

Chapter 1: Water

Impurities of water

I) Physical impurities II) Chemical impurities III) Biological impurities

I) Physical impurities

a) Colour:- Colour in water is mainly due to the presence of dissolved or colloidal or dispersed organic matter and metallic impurities like Fe, Mn, Cr etc.

Eg:- Yellowish tinge shows Presence of Cr and organic matter

Yellowish red shows presence of Fe

b) Turbidity:- Turbidity is due to colloidal, extremely fine suspension of clay, mud, dirt etc. It can be removed by sedimentation followed by coagulation, filtration etc.

C) Taste: It is due to presence of dissolved minerals in water.

E.g:-Bitter taste --- Presence of Fe, Al, Mn, sulphate or excess of lime

Soapy taste ---- Presence of NaHCO_3

d) Odour:- It is due to presence of living organism, dissolved gases, dead and decaying matter, industrial effluents containing aldehydes, phenols, ketones, esters etc.

II) chemical impurities:

a) Acidity:-It is caused by presence of free CO_2 , mineral acid and weakly dissociated acids.

b) Gases:- All Natural water contains dissolved CO_2 , its presence in water has no significance.

Presence of dissolved O_2 in industrial waste induces corrosion, but it is also essential for life of aquatic organism.

Dissolved NH_3 in water arises from decomposition of (aerobic and anaerobic) nitrogenous organic matter.

c) Mineral matter:- These includes salts of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , Mn^{2+} , CO_3^{2-} , HCO_3^- , Cl^- , F^- , SO_4^{2-} etc. They are responsible for alkalinity and hardness of water.

III) Biological impurities:-

a) Microorganism:- They are abundant in surface water but their count is low in deep water. Their growth takes place at temperature between $20\text{-}35^\circ\text{C}$.

In order to control microorganism chemical treatment like chlorination is done.

b) Water bodies: e.g Different groups of worms like flatworms, hair worms, tiny roundworms etc. They are harmful to human and fishes.

HARD WATER

"Water that produces very little lather and white curd like precipitate with soap is called hard water."

Hard water affects cleaning ability of soap. Hard water contains bicarbonate, chlorides and sulphates (any one or all) of calcium and magnesium.

SOFT WATER

"Water that produces lather with soap easily is called soft water. Soft water does not affect cleaning action of soap"

Hardness of water:

Q. What is meant by hardness of water? Distinguish between alkaline and non-alkaline water hardness.

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



White ppt of calcium sterate



White ppt of magnesium sterate



- Thus Hardness can be defined as, "**the soap consuming capacity of water sample.**"
- Other metal ions like Fe^{2+} , Mn^{2+} , and Al^{3+} also react with the soap in same manner, thus contributing to the hardness.
- But generally these are present in natural water only in traces.
- Hence, in practice, hardness of water sample is usually taken as a measure of its Ca^{2+} , Mg^{2+} content.
- When the hardness causing ions are removed as insoluble ppt, water becomes soft and forms lather.

Distinguish between hard water and soft water:

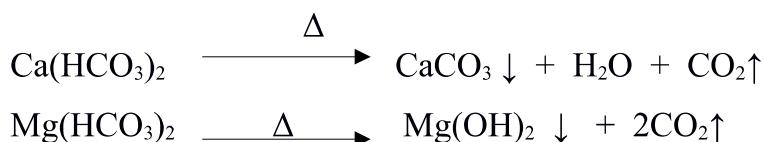
HARD WATER		SOFT WATER	
1	Water which does not produce lather with soap but forms a white curd, is called hard water.	1	Water which easily produces lather with soap is called soft water.
2	Hard water mainly contains dissolved salts of calcium and magnesium in it.	2	Soft water does not contain dissolved calcium and magnesium salts.
3	Hard water affects cleansing ability of soap and due to this a lot of soap is wasted during bathing and washing.	3	Soft water does not affect cleansing ability of soap and thus soap is not wasted.
4	Due to the presence of dissolved hardness causing salts, the boiling point of water is elevated. Hence more fuel and time are required for cooking.	4	Less fuel and time is required for cooking in soft water.
5	It is not safe for drinking as drinking hard water may affect digestive system.	5	It is safe for drinking.
6	Not suitable for industrial use.	6	Suitable for industrial use.

TYPES OF HARDNESS:

1. Temporary hardness
2. Permanent hardness

Temporary Hardness OR Carbonate Hardness OR Alkaline Hardness:

- Hardness due to bicarbonates and carbonates of Ca^{2+} , Mg^{2+} and other heavy metal ions is called as temporary hardness.
- Thus "Water that contains bicarbonates and carbonates of calcium and magnesium or of both is called temporary hard water."
- It is called alkaline hardness because the hardness causing salts like carbonates, bicarbonates and hydroxides of metals are alkaline in nature.
- Such hardness is removed by boiling followed by filtration.
- By boiling the bicarbonates are decomposed with the formation of insoluble carbonates with the evolution of CO_2 .



Permanent Hardness OR Non-carbonate Hardness OR non-alkaline hardness:

- Hardness due to chlorides, sulphates or nitrates of calcium, magnesium or other heavy metal ions is referred as permanent hardness.
- Thus water that contains chlorides, sulphates or nitrates of calcium or magnesium or of both is called Permanent hard water.
- This type of hardness thus can be removed by addition of lime $[\text{Ca}(\text{OH})_2]$ and / or soda $[\text{Na}_2\text{CO}_3]$ which precipitates the insoluble carbonate, which can be removed by filtration.

