4. Water for chemical, pulp & paper industry
 5. Waste treatment etc.
 6. Municipal and industrial waste treatment

Reverse Osmosis

When two solutions of unequal concentrations are separated by a Semipermeable membrane, solvent will flow from lower conc. to higher conc. due to osmotic pressure

This phenomenon can be reversed by making the solvent to flow in the opposite direction by applying hydrostatic pressure on the concentrated side (Reverse Osmosis)

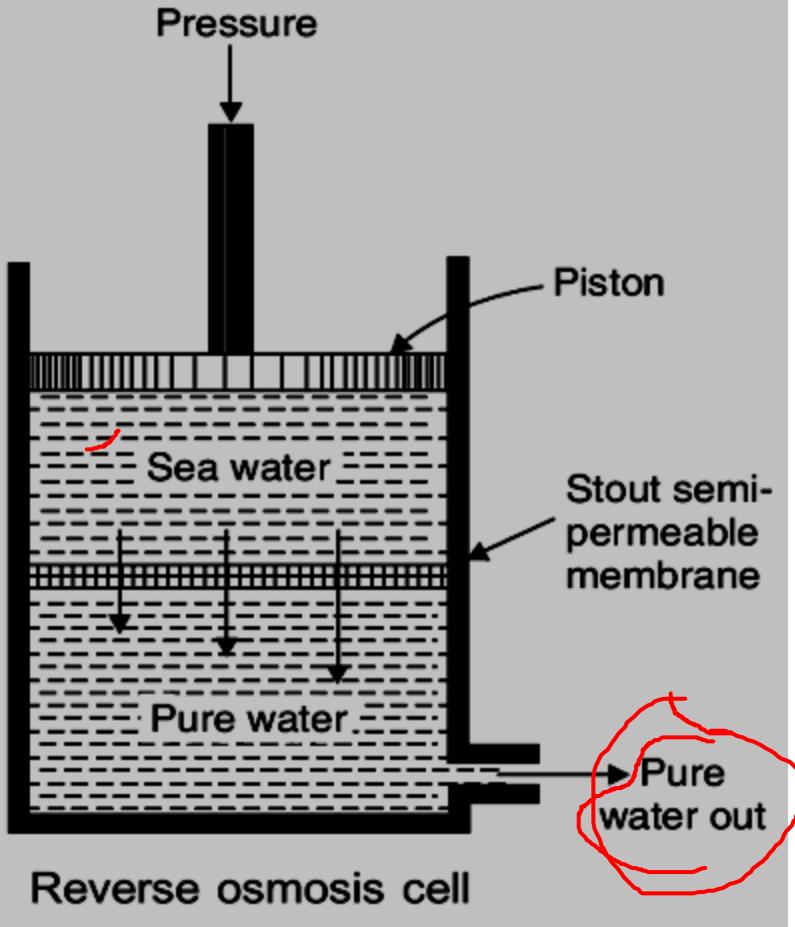
In reverse osmosis, pressure of 15-40 kg/cm² is applied on the contaminated water compartment.

The water gets forced through the semipermeable membrane leaving behind the dissolved solids.

Thus water is separated from the contaminants rather than removing contaminants from water.

Both ionic and non-ionic impurities as well as colloidal impurities are left behind.

This process is also called as "*Super-filtration*" or "*Hyper-filtration*"



