Water
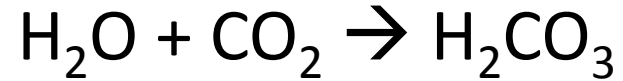
Dr. Druman Ramesh Utekar

Sources and Impurities in Water

- **Sources**

- **Impurities**

i) Physical Impurities

ii) Chemical Impurities
iii) Biological Impurities

Acidity in water

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Hardness of Water

Hardness of water is that characteristic which prevents the lathering of Soaps.

Or'

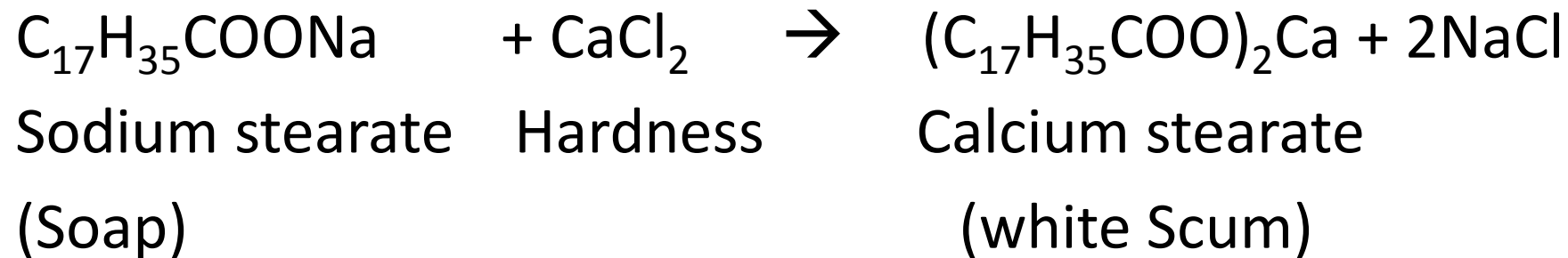It is the soap consuming capacity of water sample.

Industrial problems of water

- Boiler corrosion
- Caustic embrittlement
- Formation of scale and sludge
- Priming and foaming

Soap and Soap Consuming capacity

Soap is sodium or potassium salt of higher fatty acids like oleic, palmitic or steric acid.

Soap Consuming capacity of water

$C_{17}H_{35}COONa$ + $CaCl_2$ → $(C_{17}H_{35}COO)_2Ca$ + 2NaCl

Sodium stearate   Hardness   Calcium stearate

(Soap)   (white Scum)

Hard Water & Soft water

- The water which does not produce lather with soap solution readily is called as hard water.

- Water which lathers easily on shaking with soap solution is called soft water.

Types of hardness

- **Temporary or Carbonate or Alkaline Hardness**

The hardness caused by the presence of dissolved bicarbonates and carbonates of calcium, magnesium and other heavy metals like iron is called as temporary hardness. Eg. $CaCO_3$, $Ca(HCO_3)_2$, $MgCO_3$, $Mg(HCO_3)_2$, $FeCO_3$

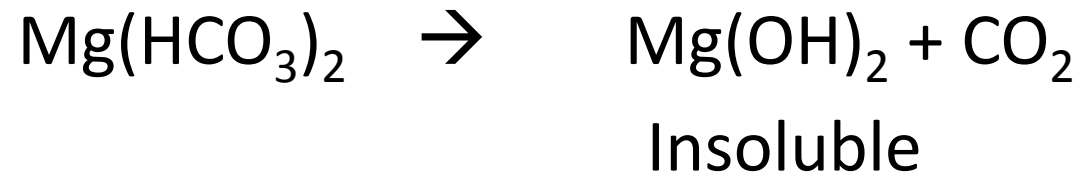$NaHCO_3$-non-hardness causing substance, SiO_2, $NaCl$, KCO_3, $KHCO_3$

- **Permanent or non-carbonate or non-alkaline hardness**

The hardness caused by the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. eg. $CaCl_2$, $MgCl_2$, $FeCl_3$, $CaBr_2$, $CaSO_4$etc

KBr-non-hardness causing substance.

- Temporary Hardness can be destroyed by boiling.
-                                    boil

$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$

                                    Insoluble

$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + CO_2$

                                    Insoluble

Permanent Hardness cannot be destroyed by boiling.

1. KHCO3

2. Mg(NO3)2= 10ppm   CaCO3 eq. =3.5ppm

3. FeSO4= 12ppm   CaCO3= 2.4ppm

4. NaAlO2

5. CaCl2= 7ppm   CaCO3 = 1.1ppm

6. Ca(NO3)2 =60ppm   CaCO3 eq. = 50ppm

Hardness of water (CaCO3 eq) = 3.5+2.4+1.1+50 =57ppm

CaCO3 is chosen as basis to express hardness of water.

Measurement of Hardness

- The extent of hardness is measured in terms of ions contributing to the hardness.

- It is expressed in terms of amount of $CaCO_3$

- Why to express hardness in terms of CaCO3?

- Ans: 1. the mol wt of CaCO3 is 100 and its equivalent wt is 50, which allows the multiplication and division in easy way when required.
  2. CaCO3 is the most insoluble salt which can be precipitated in water treatment.

The Equivalent of CaCO3

= Mass of hardness producing substance x multiplication factor(M.F.)

Where Multiplication factor

= $\dfrac{\text{Chemical eq. of CaCO3}}{\text{Chemical Eq. of hardness producing substance}}$

= 50/ 74 {for Mg(NO3)2}

Multiplication factors

Dissolved salt	Molar Mass	Chem. Eq.	M.F
1. Ca(HCO3)2	162	81	50/81 or 100/162
2. Mg(HCO3)2	146	73	50/73 or 100/146
3. CaSO4	136	68	50/68 or 100/136
4. FeCl2	127	63.5	50/63.5 or 100/127
5. CaCl2	111	55.5	50/55.5 or 100/111
6. MgSO4	120	60	50/60 or 100/120
7. MgCl2	95	47.5	50/47.5 or 100/95
8. CaCO3	100	50	1
9. MgCO3	84	42	50/42 or 100/84
10. CO2	44	22	50/22 or 100/44
11. Ca(NO3)2	164	82	50/82 or 100/164
12. Mg(NO3)2	148	74	50/74 or 100/148
13. HCO_3^-	61	61	50/61 or 100/122
14. OH-	17	17	50/17 or 100/34