Total Hardness:

$$\text{Total hardness} = \text{Permanent hardness} + \text{Temporary hardness.}$$

Q. Distinguish between Permanent hardness & Temporary hardness

Temporary hardness		Permanent hardness	
1	Hardness due to bicarbonates of Ca^{2+} , Mg^{2+} and other heavy metal ions is called as temporary hardness.	1	Hardness due to chlorides or sulphates or nitrates of calcium, magnesium or other heavy metal ions is referred as permanent hardness.
2	It is called as carbonate hardness.	2	It is called as non carbonate hardness.
3	It is called alkaline hardness because the hardness causing salts like carbonates, bicarbonates and hydroxides of metals are alkaline in nature.	3	It is called non alkaline hardness.
4	Such hardness is removed by boiling followed by filtration.	4	Such hardness cannot be removed by boiling. It can be removed by various other processes like lime-soda method, ion exchange etc.
5	Temporary hardness leads to the formation of loose deposits of carbonates and hydroxides of Ca^{2+} , Mg^{2+} respectively if used in boilers.	5	Permanent hardness leads to the formation of adherent scales.

Degree of Hardness:

What is degree of hardness of water? Why do we express hardness of water in terms of calcium carbonate equivalent?

Degree of hardness is commonly defined as the total quantity of hardness causing salts present in water.

Hardness is usually reported as an equivalent quantity of calcium carbonate (CaCO_3) because, molecular weight of CaCO_3 is 100, so the calculation becomes easy and it is the most common insoluble precipitate formed in most of the water treatments.

The calcium carbonate equivalent of any hardness causing compound can be calculated as follows:

$$\text{Equivalent of } \text{CaCO}_3 = \frac{\text{Weight of hardness producing substance} \times \text{Chemical Equivalent of } \text{CaCO}_3 (= 50)}{[\text{Chemical equivalent of hardness producing substance}]}$$

Here, Multiplication factor = $\frac{\text{Chemical equivalents of } \text{CaCO}_3 (= 50)}{\text{Chemical equivalent of hardness producing substance}}$

Units of Hardness:

Mention the common units used for expressing hardness of water. Define ppm. What is the relation between ppm and mg/lit.

Degree of hardness of given sample of water can be expressed in following different ways:

Parts per million (ppm)

It is the number of parts by weight of Calcium carbonate equivalent present per million parts by weight of water.

$$1 \text{ ppm} = \frac{1 \text{ part by weight of } \text{CaCO}_3 \text{ equivalent}}{10^6 \text{ parts by weight of water}}$$

Milligram per litre (mg/lit)

It is the number of milligrams of Calcium carbonate equivalent hardness present per litre of water.

$$1 \text{ mg/L} = \frac{1 \text{ mg of } \text{CaCO}_3 \text{ equivalent}}{\text{Litres of water}}$$

Relation between ppm and mg/L:

$$1 \text{ ppm} = 1 \text{ mg/L}$$

Numerical problems based on Calculation of hardness

Solved problem

1. Calculate the hardness of given sample of water containing following dissolved salts per litre.

$$\text{CaSO}_4 = 15.2 \text{ mg/litre}, \text{Mg}(\text{HCO}_3)_2 = 2.4 \text{ mg/litre}, \text{MgCl}_2 = 8.5 \text{ mg/litre}$$

Solution:

Step I: Calculation of CaCO_3 equivalent

Constituent s	Quantity	Molecular weight	Multiplication Factor	CaCO_3 Equivalent
CaSO_4	15.2mg/litre	136	$100/2/136/2$	$15.2 \times 100/136 = 11.18 \text{ mg/litre}$
$\text{Mg}(\text{HCO}_3)_2$	2.4 mg/litre	146	$100/2/146/2$	$2.4 \times 100/146 = 1.64 \text{ mg/litre}$
MgCl_2	8.5 mg/litre	95	$100/2/95/2$	$8.5 \times 100/95 = 8.94 \text{ mg/litre}$

Step II: Calculation of Temporary hardness

$$\begin{aligned} \text{Temporary hardness} &= \text{Hardness due to } \text{Mg}(\text{HCO}_3)_2 \\ &= 1.64 \text{ mg/litre or ppm} \end{aligned}$$

Step III: Calculation of permanent hardness

$$\begin{aligned} \text{Permanent hardness} &= \text{Hardness due to } \text{CaSO}_4 \text{ and } \text{MgCl}_2 \\ &= 11.18 + 8.94 \\ &= 20.12 \text{ mg/litre or ppm} \end{aligned}$$

Step III: Calculation of Total hardness

$$\begin{aligned} \text{Total hardness} &= \text{Temporary hardness} + \text{Permanent hardness} \\ &= 1.64 + 20.12 \\ &= 21.76 \text{ mg/litre or ppm} \end{aligned}$$