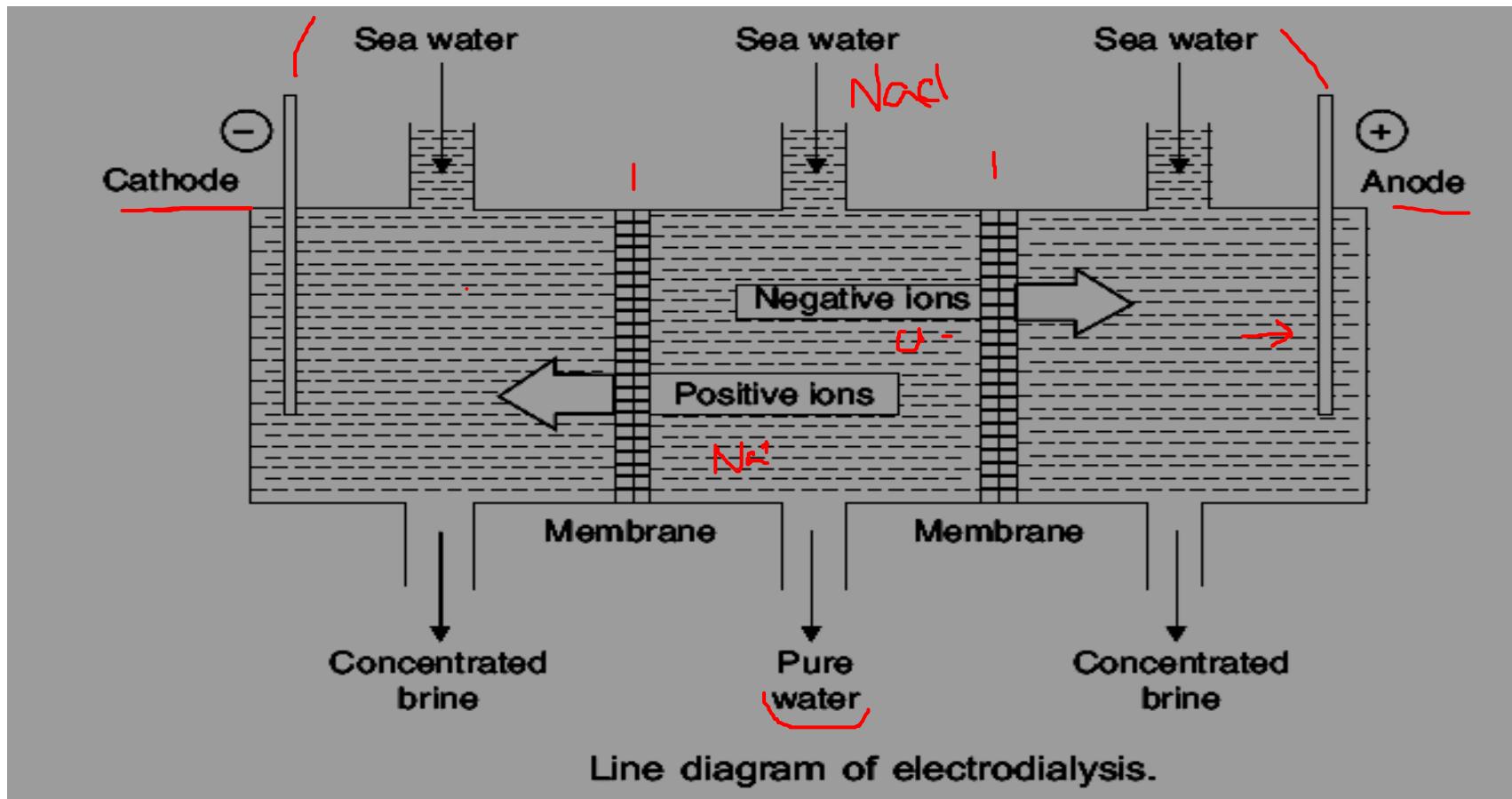
Advantages of Reverse Osmosis

- o Advantage is in removing ionic, non-ionic, colloidal and high molecular wt. organic matter.
- o It removes colloidal silica (which is not removed during demineralisation)
- o Cost is only the replacement cost of membranes (life is 2 years)
- o Membrane replacement is fast and hence uninterrupted water supply can be ensured
- o Because of the above reasons this process is being adopted for converting sea water into potable water and for high pressure boilers.
- o It can be used as desalination process for removing salt from sea water.

Desalination of brackish water

- Water containing dissolved salts with a peculiar salty (brackish) taste is brackish water
- The process of removing common salt from water is desalination
- Electrodialysis consists of a large container with two membrane separators, one permeable to positive ions and the other permeable to negative ions.
- In the outer compartments anode and cathode are arranged to pass DC Voltage.
- When DC voltage/current is passed through the cell, Na^+ will move towards cathode and Cl^- will move towards anode through the membrane.
- Hence, the concentration of salt decreases in the middle compartment and increases in the side compartments.
- Water from the middle compartment is collected and this water is desalinated water.

Electrodialysis diagram



For efficient separation, ion-selective membranes are used which selectively allow cations or anions to pass through them.

Candle filtration

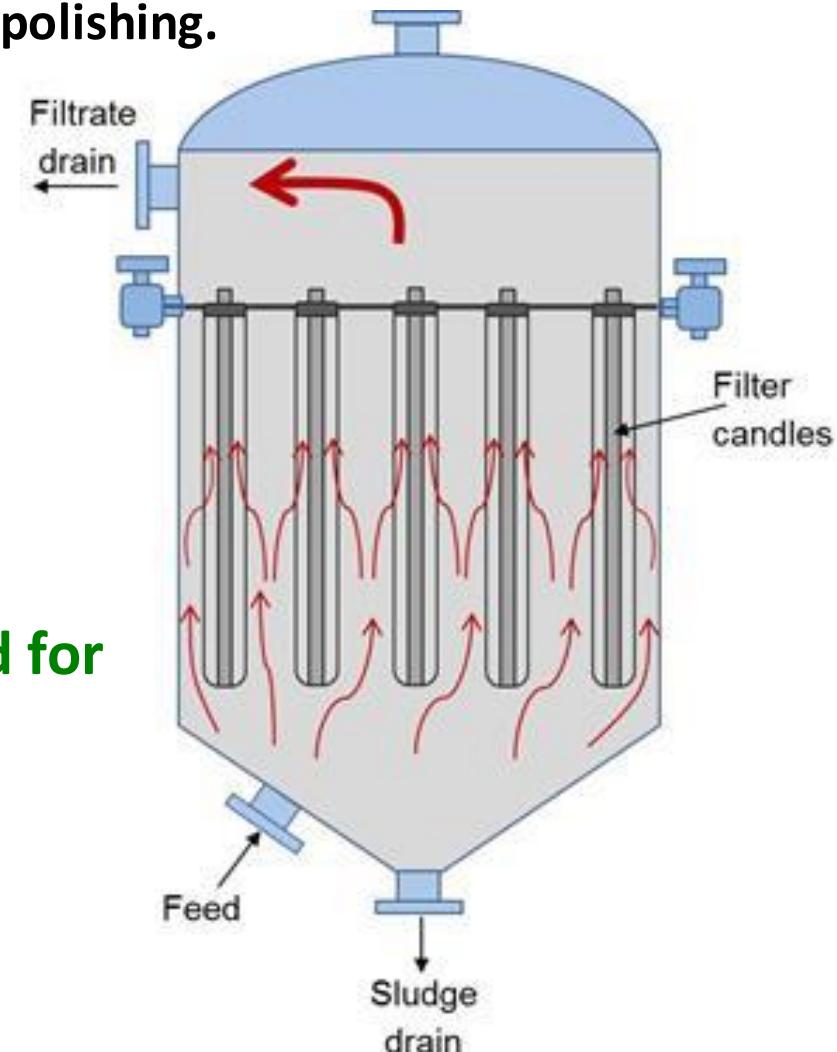
- The Candle Filters operate on a batch cycle and may be seen in process lines handling titanium dioxide, flue gas, brine clarification, red mud, china clay, fine chemicals and many other applications
- Candle filters are an alternative approach for removing fine particles.
- These are **rigid porous ceramic or metal barriers** that are usually suspended like candles in the flow stream.
- **The Candle Filter consists of following components:**
 - dip pipe for filtrates
 - perforated core with outer support tie rods,
 - filter sock for cake discharge mechanism
 - vessel
- Candle Filters are very well suited for handling flammable, toxic and corrosive materials