Dissolved salt	Molar Mass	Chem. Eq.	M.F
15. CO_3^{2-}	60	30	50/30 or 100/60
16. $NaAlO2$	82	82	50/82 or 100/164
17. $Al2(SO4)3$	342	57	50/57 or 100/114
18. $FeSO4.7H2O$	278	139	50/139 or 100/278
19. $H+$	1	1	50/1 or 100/2
20. HCl	36.5	36.5	50/36.5 or 100/73

Units of hardness

1. Parts per millions(ppm): It is the parts of $CaCO_3$ equivalent of hardness per10^6 parts of water.

2. Milligram per Litre(mg/L): it is the number of milligram of CaCO3 equivalent of hardness present per litre of water.

Mg/L = 1gx10^-3/1000mL= 1g/1000x1000 = 1:10^6

3. Clarke's Degree (°Cl): It is the number of grains (1/70000 lbs) of CaCO3 equivalent of hardness per gallon (10 lbs) of water. OR It is parts of CaCO3 equivalent per 70000 parts of water.

4. Degree French (°Fr): It is the parts of CaCO3 equivalent per 10^5 parts of water.

5. Milliequivalent per Litre(meq/L): It is the number of milliequivalent of hardness present per litre of water.

Relationship between various units of hardness

1ppm = 1mg/L = 0.1°Fr = 0.07°Cl = 0.02 meq/L

Numerical 1: Convert the total hardness of water samples in ppm and meq/L from the following.

i)   20.23°Cl

ii)   31.3°Fr

Numerical 2: A sample of water has hardness 208ppm of CaCO3 equivalents. Find the hardness in terms of

i)   mg/L ii) °Fr   iii) °Cl   iv) meq/L

Numerical 3: How many grams of FeSO4 dissolved per litre gives 210.5ppm of hardness? (Fe = 56, S =32, O =16, Ca =40, C = 12)

Soln: Mol. Wt of CaCO3 = 100g and mol. Wt of FeSO4 = 152g

100g of CaCO3 = 152g of FeSO4

100ppm of CaCO3 = 152ppm of FeSO4

Hence, 210.5ppm of hardness = 152 x 210.5/100 ppm of FeSO4

= 319.96 mg/L

=0.320g/L of FeSO4

Numerical 4: Calculate Temporary hardness and permanent hardness of water sample from the following data: Mg(HCO3)2 = 16.8mg/L, MgCl2 = 19mg/L, MgSO4 = 24mg/L, Mg(NO3)2 = 29.6mg/L, CaCO3 = 4mg/L, MgCO3 = 10mg/L.

Solution:

Constituent (mg/L)	Multiplication Factor	CaCO3 Eq.	Hardness
1. Mg(HCO3)2 = 16.8	50/73	11.5	T
2. MgCl2 = 19	50/47.5	20	P
3. MgSO4 = 24	50/60	20	P
4. Mg(NO3)2= 29.6	50/74	20	P
5. CaCO3 = 4	1	4	T
6. MgCO3 = 10	50/42	11.9	T

Temporary Hardness = hardness due to Mg(HCO3)2 +CaCO3 + MgCO3

= 11.5 + 4 + 11.9 = 27.4 ppm or 27.4 mg/L

Permanent Hardness = hardness due to MgCl2 + MgSO4 + Mg(NO3)2

= 20 + 20+ 20 = 60mg/L = 60ppm

Numerical 5: A water sample analysis has been found to contain following impurities in ppm: $Mg(HCO_3)_2$ =14.6, $Mg(NO_3)_2$ = 29.6, $Ca(HCO_3)_2$= 8.1, $MgCl_2$ = 19, $MgSO_4$ = 24. calculate the temporary & permanent hardness of water.

Numerical 6: How many grams of $CaCl_2$ dissolved per litre gives 150ppm hardness?

Numerical 7: Classify the following impurities into temporary permanent and non-hardness causing impurities.

$Ca(HCO_3)_2$, $MgSO_4$, $CaCl_2$, CO_2, HCl, $Mg(HCO_3)_2$

Determination of hardness of water by EDTA method

- Hardness of water can be readily determined by titration with the chelating agent EDTA.

- EDTA is ethylene diamine tetra acetic acid. It is a weak acid that can lose four H+ ions on complete neutralization. Its formula is
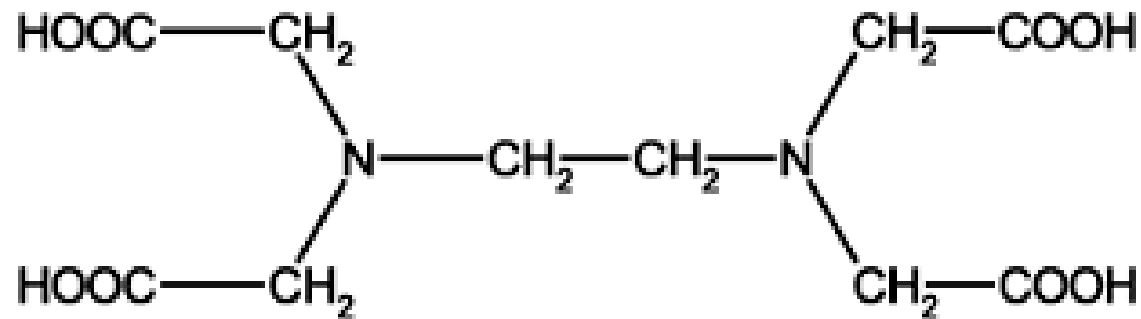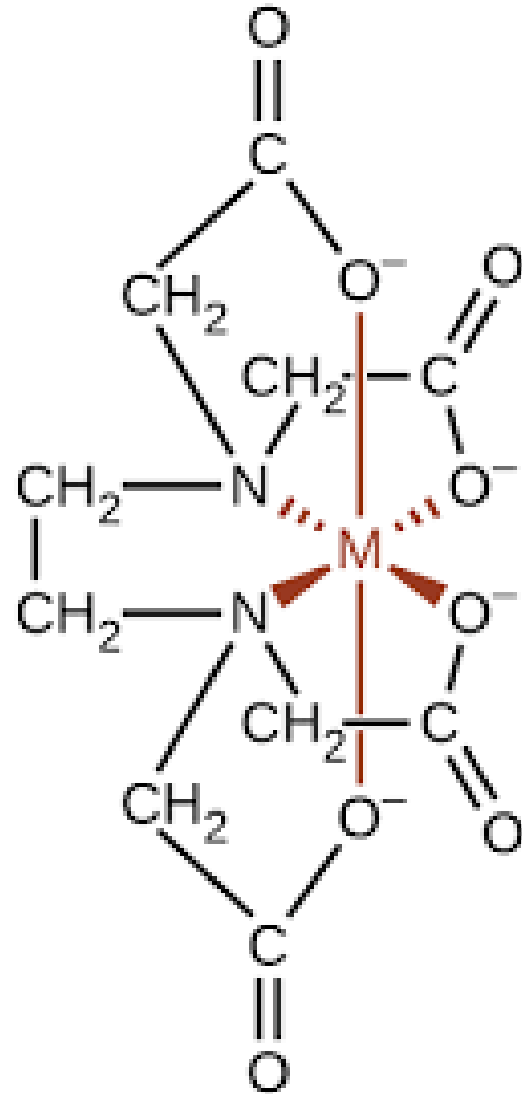