Problems for Practice

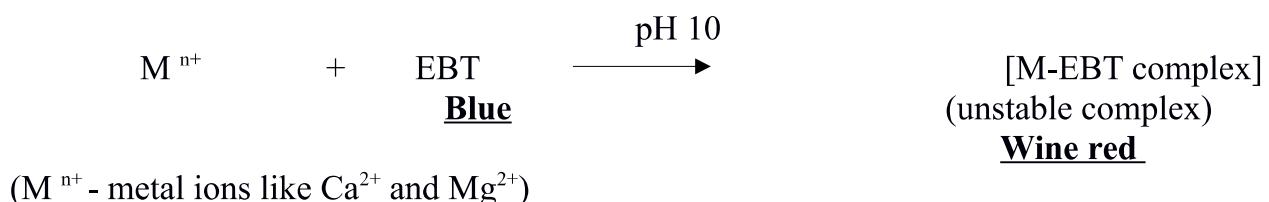
- Calculate the temporary and permanent hardness in water from the following data.
 $Mg(HCO_3)_2 = 14.6 \text{ mg/litre}$, $Ca(HCO_3)_2 = 8.1 \text{ mg/litre}$, $Mg(NO_3)_2 = 29.6 \text{ mg/litre}$,
 $MgSO_4 = 24 \text{ mg/litre}$, $MgCl_2 = 19.0 \text{ mg/litre}$.
Ans: Temporary Hardness- 15 ppm, Permanent Hardness- 60 ppm
- Calculate the temporary and total hardness of a sample of water containing following salts:
 $Mg(HCO_3)_2 = 7.3 \text{ mg/litre}$, $Ca(HCO_3)_2 = 16.2 \text{ mg/litre}$, $MgCl_2 = 9.5 \text{ mg/litre}$, $CaSO_4 = 13.6 \text{ mg/litre}$.
Ans: Temporary Hardness- 15 ppm, Permanent Hardness- 20 ppm
- Three water samples A, B, C were analyzed for their salt content. Sample A was found to contain 168 mg/litre $MgCO_3$. Sample B was found to contain 82 mg/litre of $Ca(NO_3)_2$ and 2 mg/litre silica, sample C was found to contain 20 mg/litre of potassium nitrate and 20 mg of $CaCO_3$ per 500 ml. Determine the hardness in all the above three water samples A, B, C.
Ans: Hardness in A = 200 ppm, B = 50 ppm, C = 40 ppm.
- Calculate the temporary and permanent hardness of a water sample having the following analysis.
 $Mg(HCO_3)_2 = 73 \text{ mg/litre}$, $MgCl_2 = 95 \text{ mg/litre}$, $Ca(HCO_3)_2 = 162 \text{ mg/litre}$, $CaSO_4 = 136 \text{ mg/litre}$, $CaCl_2 = 111 \text{ mg/litre}$, $NaCl = 100 \text{ mg/litre}$.
- A water sample contains: $Ca(HCO_3)_2 = 32.4 \text{ mg/litre}$, $Mg(HCO_3)_2 = 29.2 \text{ mg/litre}$, $CaSO_4 = 13.5 \text{ mg/litre}$. Calculate the temporary, permanent and total hardness.
- How many gms of $CaCl_2$ dissolved per liter gives 150 ppm of hardness? (Dec 2011)
Ans: 0.1665 g/L
- How many grams of $FeSO_4$ dissolved per litre gives 210.5 ppm of hardness? (At. wt.: Fe – 56, S – 32, Ca – 40, O – 16, C – 12) **Ans.** 0.319 g/L.
- Two samples of water were analyzed for their salt content:
i) Sample A was found to contain 168 mg $MgCO_3$ per litre.
ii) Sample B was found to contain 820 mg $Ca(NO_3)_2$ per litre and 2 mg SiO_2 per litre.
Calculate the total hardness of each sample and state which sample is more hard.
Ans. A = 200 ppm, B = 500 ppm
- Classify the following salts into temporary and permanent hardness causing salts and also calculate their calcium carbonate equivalent
 - $Ca(HCO_3)_2 = 16.2 \text{ mg/litre}$
 - $MgSO_4 = 1.2 \text{ mg/litre}$
 - $FeCl_2 = 12.7 \text{ mg/litre}$
 - $NaCl = 94 \text{ mg/litre}$

Estimation of Hardness of water by EDTA method (complexometric method)

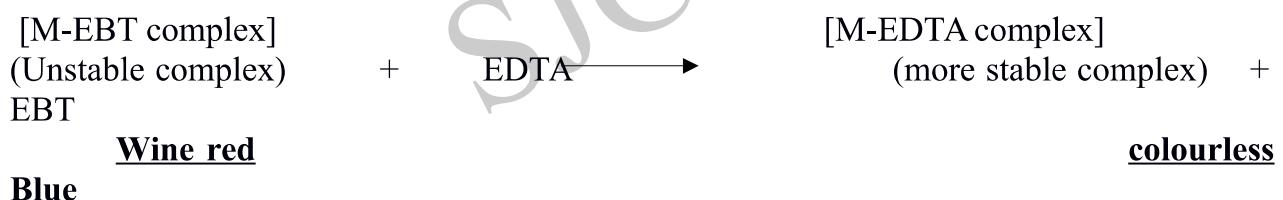
This method is also called as complexometric methods since it involves metal complex with reagent used in the determination.

Principle:

The EDTA method for determination of total hardness of water is based on the fact that when blue dye Eriochrome Black T is added to hard water in alkaline medium (buffer pH 10), it gives a wine red coloured unstable complex with metal ions like Ca^{2+} and Mg^{2+} .