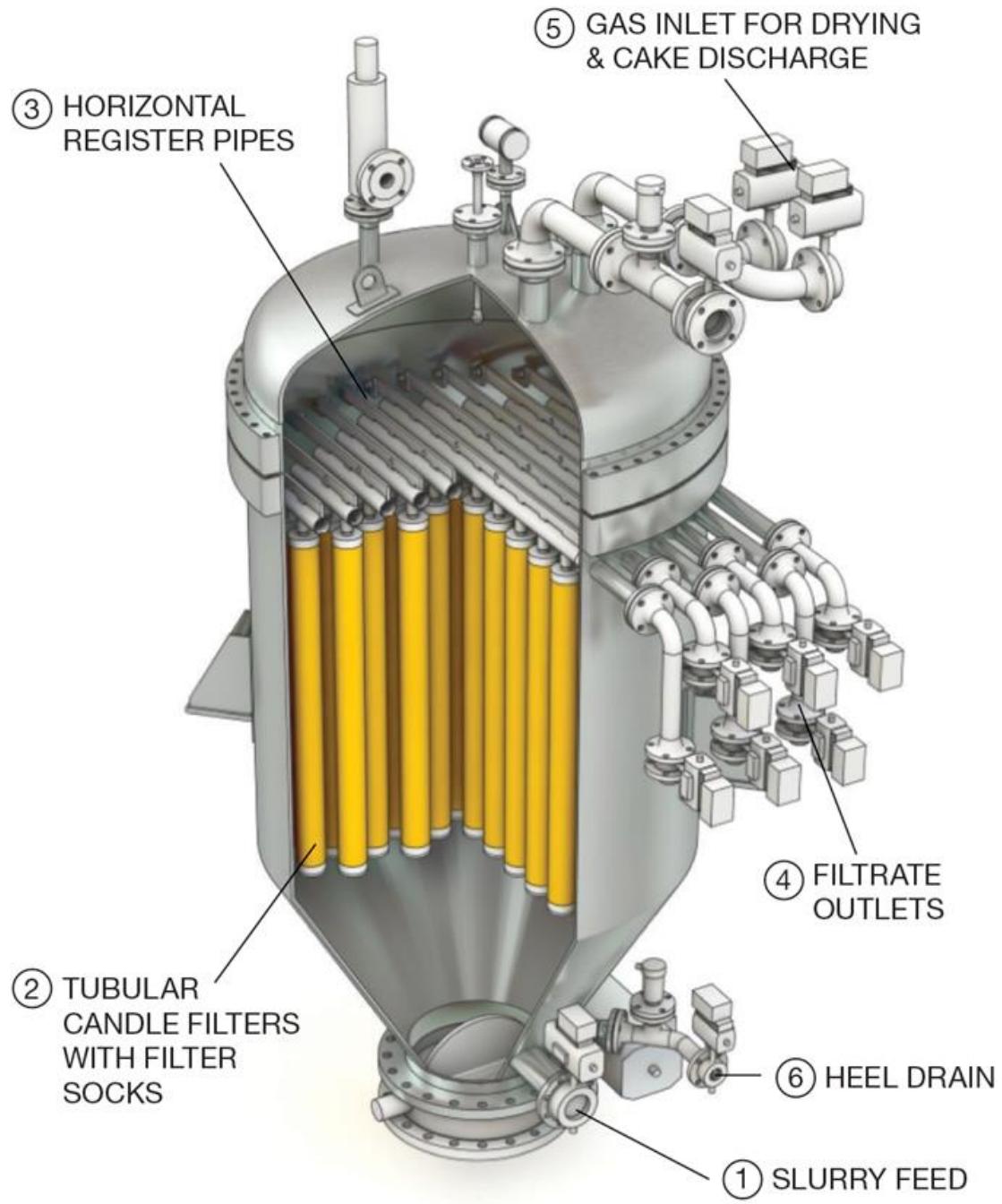
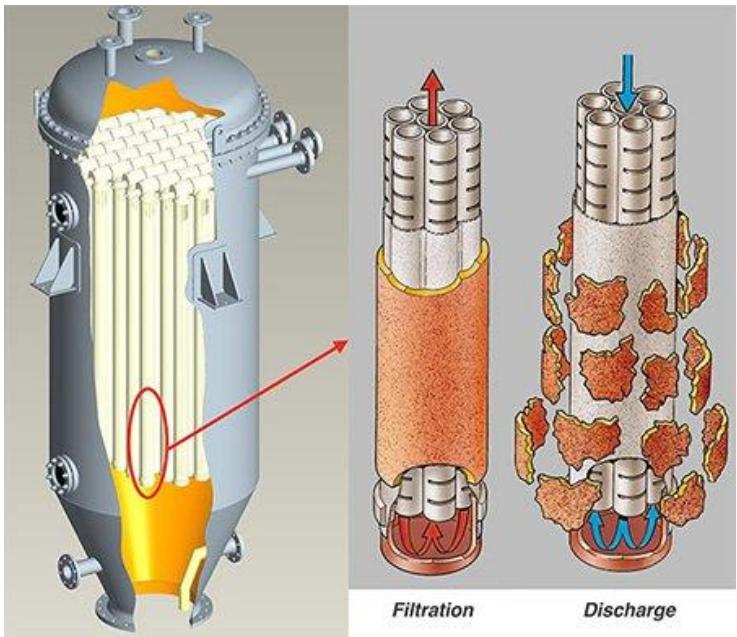
Candle Filtration