Figure 1. Molecular structure of EDTA

- M-EDTA Complex structure: Stable at pH=10 Octahedral complex

Theory or Principle:

- The process involves the titration of metal ion solution with standardized EDTA soln. Indicator used is Eriochrome Black-T (EBT).

- EBT is alcoholic solution of blue eye. It forms an unstable wine-red complex with Ca^{2+} & Mg^{2+} at pH =10. A buffer solution of NH_4OH & NH_4Cl is used to maintain the pH = 10.

- **Initial reaction:** When EBT indicator is added to hard water buffered to pH =10, a wine red unstable complex is formed. pH = 10

$$M^{2+} \quad + \quad EBT \quad \rightarrow \quad [\text{M-EBT}] \text{ complex (Unstable)}$$
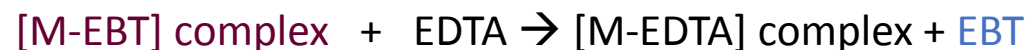
$$\text{(Wine red)}$$

Titration Reaction: During the course of titration with EDTA soln, EDTA combines with M2+ ions to form stable complex M-EDTA & releases free EBT indicator, which immediately combines with remaining M2+ ions present in solution. Thus wine red colour retained.

$$[\text{M-EBT}] \text{ complex} \quad + \quad EDTA \rightarrow [\text{M-EDTA}] \text{ complex} + EBT$$

$$pH = 10$$
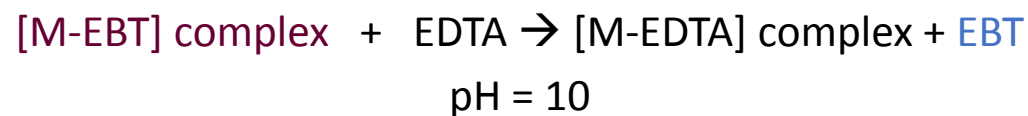
$$M^{2+} \quad + \quad EBT \quad \rightarrow \quad [\text{M-EBT}] \text{ complex}$$

End point Reaction: At end point all of the cations formed M-EDTA complex, where last drop of EDTA added displaces the EBT indicator from M_EBT complex and wine red colour changes to blue due to presence of only free EBT. Thus the colour change is wine red to blue at the end point of titration.

$$pH = 10$$

$$[\text{M-EBT}] \text{ complex} \quad + \quad EDTA \rightarrow [\text{M-EDTA}] \text{ complex} + EBT$$

Colour change : Wine red to Blue

Practical Colour change: Wine red to purple to blue

Experimental Procedure:

A) Preparations of solutions

i) Preparation of Standard Hard water (SHW):

Dissolve 1g of $CaCO_3$ in minimum amount of dil. HCl till all solid dissolves and evaporated to dryness. Dissolve this residue in 1L distilled water. Each mL of this solution contains 1mg of $CaCO_3$ equivalent hardness.

1g of $CaCO_3$ in 1L of water= 1000mg of $CaCO_3$ in 1L = 1000ppm soln

1mL of SHW ($CaCO_3$) soln = 1mg of $CaCO_3$

100mL of SHW = _100__mg of $CaCO_3$

1ppm = 1mg/L

ii) Preparation of EDTA solution: Dissolve 3.72g of pure EDTA + 0.1 mg $MgCl_2$ in 1L of distilled water.

iii) Preparation of indicator: dissolve 0.5g of EBT indicator in 100ml of alcohol.

iv) Preparation of Buffer soln: Add 67.5g of NH_4Cl to 570mL of ammonia soln and then dilute with distilled water to 1L.

B) **Procedure: it has three steps:**

Step 1: Standardization of Hard water: Pipette out 50mL of SHW in a conical flask. Add 10mL of buffer soln and 4 to 5 drops of EBT indicator. Titrate with EDTA soln till wine red colour changes to blue. Let the volume used be V1 mL.

50mL of SHW = V1 mL of EDTA

1ml of EDTA = ____mg of CaCO3

Step 2: Titration of unknown hard (bore well) water: Titrate 50mL of sample water just same as given instep 1. Let the volume used be V2 mL.

50mL of sample HW = V2 mL of EDTA

Total Hardness

Step 3: Titration of permanent hardness: Take 50mL of water sample in a beaker and boil it till volume reduces to half. (where all bicarbonates are decomposed to insoluble CaCO3 and Mg(OH)2.) Filter the solution and titrate the filtrate as given in step 1. Let the volume used be V3 mL.

50ml of boiled sample HW = V3 mL of EDTA

Permanent Hardness

Calculations:

50ml of SHW = V1 mL of EDTA soln

Since 1 mL SHW contains 1mg of CaCO3,

50mg of CaCO3 = V1 mL of ETDA soln.

Hence, **1mL of EDTA = 50/V1 mg of CaCO3 eq.**

A) Total Hardness

50mL of sample hard water = V2 mL of EDTA soln

$\qquad\qquad\qquad$ = V2 x 50/V1 mg of CaCO3 eq.

Hence 1000mL of sample hard water = 1000 V2x 50/V1 x 1/50   mg of CaCO3 eq.