When sodium salt of EDTA is added to the flask content, since EDTA has more affinity to form stable complex with metal ions, the metal-EBT unstable complex (wine red) dissociates to form more stable metal-EDTA complex (colourless), releasing the EBT dye (blue colour).



If some free metal ions are present in the flask solution, then they will react with this EBT dye forming M-EBT complex again which in turn reacts with EDTA to form stable complex. When all these free ions are reacted, the last drop of EDTA gives end point of the titration, i. e. colour change from wine red to blue. Thus amount of EDTA used corresponds to the hardness of water.

Why to use buffer of pH 10?

The colour of dye metal complex (M-EBT) and dye (EBT) are different. However change in pH is sharper at pH 10 than at other pH ranges. The metal dye complex has wine red colour at pH 10 while dye itself is blue colour at pH 10. Also the M-EDTA complex has high stability at pH 10.

Various steps involved in this are:

1. Preparation of solutions:

This step involves preparation of standard hard water, buffer solution, EBT indicator and EDTA solution.

{Preparation of standard hard water:

Dissolve 1.0 gm of pure and dry CaCO_3 in minimum quantity dil. HCl and then evaporate the solution to dryness on a water bath. Dissolve the solution in a distilled water to make 1 litre solution. (So that each ml of this solution contains 1 mg. CaCO_3 equivalent hardness)

Preparation of Buffer solution:

Add 67.5 gm of NH_4Cl to 570 ml of concentrated (liquor) ammonia solution and then dilute with distilled water to 1 lit.

Preparation Eriochrome Black T:

Dissolve 0.5 gm of Eriochrome Black T in 100 ml of pure alcohol. 2 to 3 drops of indicator are sufficient.

Preparation of EDTA:

Dissolve 4 gm of EDTA in 1 lit of distilled water & 0.1 gm of MgCl_2 is generally added to ensure proper colour development with dye.

Student need not have to explain these steps. This is only for their understanding}

2. Standardization of EDTA

Rinse and fill the Burette with EDTA solution. Pipette out 50 ml of standard hard water in a conical flask. Add to it 5-10 ml of buffer solution and 4-5 drops of indicator. Titrate the flask solution with EDTA solution till wine red colour changes to clear blue.

Let the volume of EDTA solution used be V_1 ml.

3. Titration of unknown hard water (for Total hardness)

Titrate 50 ml of sample water using Eriochrome Black T indicator exactly in the above manner.

Let the volume of EDTA solution used be V_2 ml.

4. Titration of boiled water sample (for permanent hardness)

Boil 250 ml of sample water in a beaker till the volume is reduced to 50 ml to convert all the bicarbonates into carbonate. Filter off the precipitate with distilled water and collect the filtrate and washings in 250 ml of measuring flask.

Make up the volume 250 ml with distilled water. Titrate 50 ml of this solution against EDTA solution using Eriochrome Black T as indicator.

Let the volume of EDTA solution used be V_3 ml.

Numerical problems based on Determination of hardness by EDTA method:

Solved problem

1. 50 ml of standard hard water containing 1 mg of pure CaCO_3 per ml consumed 20 ml of EDTA solution. 50 ml of the given water sample required 25 ml of same EDTA solution. 50 ml of the boiled sample required 15 ml of EDTA solution. Calculate total, permanent and temporary hardness of water sample.

Solution:

Step I: Determination of strength of EDTA solution.

$$1 \text{ ml of standard hard water} = 1 \text{ mg CaCO}_3$$

$$50 \text{ ml standard hard water} = 50 \text{ mg of CaCO}_3 \dots\dots\dots (1)$$

$$\text{Also, } 50 \text{ ml standard hard water} = 20 \text{ ml EDTA solution} \dots\dots\dots (2)$$

From equation (1) and (2),

$$20 \text{ ml EDTA solution} = 50 \text{ mg CaCO}_3$$

$$1 \text{ ml EDTA} = 50 / 20 = 2.5 \text{ mg of CaCO}_3$$

Step II: Calculation of total hardness

$$50 \text{ ml of given water sample} = 25 \text{ ml of EDTA solution} \dots\dots\dots (3)$$

$$\text{But, } 1 \text{ ml of EDTA solution} = 2.5 \text{ mg of CaCO}_3 \quad 25 \text{ ml of EDTA solution} = 2.5 \times 25 = 62.5 \text{ mg of CaCO}_3 \dots\dots\dots (4)$$

From equation (3) and (4),

$$50 \text{ ml of water sample} = 62.5 \text{ mg of CaCO}_3$$

$$1000 \text{ ml water sample} = \frac{1000 \times 62.5}{50}$$

$$= 1250 \text{ mg of CaCO}_3$$

$$= 1250 \text{ mg/litre or ppm}$$

$$\text{Total hardness of water sample} = 1250 \text{ ppm}$$

Step III: Calculation of Permanent Hardness

50 ml of given water sample = 15 ml of EDTA solution..... (5)

But, 1 ml of EDTA solution = 2.5 mg of CaCO_3

15 ml of EDTA solution = $2.5 \times 15 = 37.5$ mg of CaCO_3 (6)