The Candle Filters are, like all pressure filters, operating on a batch cycle and may be seen in process lines handling titanium dioxide, flue gas, brine clarification, red mud, china clay, fine chemicals and many other applications that require efficient low moisture cake filtration or high degree of polishing.

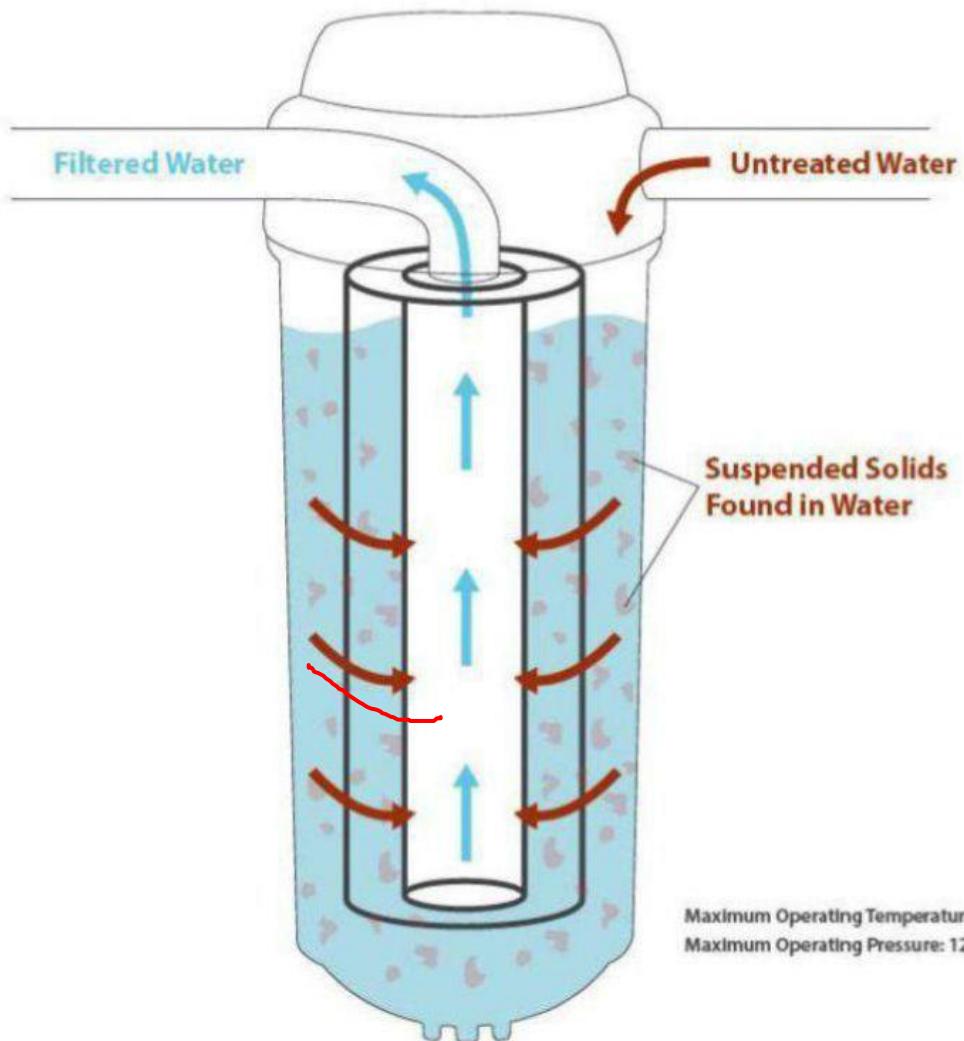
The Candle Filter consists of three major components:

- The vessel
 - The filtering elements
 - The cake discharge mechanism
-
- Candle Filters are very well suited for handling flammable, toxic and corrosive materials.





Filtration Process.



Maximum Operating Temperature: 100°F (38°C)
Maximum Operating Pressure: 125 Psi (8.61 Bars)

The cartridge structure traps & incinerates particles for easy disposal.
It can be used as pretreatment to residential and commercial RO systems.