$\qquad$ there fore, **Total Hardness = V2/V1 x 1000 ppm**

B) Permanent Hardness:

Now, 50ml of boiled sample water = V3 mL of EDTA

$\qquad\qquad\qquad$ = V3 x 50/V1 mg of CaCO3

Hence 1000mL of Sample hard water = V3/V1 x 1000 mg of CaCO3

$\qquad$ Therefore, Permanent hardness = V3/V1 x 1000 ppm

C) Temporary hardness = Total hardness – Permanent hardness

Advantages of EDTA method

- This method is preferable to the other methods, because of

i)   Greater accuracy

ii)   Convenience

iii)   More rapid procedure

Numerical 1: 50mL of standard hard water requires 38mL of EDTA solution. 100 mL of water sample consumes 21mL of EDTA soln. 100mL of boiled water sample consumes 10mL of EDTA soln. Find all types of hardness.

Solution:

50 mL of SHW = _50_mg of $CaCO_3$

50mL of SHW = 38 ml of EDTA soln.

There fore, 38mL of EDTA = 50mg of $CaCO_3$

$\qquad$ 1mL of EDTA = _50/38__mg of $CaCO_3$

$\qquad$ **1mL of EDTA = 1.316mg of $CaCO_3$**

Total Hardness:

100mL of sample HW =21 mL of EDTA solution

$\qquad$ = 21 x 1.316 mg of $CaCO_3$

$\qquad$ = 27.636 mg of $CaCO_3$

1000mL of sample HW = 27.636 x 1000/100

$\qquad$ = 276.36mg of $CaCO_3$/L = 276.36ppm

There fore **Total hardness = 276.36ppm**

Permanent hardness:

100mL of Boiled sample HW = 10mL of EDTA

$\qquad$ = 13.16 mg of $CaCO_3$

1000mL of boiled sample HW = 13.16 x 1000/100 = 131.6mg of $CaCO_3$ / L

Permanent hardness = 131.6ppm

Temporary Hardness = Total hardness – permanent hardness

Numerical 2: 50 mL of Standard hard water required 21mL of EDTA solution. 50mL of sample Water requires 21mL of EDTA solution. 50mL of boiled sample water requires 7mL of EDTA soln. calculate all the types of hardness.

Soln:

50mL of SHW = 50mg of CaCO3

50mL of SHW = 21mL of EDTA

There fore 21 mL of EDTA soln = 50mg of CaCO3

Hence   **1mL of EDTA soln = 50/21 = 2.381mg of CaCO3 eq.**

Total Hardness

50mL of sample HW = 21mL of EDTA soln

                = 21 x 2.381 = 50.001 mg of CaCO3 eq.

1000mL of sample HW = 50.001 x 1000/50 = 50.001 x 20

                    = 1000.02mg CaCO3/L

Hence Total hardness = 1000.02ppm

Permanent Hardness

50mL of boiled sample HW = 7mL of EDTA soln

                    = 7 x 2.381 = 16.667mg of CaCO3/L

1000mL of boiled sample HW = 16.667 x 1000/50 = 16.667 x 20 =333.34mg of CaCO3

Hence permanent hardness = 333.34ppm

Temporary Hardness = total hardness – permanent hardness = 1000.02 -333.34 = 666.68 ppm

Numerical 3: 0.38g of CaCO3 was dissolved in HCl and the solution made up to 1Litre with distilled water. 100 mL of the above soln required 25mL of EDTA soln. 100 mL of hard water sample required 37mL of EDTA soln. 100mL of boiled hard water sample required 10mL of EDTA soln. Calculate each type of hardness.

Soln

~~1ml of SHW = 1mg of CACO3~~

SHW = 0.38g of CaCO3/ 1000mL = 380mg of CaCO3 / 1000mL

1mL of SHW = 0.38mg of CaCO3......using 1st statement of numerical

100mL of SHW = 25mL of EDTA

100mL of SHW = 38 mg of CaCO3

There fore 25mL of EDTA = 38mg of CaCO3

Hence   **1mL of EDTA = 38/25 =1.52mg of CaCO3 ......using 2nd statement of numerical**

Total Hardness

100mL of sample HW = 37mL of EDTA

                            = 37 x 1.52 = 56.24 mg of CaCO3

1000ml of sample HW = 56.24 x 1000/100 = 562.4 mg of CaCO3 /L

Hence Total hardness = 562.4ppm

Permanent hardness

100mL of Boiled sample HW = 10 ml of EDTA

                            = 10 x 1.52 = 15.2 mg of CaCO3

1000mL of Boiled sample HW = 15.2 x 1000/100 = 152 mg of CaCO3

        Hence permanent hardness = 152ppm

Temporary Hardness = total Hardness – permanent hardness = 562.4-152 = 410.4ppm

Numerical 4: 1.2g of CaCO3 was dissolved in HCl and the solution made up to 1Litre with distilled water. 50 mL of the above soln required 30 of EDTA soln. 100 mL of hard water sample required 27mL of EDTA soln. 100mL of boiled hard water sample required 11mL of EDTA soln. Calculate each type of hardness.

Soln:

Numerical 5: 0.55g of CaCO3 was dissolved in HCl and the solution made up to 1Litre with distilled water. 20 mL of the above soln required 10 of EDTA soln. 50 mL of hard water sample required 17mL of EDTA soln. 10mL of boiled hard water sample required 1.1mL of EDTA soln. Calculate each type of hardness.

Ans:

Numerical 6: 50mL sample of water require 10.2mL of M/20 disodium EDTA for titration. After boiling and filtration the same volume required 6.5mL of EDTA. Calculate all the types of hardness in it.

Numerical 6: 50mL sample of water require 10.2mL of M/20 disodium EDTA for titration. After boiling and filtration the same volume required 6.5mL of EDTA. Calculate all the types of hardness in it.

Soln:

1mL of 0.05M EDTA = ____mg of $CaCO_3$

M/20 EDTA = 1/20M EDTA = 0.05M EDTA

Std relationships says that,

1000mL of 1M EDTA = 100g of $CaCO_3$......due to Avogadro's numbers of molecules

1mL of 1M EDTA = 100mg of $CaCO_3$

1mL of 0.05M EDTA = 100 x 0.05 = 5mg of $CaCO_3$

Total Hardness:

50 mL of sample HW = 10.2mL of 0.05M EDTA soln

$$= 10.2 \text{ x } 5 = 51mg \text{ of } CaCO_3 \text{ eq.}$$

1000mL of sample HW = 51 x 1000/50 = 51 x 20 = 1020mg of $CaCO_3$

Hence Total Hardness = 1020ppm

Permanent Hardness:

50mL of Boiled sample HW = 6.5mL of 0.05M EDTA

$$= 6.5 \text{ x } 5 = 32.5mg \text{ of } CaCO_3 \text{ eq.}$$

1000mL of boiled Sample HW = 32.5 x 20 = 650mg of $CaCO_3$ eq

Hence Permanent Hardness = 650ppm

So, temporary hardness = 1020-650 = 370ppm

Numerical 7: 50mL sample of water require 15.3mL of M/15 disodium EDTA for titration. After boiling and filtration the same volume required 9.5mL of EDTA. Calculate all the types of hardness in it.