From equation (5) and (6),

50 ml of water sample = 37.5 mg of CaCO_3

$$1000 \text{ ml water sample} = \frac{1000 \times 37.5}{50}$$

$$= 750 \text{ mg of } \text{CaCO}_3$$

$$= 750 \text{ mg/litre or ppm}$$

Permanent hardness of water sample = 750 ppm

Step IV: Determination of temporary hardness

$$\begin{aligned}\text{Temporary Hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ &= 1250 - 750 \\ &= 500 \text{ mg/litre or ppm}\end{aligned}$$

Problems for practice

1. In the determination of hardness by EDTA method, 50 ml of standard hard water (containing 1 mg of CaCO_3 hardness per ml. of solution) required 45 ml of EDTA solution. While 50 ml of sample hard water consumed 20 ml of EDTA solution. After boiling and diluting, 50 ml of the same sample of water required 10 ml of EDTA solution. Calculate various hardness in ppm.

(Ans. Total Hardness = 444.44 ppm, Perm. Hardness = 222.22 ppm, Temp. Hardness = 222.22 ppm)

2. Calculate the hardness in ppm in a given sample of water from the following data:

50 ml of standard hard water containing 1 mg of pure CaCO_3 per ml consumed 20 ml of EDTA.

50 ml of water sample consumed 30 ml of EDTA solution using EBT indicator. 50 ml of sample of water after boiling and filtering consumed 20 ml of EDTA solution using EBT indicator.

(Ans. Total Hardness = 1500 ppm, Perm. Hardness = 1000 ppm, Temp. Hardness = 500 ppm)

3. 0.28 g of CaCO_3 was dissolved in HCl and solution is made up to 1 litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution. 100 ml hard water required 33 ml of same EDTA solution on titration. After boiling 100 ml of this was required 10 ml of EDTA solution on titration. Calculate the temporary and permanent hardness of water.

(Ans. Total Hardness = 330 ppm, Perm. Hardness = 100 ppm, Temp. Hardness = 230 ppm)

4. Calculate the hardness of water sample whose 20 ml required 30 ml of EDTA solution. 10 ml CaCl_2 solution (strength 300 mg CaCO_3 per 200 ml) required 20 ml of EDTA solution.

(Ans. Hardness = 1125 ppm)

5. 50 ml of hard water (1.1 mg of CaCO_3 per ml) requires 38 ml of disodium EDTA.

100 ml of a water sample consumes 21 ml of EDTA during titration. Find the degree of hardness of the water sample.

(Ans. Degree of Hardness = 303.9 mg/l)

6. Calculate the hardness in ppm of water sample from the following data. 100 ml of water containing 1 mg/ml of pure CaCO_3 consumed 40 ml of EDTA solution. 50 ml of water sample consumed 30 ml of EDTA solution using EBT indicator.

(Ans. Hardness = 1500 ppm)

7. 0.5g of CaCO_3 was dissolved in HCl and solution is made up to 500ml with distilled water. 50ml of the above solution required 48 ml of EDTA solution. 50ml hard water required 15ml of same EDTA solution on titration. After boiling 50ml of this was required 10 ml of EDTA solution on titration. Calculate the temporary and permanent hardness of water.

(Ans. Total hardness = 312ppm, permanent hardness = 208ppm, temporary hardness = 104ppm)

8. 20ml of standard hard water containing 15g/L CaCO_3 required 25ml of EDTA solution. 100ml of hard water sample required 18ml of EDTA solution. Same sample on boiling required 12ml of EDTA solution. Calculate temporary hardness of the water.

(Ans. Total hardness = 2160ppm, permanent hardness = 1440ppm, temporary hardness = 720ppm)

9. 50 ml water sample required 6.2ml of N/20 EDTA for titration. After boiling and filtration the same volume required 4ml of EDTA. Calculate both the type of hardness.
(Dec 2011)

(Ans. Total hardness = 310ppm, permanent hardness = 200ppm, temporary hardness = 110ppm)

10. 50 ml of sample hard water required 15ml of 0.01M EDTA for titration. After boiling and filtration the same sample required 5ml of same EDTA. Calculate the total, temporary and permanent hardness of water

(Ans. Total hardness = 300ppm, permanent hardness = 100ppm, temporary hardness = 200ppm)

Softening of water

Definition:

The process of removal of hardness of water, irrespective of whether it is permanent or temporary hardness is called softening.

The main principle involved in such softening is the conversion of soluble salts present in water to some insoluble ones which can then be easily removed by simple filtration.

Demineralization or Ion Exchange process

Principle:

In this process, cations like Ca^{2+} , Mg^{2+} of hard water are exchanged with H^+ ions of the cation exchanger resin (RH_2) and anions like Cl^- , SO_4^{2-} etc. of hard water are exchanged with OH^- of anion exchanger resin $\text{R}'(\text{OH})_2$.

{Ion exchange resins

These are high molecular weight; cross linked, insoluble, long chain organic polymers with micro porous structure and the functional group attached to the chain are responsible for the ion exchanging properties.}

Process:

The process of softening in the ion exchange involves passing raw water first through the cation exchanger and then through the anion exchange resin.

The hard water is passed first through the cation exchange resin, it removes all the cations like Ca^{2+} , Mg^{2+} from it and equivalent amount of H^+ ions are released from this column to water.



The treated water is now free of cations but is too acidic and cannot yet be used in the boiler.