Candle Filtration

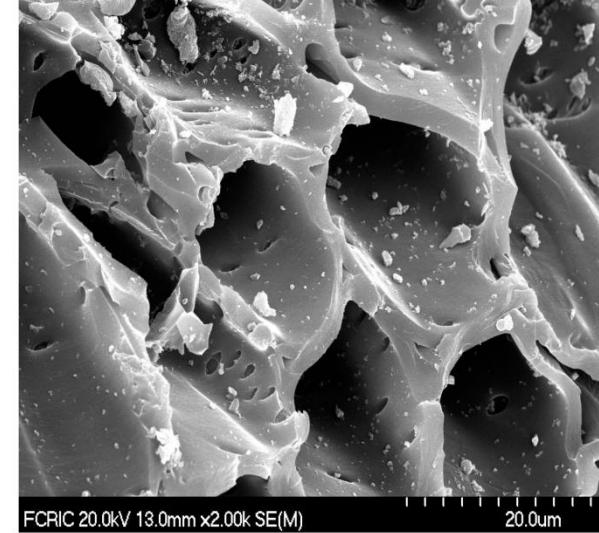
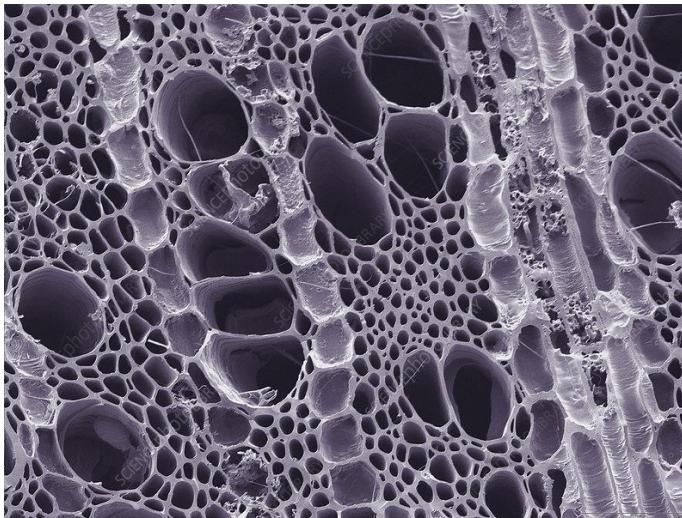
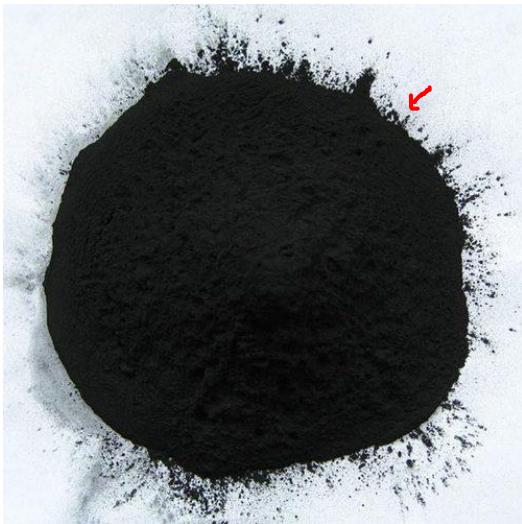
- **Advantages**
- Excellent cake discharge.
- Adapts readily to slurry thickening.
- Minimum floor space.
- Mechanically simple since there are no complex sealing glands or bearings.
- **Disadvantages**
- High headroom is required for dismantling the filtering elements.
- The emptying of the vessel in between cake filtration, washing and drying requires close monitoring of the pressure inside the vessel to ensure that the cake holds on to the candles.

Activated carbon filtration

- Activated carbon is produced from carbonaceous source materials such as **nutshells, coconut husk, peat, wood, coir, lignite, coal, etc.**
- Activated carbon is derived mostly from charcoal that has been treated with oxygen
- Activated carbon is a **highly porous material**; therefore, it has an **extremely high surface area** for contaminant adsorption.
- Two basic kinds of carbon filters **Granular Activated Carbon(GAC)** and **Solid Block Activated Carbon (SBAC)**
- Activated carbon **works via a process called adsorption**, whereby pollutant molecules in the fluid to be treated are trapped inside the pore structure of the carbon substrate
- **Most effective at removing chlorine, sediment, volatile organic compounds (VOCs), taste, color and odor from water**
- **Not effective in removing minerals, salts and dissolved inorganic compounds**

Activated carbon (AC)

- Extremely porous with high surface area: $500 \text{ m}^2/\text{g}$.
- The rate of adsorption for a surface area of a just one pound (0.45kg) of Activated Carbon is equal to 60-150 acres
- Coconut shells and coal (anthracite or bituminous) are both organic sources of activated carbon



- | | | |
|--------------------|--------------------|---------------------|
| ■ Water treatment | ■ Medicine | ■ Gold purification |
| ■ Air treatment | ■ Sewage treatment | ■ Metal extraction |
| ■ Gas purification | ■ Gas masks | ■ Filter masks |