Solution

Softening of Water by Lime-Soda Method

The process of removing or reducing the concentrations of hardness causing ions/ salts from hard water is called as Softening of water.

Principle

In this method hard water is treated with calculated amounts of slaked Lime[Ca(OH)2] and soda ash Na2CO3 in reactions tanks. So as to convert hardness producing chemicals into insoluble compounds, which are then removed by settling and filtration.

Convert Ca^{2+} in $CaCO_3$ and Mg^{2+} into $Mg(OH)_2$, $Fe^{2+} \rightarrow Fe(OH)_2$

Constituent	Reactions Soda = Na_2CO_3 and Lime = $Ca(OH)_2$	Requirement L or S
1) Ca^{2+} (perm.) Eg. $CaCl_2$, $CaSO_4$	$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$	S
2) Mg^{2+} (perm.) Eg. $MgCl_2$, $MgSO_4$	$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$	L + S
3) HCO_3^- Eg. $NaHCO_3$	$2HCO_3^- + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O + CO_3^{2-} = Na_2CO_3$	L – S
4) $Ca(HCO_3)_2$ Temp.	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$	L
5) $Mg(HCO_3)_2$ Temp.	$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$	2L
6) CO_2	$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$	L
7) H^+	$2H^+ + Ca(OH)_2 \rightarrow 2H_2O + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$	L + S
8) $FeSO_4$	$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$ $Fe(OH)_2 + O_2 + H_2O \rightarrow Fe(OH)_3$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$	L+S

Constituent	Reactions	Requirement L or S
9) $Al_2(SO_4)_3$	$2Al^{3+} + 3\,Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3Ca^{2+}$ $3Ca^{2+} + 3Na_2CO_3 \rightarrow 3CaCO_3 + 6Na^+$	L + S
10) $NaAlO_2$	$NaAlO_2 + H_2O \rightarrow Al(OH)_3 + NaOH$	-L

Equivalence

$CaCO_3$ = $Ca(OH)_2$ = Na_2CO_3

100 = 74 = 106
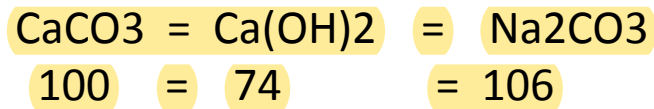
Lime required = 74/100 [Mg^{2+} perm. + HCO_3^- + Ca^{2+} temp. + 2 Mg^{2+} temp. + CO_2 + H^+ + Fe^{2+} + Al^{3+} -$NaAlO_2$] mg/L

$$= \frac{74\,[\,Mg^{2+}\,perm. + HCO_3^- + Ca^{2+}\,temp. + 2\,Mg^{2+}\,temp. + CO_2 + H^+ + Fe^{2+} + Al^{3+} - NaAlO_2]\, \times \text{Volume of wat}}{100 \times 1000 \times \%\,Purity}$$

= g of Lime

Soda required = $\dfrac{106\,[\,Ca^{2+}\,perm. + Mg^{2+}\,perm - HCO_3^- + H^+ + Fe^{2+} + Al^{3+}]\, \times \text{volume of water} \times 100}{100 \times 1000 \times \%\,purity}$

= ___g of Soda

Numerical 1: Calculate the amount of lime (74% pure) & Soda (90% Pure) for softening of 6000 litres of water containing following impurities.

$Mg(HCO_3)_2$ =73mg/L, $CaCl_2$ = 222mg/L, $MgSO_4$ = 120mg/L, $Ca(NO_3)_2$ = 164mg/L.

Soln

Impurities	Multiplication Factor	$CaCO_3$ eq.	Requirement
1) $Mg(HCO_3)_2$ = 73mg/L	100/ 146 or 50/73	= 73 x 50/73 =50	2L
2) $CaCl_2$ = 222mg/L	100/111 or 50/55.5	222 x 100/111 = 200	S
3) $MgSO_4$ = 120mg/L	100/120 or 50/60	120 x 100/120 = 100	L + S
4) $Ca(NO_3)_2$ = 164mg/L	100/164 or 50/82	164x 100/164 = 100	S

Lime required = 74 x [CaCo3 eq of 2x Mg(HCO3)2 + MgSO4] x volume of water x 100

100 x 1000 x % purity

= 74 x [2 x 50+ 100] x 6000 x 100 = 200 x 6 = 1200g = 1.2Kg

100 x 1000 x 74

Soda Required = 106 x [CaCO3 eq of CaCl2 + MgSO4 + Ca(NO3)2] x vol. of water x 100

100 x 1000 x % purity

= 106 x [200+100+100] x 6000 x 100 = 2826.67g = 2.827Kg

100 x 1000 x 90

Numerical 2: Calculate the quantity of soda and lime needed to soften 10000 litres of water containing following impurities. Na2SO4 =7mg/L, SiO2 = 2mg/L, CaCl2 = 22.2mg/L, MgSO4 = 2.0mg/L, Mg(HCO3)2 = 5.0mg/L.