This acidic water emerging from cation exchanger is passed through the anion exchanger which removes all the anions like SO_4^{2-} , Cl^- etc. present in the water and equivalent amount of OH^- ions are released from this column to water.

Anion exchange

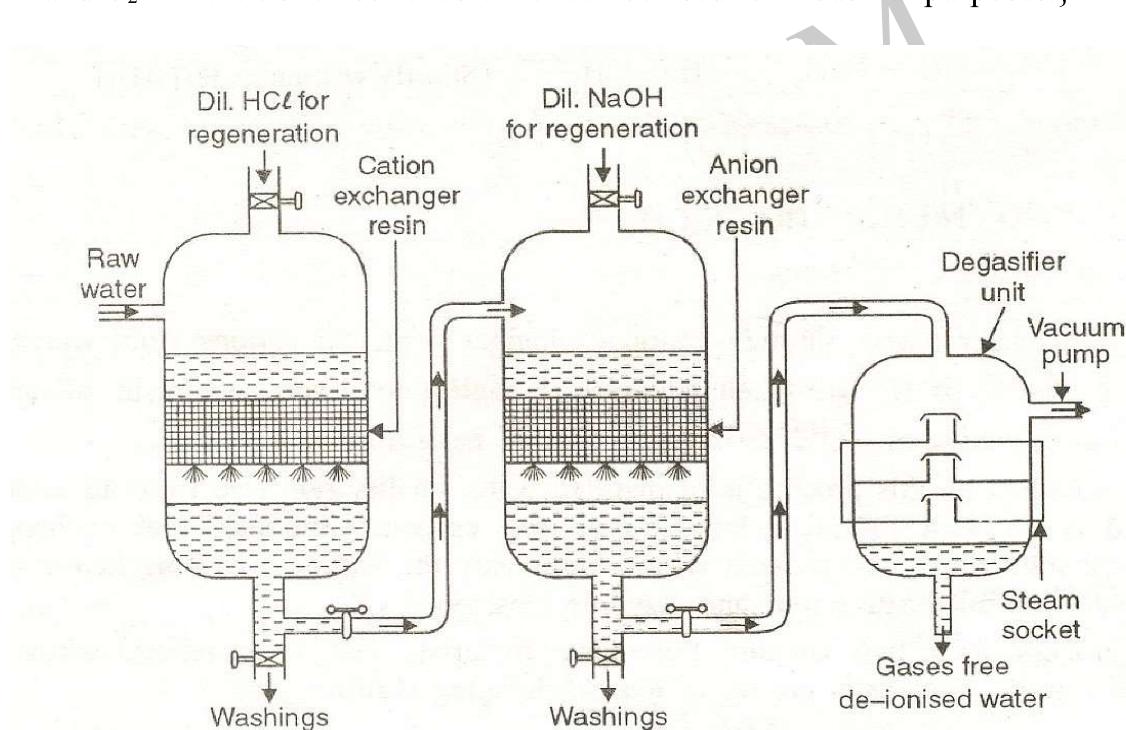


In this way, the water coming out from both cation and anion exchanger is free from both cations and anions and is virtually distilled water.



It means it does not have any hardness at all. However water may contain some dissolved gases. In order to remove the dissolved gases, water is passed through degasifier.

{Degasifier is a tower whose both sides are heated with steam jacket and is connected to vacuum pump. High temperature and low pressure reduces the quantity of dissolved CO_2 and O_2 in water. Such softened water can be used for industrial purposes.}



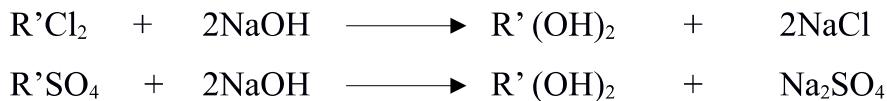
The exhausted cation exchange is regenerated by passing dil. HCl or H_2SO_4 through the first tower. The reactions in regeneration can be represented as



The washing containing CaCl_2 , MgCl_2 or CaSO_4 , MgSO_4 etc., is also passed to drain.

Regeneration of anion exchanger

The exhausted anion exchanger is regenerated by passing dilute solution of NaOH or KOH through the second tower. The reactions in regeneration can be represented as-



Advantages of ion exchange process

1. The process can be used for highly acidic or alkaline water
2. By this process water of zero hardness can be obtained.
3. Water obtained can be used for high pressure boilers.

Disadvantages of ion exchange process

1. Capital cost is high since equipment and chemicals both are costly.
2. If water contains turbidity, then, the efficiency of the process reduced.

Problems for practice (Ion exchange)

1) An ion exchanger required 50 litres of N/20 HCL and 50 litres of N/20 NaOH for regeneration of cation and anion exchanger after softening 2000 litres of water. Find the hardness of the above water sample.

Ans: 62.5 mg/litre.

2) An ion exchanger required 20 litres of 1M HCL and 20 litres of 1M NaOH for regeneration of cation and anion exchanger after softening 10000 litres of water. Find the hardness of the above water sample.

Ans : 200 mg/litre

Desalination of Brackish water by Electrodialysis:

Principle:

Electrodialysis is an electrochemical process in which ions migrate through ion selective membrane as a result of their attraction towards two electrically charged electrodes.