Principal mechanisms for Purification

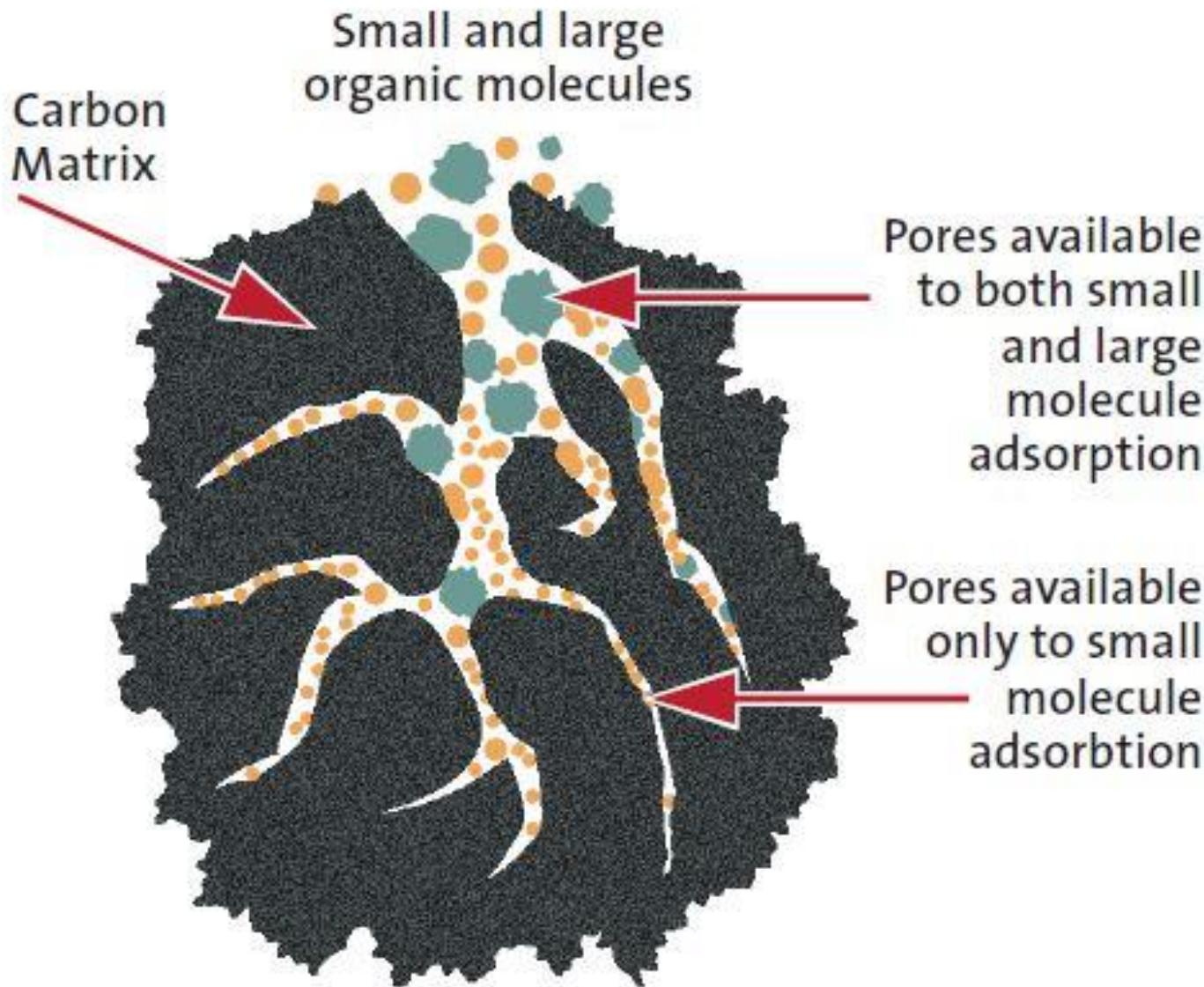
(a) physical removal , (b) adsorption and (c) catalytic reduction

- Physical removal of contaminant particles: Blocking any that are too large to pass through the pores (obviously, filters with smaller pores are more effective)
- Adsorption: By which a variety of dissolved contaminants are attracted to and held (adsorbed) on the surface of the carbon particles. The characteristics of the carbon material (particle and pore size, surface area, surface chemistry, density, and hardness) influence the efficiency of adsorption
- Organics are removed by adsorption. Organic material in public water supplies comes from decaying plant life, which becomes more soluble in water over time and exists as large, high-molecular weight organic acids.

■ Catalytic reduction: Residual disinfectants removal.