Soln:

Impurities	Multiplication Factor	CaCO3 eq.	Requirement
1) Na2SO4 = 7mg/L	Non-hardness causing		
2) SiO2= 2mg/L	Non-hardness causing		
3) CaCl2 = 22.2mg/L	100/111 or 50/55.5	= 22.2 x 100/111 =20	S
4) MgSO4 =2.0mg/L	100/120 or 50/60	= 2 x 100/120 =1.67	L + S
5) Mg(HCO3)2 = 5.0mg/L	100/146 or 50/73	= 5.0 x 100/146 = 3.42	2L

Lime Required = $\underline{74 \times [CaCo3\ eq\ of\ MgSO4 + 2x\ Mg(HCO3)2 \times 10000}$

$\qquad\qquad$ 100 x 1000

$\qquad = \underline{74 \times [1.67 + 3.42 \times 2] \times 10000} = 62.974g$

$\qquad\qquad$ 100 x 1000

Soda Required = $\underline{106 \times [CaCo3\ eq.\ of\ CaCl2 + MgSO4] \times vol\ of\ water}$

$\qquad\qquad$ 100 x 1000

$\qquad = 229.702g$
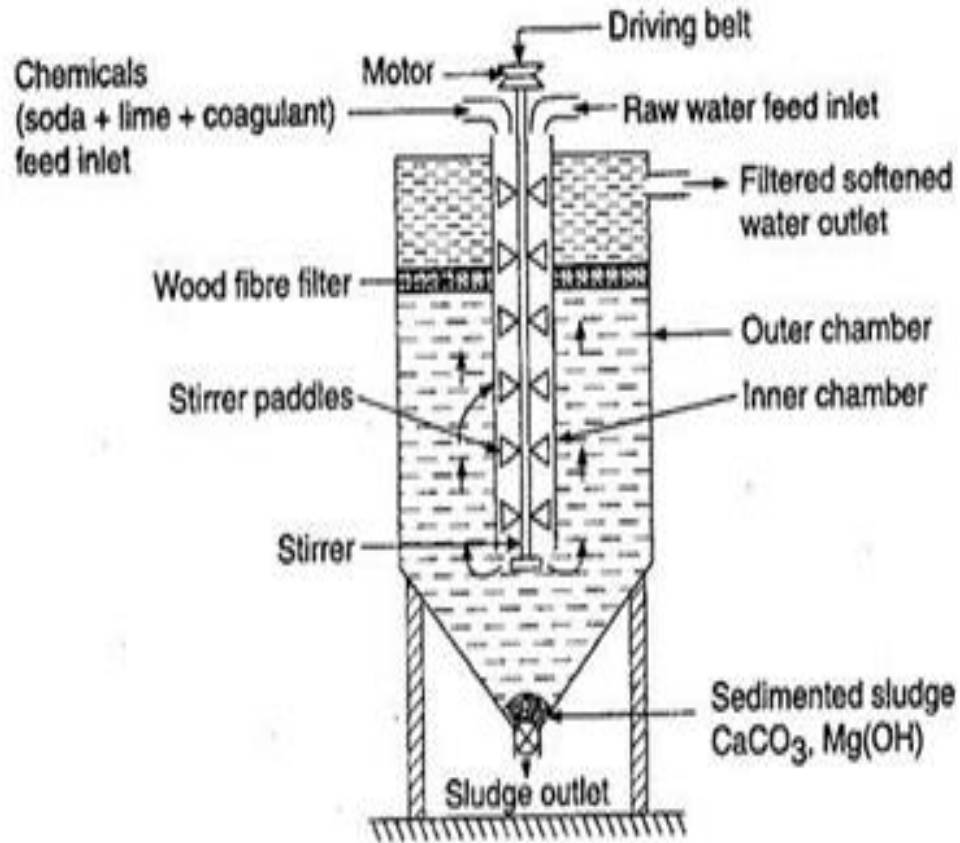
Numerical 3: Calculate amount of lime (90% pure) and Soda (98% Pure)for the treatment of 1 million litres ofwater containing Ca(HCO3)2 = 8.1ppm, CaCl2=33.3ppm, HCO3-= 91.5ppm, MgCl2 = 38ppm, Mg(HCO3)2 = 14.6ppm. The coagulant Al2(SO4)3 was added at the rate of 17.1ppm.

Impurities	Multiplication Factor	CaCO3 eq.	Requirement
1) Ca(HCO3)2 = 8.1mg/L	= 100/162 or 50/81	5	L
2) CaCl2 = 33.3mg/L	100/111 or 50/55.5	30	S
3) HCO3- = 91.5mg/L	=100/122 or 50/61	75	L - S
4) MgCl2 =38.0mg/L	100/95 or 50/47.5	40	L + S
5) Mg(HCO3)2 = 14.6mg/L	100/146 or 50/73	10	2L
6) Al2(SO4)3 = 17.1mg/L	100/114 or 50/57	15	L + S

Types of Lime Soda Processes

- Hot Lime-Soda Method
- Cold Lime-Soda Method

Cold Lime Soda Method

Driving belt

Chemicals (soda + lime + coagulant) feed inlet

Motor

Raw water feed inlet

Filtered softened water outlet

Wood fibre filter

Outer chamber

Stirrer paddles

Inner chamber

Stirrer

Sedimented sludge $CaCO_3$, $Mg(OH)$

Sludge outlet

Principle:

In this process calculated quantities of lime and soda are mixed with hard water at room temperature.

The precipitate formed are finely divided and there fore do not settle down easily and cant be filtered easily.

Thus it is essential to add small quantities of coagulants like alum, aluminum sulphate, sodium aluminates.