Process:

- The unit consists of electrodes (anode & cathode) and thin rigid ion-selective membranes which are permeable to either cation or anion.

- The anode is placed near anion selective membrane while the cathode is placed near cation selective membrane.
- Under the influence of applied e.m.f. across the electrode, the cations (Na^+) move towards cathode through cation selective membrane while the anions (Cl^-) move towards anode through anion selective membrane.
- The net result is depletion of ions in the central compartment while increase in the concentration in the two side compartments.
- Desalinated water is periodically drawn out from central compartment, while the concentrated brackish water is replaced by fresh sample.

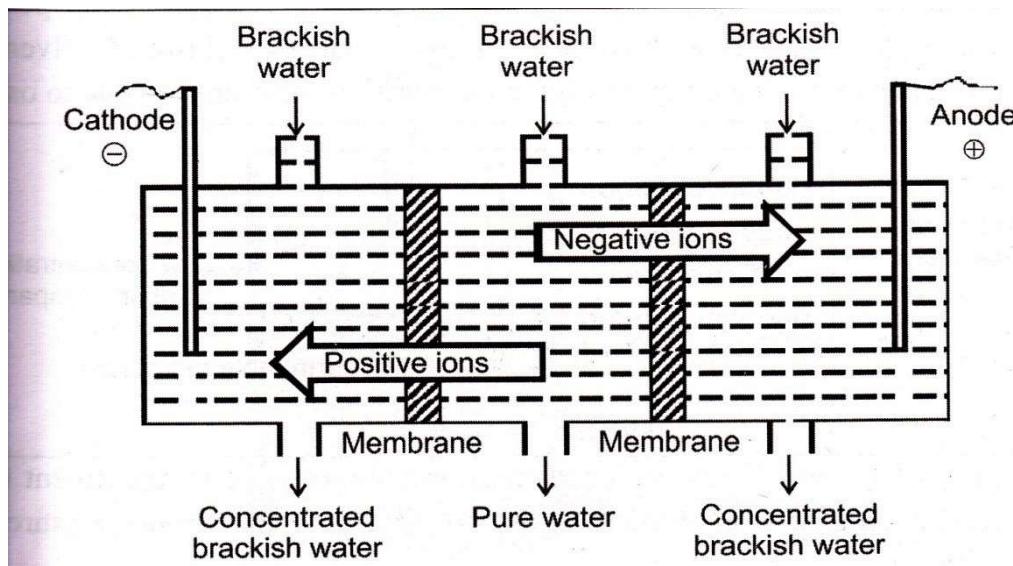


Fig. 1.10: Electro Dialysis of Brackish Water

Advantages:

1. The process is economical.
2. The unit is compact.

Reverse osmosis

What is osmosis?

During natural osmosis, water flows from a less concentrated solution through a semi permeable membrane to a more concentrated saline solution until concentrations on both sides of the membrane are equal

What is Reverse Osmosis (RO)?

Reverse osmosis is the reversal of the natural flow of osmosis. It occurs when the water is moved across the membrane from high concentration to lower concentration under the influence of applied pressure.

Method:

1. In this process, pressure is applied to impure water. Because of this pressure impure water is forced out through the semi permeable membrane; leaving behind the dissolved solids.
2. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube.
3. The material of the membrane is semi-permeable; it allows water molecules to pass through while acting as a barrier to dissolved solids.
4. The remaining contaminants are concentrated and washed from the surface of the membrane down the drain.
5. Ultimately the membrane could become blocked by salt and other impurities.
6. To solve this problem, the membranes are configured to split the feed water into two streams. One part to be purified and the other part to wash away the particles rejected by the membrane.

Advantages of reverse osmosis:

1. Reverse osmosis possesses a distinct advantage of removing ionic as well as non ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization.
3. The maintenance cost is less.
4. The life time of membrane is quite high, about 2 years.
5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.

Ultra filtration (UF)

Give an account of ultra-filtration. (3M) May 09.

1. Ultra filtration uses a membrane very similar in design to reverse osmosis systems except that the ultra filter's pores are slightly larger having pore size in the range of 0.0025 to 0.1 microns.
2. The ultra filter is used to remove pyrogens and other long chain organic molecules, salts, proteins and other impurities.

3. Because of the larger pore size in the membrane, UF requires a much lower operating pressure: 10 to 100 psi.
4. The type of membrane media determines how much pressure is needed to drive the water through and what sizes of micro-organisms can be filtered out.
5. Since a high percentage of the water passes through the ultra filters, it will eventually plug if not carefully maintained.
6. In a properly designed system, the ultra filter is regularly and tangentially washed free of contaminants.
7. With this type of design, ultra filtration is an outstanding technology for ensuring very consistent ultra pure water quality.

Advantages:

1. Effectively removes most particles, pyrogens, microorganisms, and colloids above their rated size.
2. Produces highest quality water for least amount of energy.
3. Regenerated using a hot (50°C) 5% caustic solution, solving the problem of fouling

Disadvantages:

It will not remove dissolved inorganic materials.

Applications:

1. Selective concentration of milk constituents (fat and true proteins)
2. Concentration of fruit juices.
3. Clarification of sugarcane juice.
4. Soya bean milk purification.
5. Removal of colloidal particles from surface water.
6. Purification of drinking water.