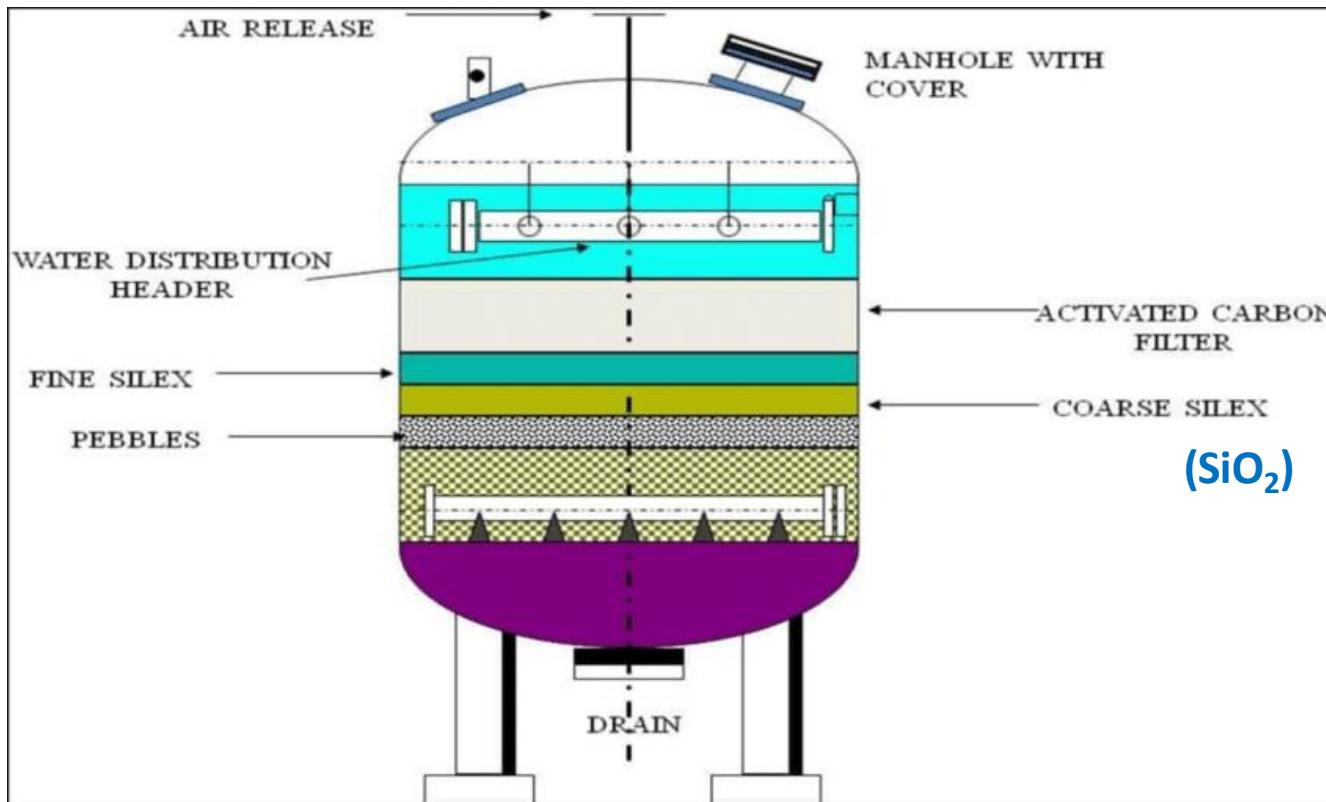
- Activated carbon can remove and destroy residual disinfectants (chlorine and chloramine) through a catalytic reduction reaction.
- This is a chemical reaction that involves a transfer of electrons from the activated carbon surface to the residual disinfectant.
- Activated carbon's removal of chlorine reduces the chlorine to a non-oxidative chloride ion. $\text{Cl}_2 \rightarrow 2\text{Cl}^-$
- The reaction is very fast and takes place in the first few inches of a new activated carbon bed. (Where removal of organics by activated carbon takes minutes, removal of chlorine literally takes seconds). Chloramine removal by activated carbon is a much slower reaction.
- The predominant species of chloramine in city water supplies (pH about 7 to 8) is monochloramine. The reaction with activated carbon and monochloramine also renders a non-oxidative chloride ion.

How activated carbon works for water filtration?