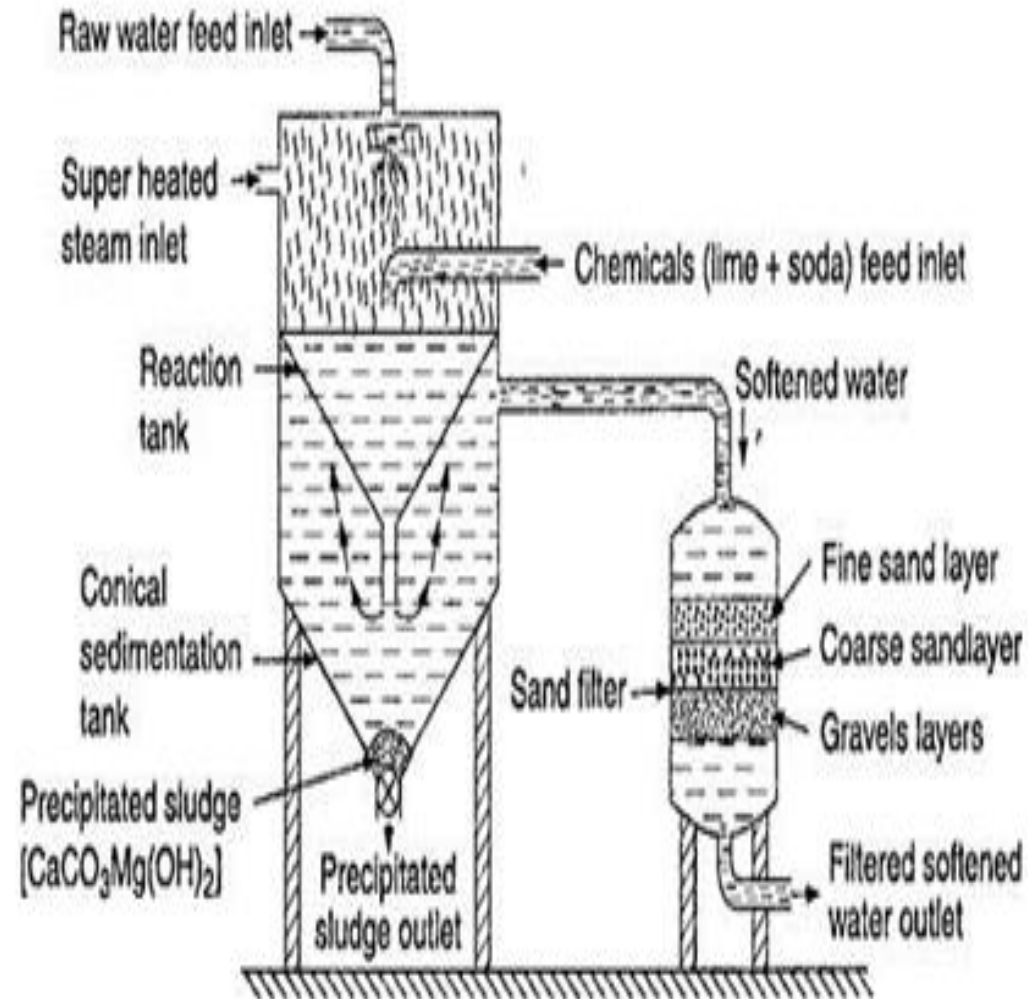These hydrolyze to gelatinous ppt of aluminum hydroxide and entrap fine precipitate.

If sodium aluminate is used as coagulant, silica as well as oil present in water are also removed.

Cold lime soda process provides water containing a Residual hardness of 50 to 60 ppm.

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

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

Hot Lime Soda Method

Raw water feed inlet
Super heated steam inlet
Chemicals (lime + soda) feed inlet
Reaction tank
Softened water
Conical sedimentation tank
Fine sand layer
Coarse sandlayer
Sand filter
Gravels layers
Precipitated sludge [CaCO₃Mg(OH)₂]
Precipitated sludge outlet
Filtered softened water outlet

Principle:
In this method water is treated with softening chemicals like soda and Lime at a temp. of 80°C to 150°C. this process is operated at a temp close to boiling point of the solution. Hence the reaction proceeds faster, the softening capacity Of the process increased many fold, the precipitate and sludge formed settle down rapidly and hence no coagulants are required.

Much of the dissolved gases like CO2 & air are driven out of water.

Viscosity of soften water is lowered therefore filtration of water becomes much easier.

This method produces water of comparatively lower residual hardness of 15 to 30 ppm.
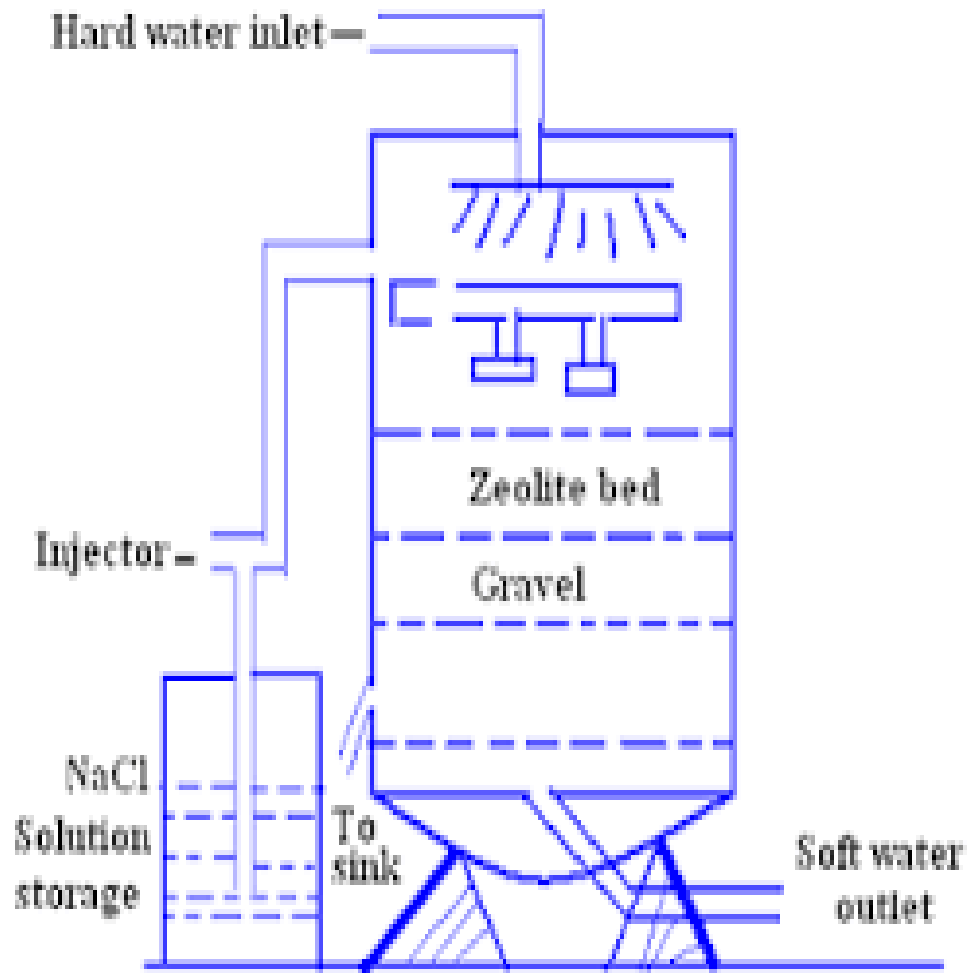
Advantages of Lime Soda Process

- It is very Economical
- If the process is combined with sedimentation & coagulation, lesser amounts of coagulants shall be needed.
- The process increases the pH value of the treated water, thereby corrosion of the distribution pipe is reduced.
- Besides the removal of hardness, the quantity of minerals in the water is reduced.
- To a certain extent, iron and manganese are also removed from the water.
- Due to alkaline nature of treated water, the amount of pathogenic bacterial in water is considerably reduced.