Methods to determine extent of water pollution:

1. Biological Oxygen Demand:

Definition:

BOD of sewage is defined as "**the amount of free oxygen in water required for the biological oxidation of organic matter under aerobic conditions at 20°C and for a**

period of 5 days."BOD is expressed in Mg/liter or ppm. Drinking water has less than 1 ppm BOD. An average sewage has the BOD of 100-150 mg oxygen/litre.

Determination of BOD:

This test is based on determination of dissolved O₂. A known volume of sewage sample is diluted with a known volume of saline solution. (Water containing nutrients for the growth of bacteria), whose dissolved oxygen content is pre-determined. The whole solution is incubated in a closed bottle at 20°C for a period of 5 days. After this, the unused oxygen is determined. The difference between the original oxygen content in saline solution and unused oxygen at solution after 5 days give BOD.

Importance or significance of BOD:

1. BOD test is the most important in sewage treatment as it indicates the amount of decomposable organic matter in sewage. Larger the concentration of decomposable matter, greater is the BOD and consequently, more the pollution of water.
2. It is also a means of checking on the quantity of effluents discharged into surface water.

BOD = [Dissolved Oxygen before incubation- Dissolved Oxygen after incubation] x Dilution Factor

OR

$$\text{BOD} = [\text{DO}_b - \text{DO}_a] \times \text{Dilution Factor}$$

Dilution Factor = Volume of waste water after dilution/ Volume of waste water after dilution

Numericals On BOD

1. 100 mL of waste water(containing 920 ppm dissolved oxygen) was diluted with 100 mL of distilled water and kept in a bottle at 20° C for 5 days. The oxygen content of resulting water was then found to be 260 ppm. Calculate BOD of the sample.

$$\text{BOD} = [\text{DO}_b - \text{DO}_a] \times \text{Dilution Factor}$$

$$\text{BOD} = [920 - 260] \times 200 / 100$$

$$\text{BOD} = 1320 \text{ ppm.}$$

2. A 50 mL Sample contains 840 ppm of dissolved oxygen after 5 days the dissolved oxygen value become 230 ppm after the sample has been diluted to 80 mL calculate BOD of the sample.

2. Chemical Oxygen Demand

Definition:

It is an amount of oxygen required for the chemical oxidation of organic matter in sewage". In other words, it is a measure of oxidisable impurities present in the sewage.

Determination of COD

The chemical oxygen demand is measure of the oxygen equivalent of that portion of organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. A measured quantity of the sample is reflux with a known amount of $K_2Cr_2O_7$ and H_2SO_4 (Most type of organic matter are completely oxidized by a boiling mixture of chromic and sulphuric acid to produce CO_2 and H_2O .) and the excess of dichromate remaining un-reacted is titrated with ferrous ammonium sulphate $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$. The $K_2Cr_2O_7$ consumed is proportional to the amount of oxidisable organic matter measured as oxygen equivalent.

$$\text{COD of the sample water} = \frac{(V_{\text{blank}} - V_{\text{sample}}) N \times 8000}{X}$$

Where V_{blank} = Volume of FAS solution run down in blank titration

V_{sample} = volume of FAS solution run down in the sample test titration.

N = normality of FAS solution.

X = Volume of test sample taken.

Importance of COD

1. BOD is just the measure of oxygen required for the oxidation of organic matter while COD is measure of both, the biologically oxidisable and the biologically inert organic matter (like cellulose). Thus, COD value is generally found higher than BOD.
2. COD determination gets completed in comparatively less time (i.e. 3 hours) than BOD determination (which takes 5 days).
3. On the basis of COD value, approximate BOD value can be estimated.
4. It helps in designing water treatment plant.

Numericals On COD

1) A 25 ml of sewage water sample was refluxed with 10ml of 0.25N $K_2Cr_2O_7$. The unreacted dichromate required 6.5 ml of 0.1N FAS. 10 ml of same $K_2Cr_2O_7$ solution and 25 ml of distilled water under the same conditions required 27 ml of 0.1N FAS. Calculate COD of sewage water sample.

Given: $V_{blank} = 27\text{ml}$

$V_{sample} = 6.5 \text{ ml}$

Normality=0.1

Volume of sewage sample (X)=25ml

$$\text{COD} = \frac{(V_{blank} - V_{sample}) \times \text{Normality} \times 8000}{\text{Volume of sewage sample}}$$

$$= \frac{(27 - 6.5) \times 0.1 \times 8000}{25}$$

$$= 656 \text{mg/litre or } 656 \text{ ppm}$$

2) A 10 ml of waste water sample was refluxed with 20ml of $K_2Cr_2O_7$ solution after refluxing the excess unreacted dichromate required 26.2 ml of 0.1N FAS solution. A blank of 10 ml distilled water on refluxing with 20ml of $K_2Cr_2O_7$ solution required 36 ml of 0.1N FAS. Calculate COD of water sample.

Ans: 784 ppm

3) A 5 ml of waste water sample was refluxed with 30ml of $K_2Cr_2O_7$ solution after refluxing the excess unreacted dichromate required 23 ml of 0.1N FAS solution. A blank of 5 ml distilled water on refluxing with 30ml of $K_2Cr_2O_7$ solution required 36 ml of 0.1N FAS. Calculate COD of water sample.

Ans: 2080 ppm