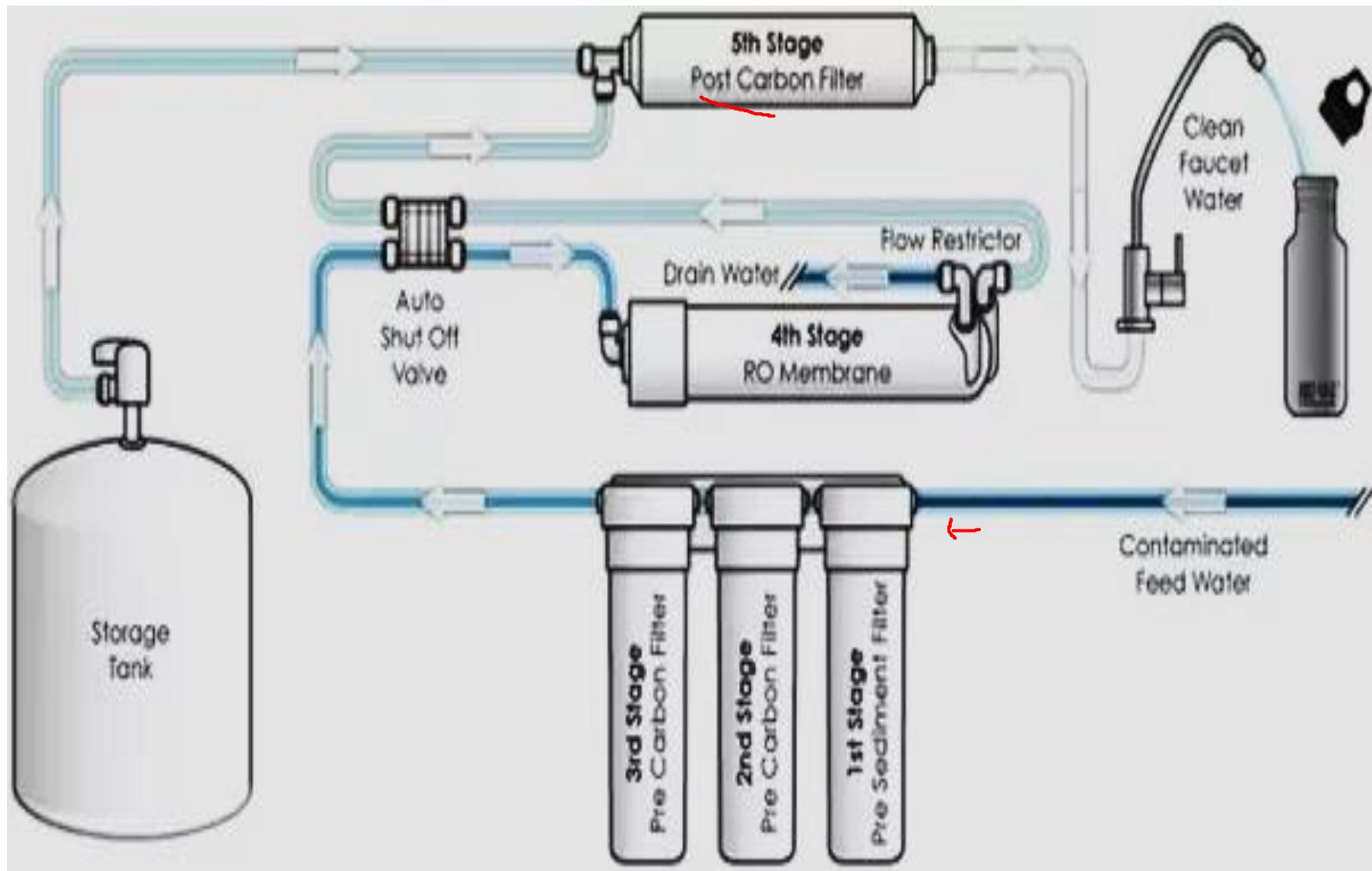


Activated Carbon Filtration

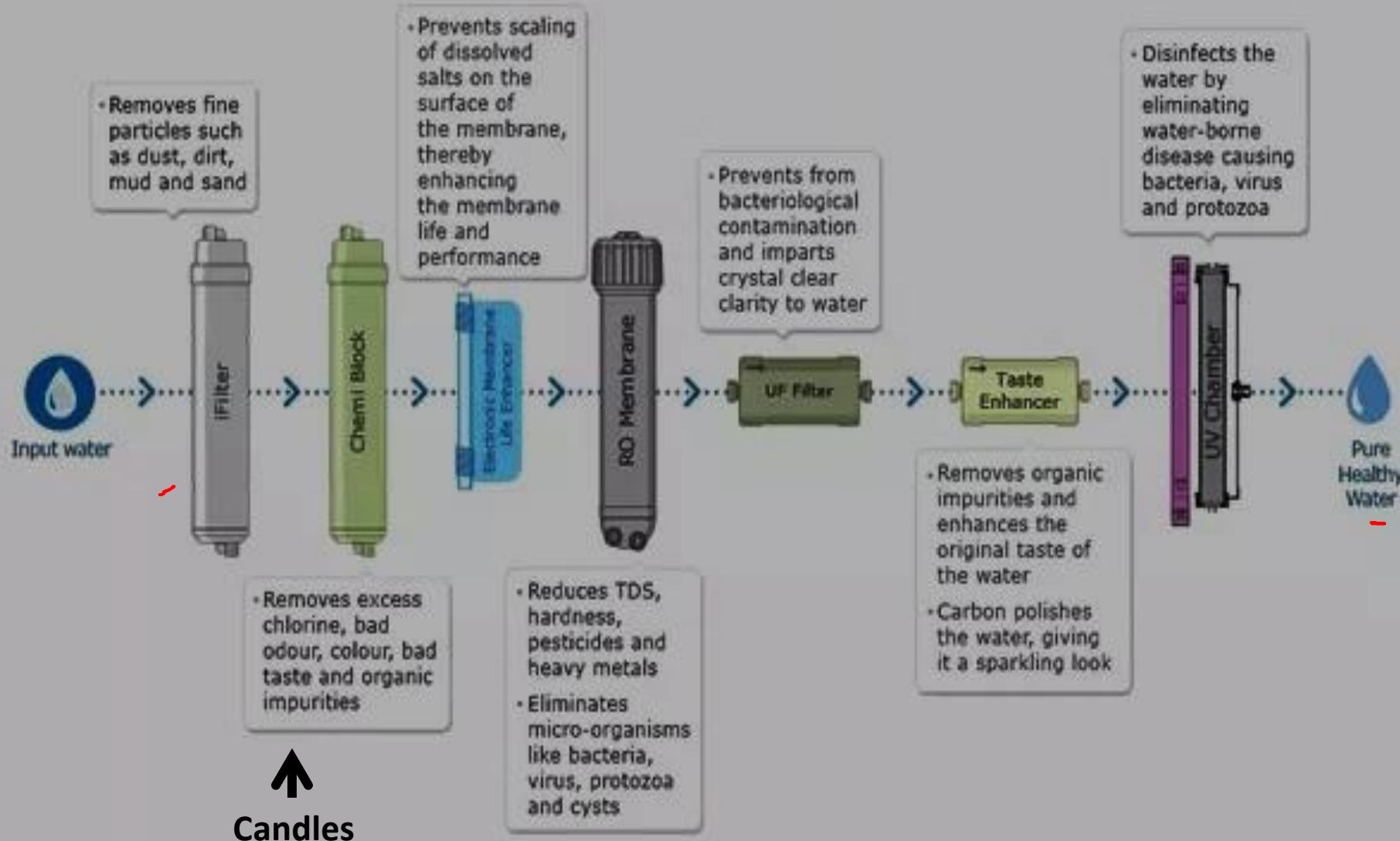
- Activated carbon filters are generally used in the process of removing organic compounds and/or extracting free chlorine from water.
- Coconut shells and coal (anthracite or bituminous) are both organic sources of activated carbon.



Domestic water purification system



Aquaguard Geneus Purification Process



Working Mechanism in the fabrication of Activated Carbon

- Carbon forms when an organic source is burned in an environment without oxygen. This process leaves only about 30% of the organic mass intact, driving off heavy organic molecules.
- Prior to being used for water treatment, the organic mass must then be "activated by either Steam Activation (800°C-1000°C) or Chemical Activation (a powerful dehydrating agent like phosphoric acid (P_2O_5) or zinc chloride ($ZnCl_2$)."
- The process of activation opens up the carbon's massive number of pores and further drives off unwanted molecules. The open pores are what allow the carbon to capture contaminants, through **adsorption**.
- The rate of adsorption for a surface area of a just one pound (0.45 kg) of Activated Carbon is equal to 60-150 acres!