Disadvantages

- For efficient and economical softening, careful operation & skilled supervision is required.

- Disposal of large amounts of sludge poses a problem. However the sludge may be disposed off in raising low lying areas of the city.

- This can remove hardness only up to 15ppm which is not good for boilers.

Softening of water by zeolite process

- Sodium zeolite: $Na_2O.\ Al_2O_3.xSiO_2.yH_2O$

- Where x = 2-10 and y = 2-6

- Zeolite is sodium alumino silicate capable of exchanging reversibly its sodium ions for hardness producing ions present in water.

- Types of zeolite

- Natural Zeolite: are non porous eg. Natrolite $Na_2O.Al_2O_3.4SiO_2.2H_2O$

- Synthetic Zeolite: are porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash.

Softening Process :

$$Na_2ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2\ NaHCO_3$$
$$Na_2ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2\ NaHCO_3$$

Regeneration :

$$CaZe + 2\ NaCl \longrightarrow Na_2ze + CaCl_2$$
$$MgZe + 2\ NaCl \longrightarrow Na_2ze + MgCl_2$$

Advantages of zeolite process

- It removes the hardness almost completely and water of about 10ppm hardness is produced.

- The equipment used is compact, occupying small space.

- No impurities are precipitated, so there is no danger of sludge formation in treated water at a later stage.

- The process automatically adjusts itself for variation in hardness of incoming water.

- It is quite clean process.

- It requires less time for softening.

- It requires less skill for maintenance as well as operation.

Disadvantages

- The treated water contains more sodium salts than in lime soda process.

- The method only replaces Ca2+ and Mg2+ ions by Na+ ions but leaves all the acidic ions like HCO_3- and CO_32- as such in the softened water.

- When such soften water is used in boilers for steam generation, sodium carbonate decomposes producing CO2, which cause corrosion and sodium carbonate hydrolyses to sodium hydroxide which cause caustic embrittlement.

- High turbidity water cannot be treated efficiently by this method.

Numerical 1: The hardness of 10000 litres of hard water sample was completely removed by passing it through a zeolite softener. The zeolite softener required 5000litres of NaCl soln containing 1170mg of NaCl/L. Determine hardness of water sample.

Solution:

5000 L of NaCl soln = 5000 x 1170mg of NaCl

= 5850000mg of NaCl

1eq of NaCl = 1eq of CaCO3

58.5mg of NaCl = 50mg of CaCO3

5850000mg of NaCl = 5000000 mg of CaCO3

There fore,

10000L of Hard water = 5000000mg of CaCO3

1L of Hard water = 5000000/10000 = 500mg of CaCO3

Hence Hardness of water = 500ppm.

Numerical 2: An Exhausted zeolite softener was regenerated by passing 75L of NaCl soln having strength of 75g/L. If 1.6×10^4 hard water was passed though zeolite bed, what will be the hardness of water.

Soln:

75L of NaCl = 75 x 75 g of NaCl = 5625g of NaCl

$$= 5625 \times 10^3 \text{ mg of NaCl}$$

1eq of NaCl = 1eq. Of CaCO3

58.5mg of NaCl = 50mg of CaCO3

5625×10^3 mg of NaCl = $5625 \times 10^3 \times 50/58.5$ mg of $CaCO_3$

$$= 4.81 \times 10^6 \text{ mg of } CaCO_3$$

1.6×10^4 L of hard water = 4.81×10^6 mg of CaCO3

1L of hard water = 4.81×10^6 / 1.6×10^4

$$= 300\text{ppm}$$

Numerical 3: An exhausted zeolite softener was regenerated by passing 125L of NaCl having strength 50gNaCl/L. If the hardness of water is 350ppm, then calculate the total volume of water sample.

Soln:

125L of NaCl = 125 x 50g of NaCl

= 6250g = 6250000mg of NaCl

58.5mg of NaCl = 50mg of CaCO3

6250000mf of NaCl = 6250000x50/58.5

= 5341880mg of CaCO3

1L of hard water = 350mg of CaCO3

Therefore,

x L of Hard water = 5341880mg of CaCO3

Hence volume of hard water = 5341880/350

= 15262.5L

- Numerical4: Calculate the volume of NaCl (12.5g/L) in L for regeneration of zeolite, the 200ppm of 10000L of hardwater was passed through it to get zeolite exhausted.

Softening of Water by Ion-Exchange Process Or Demineralization process
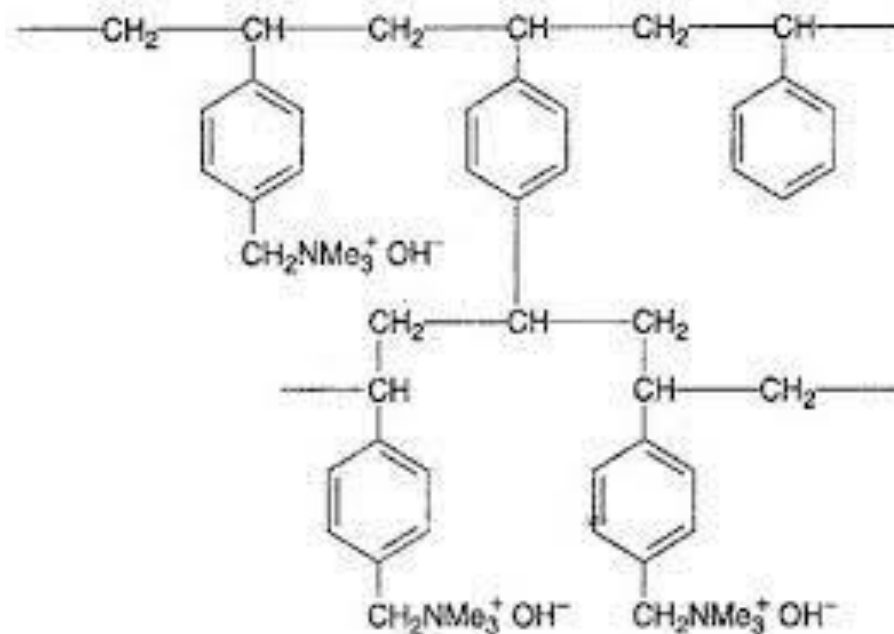
- Ion e[...] organic poly[...]

- **Catio** [...] ers which on s[...] nging their hydr[...]
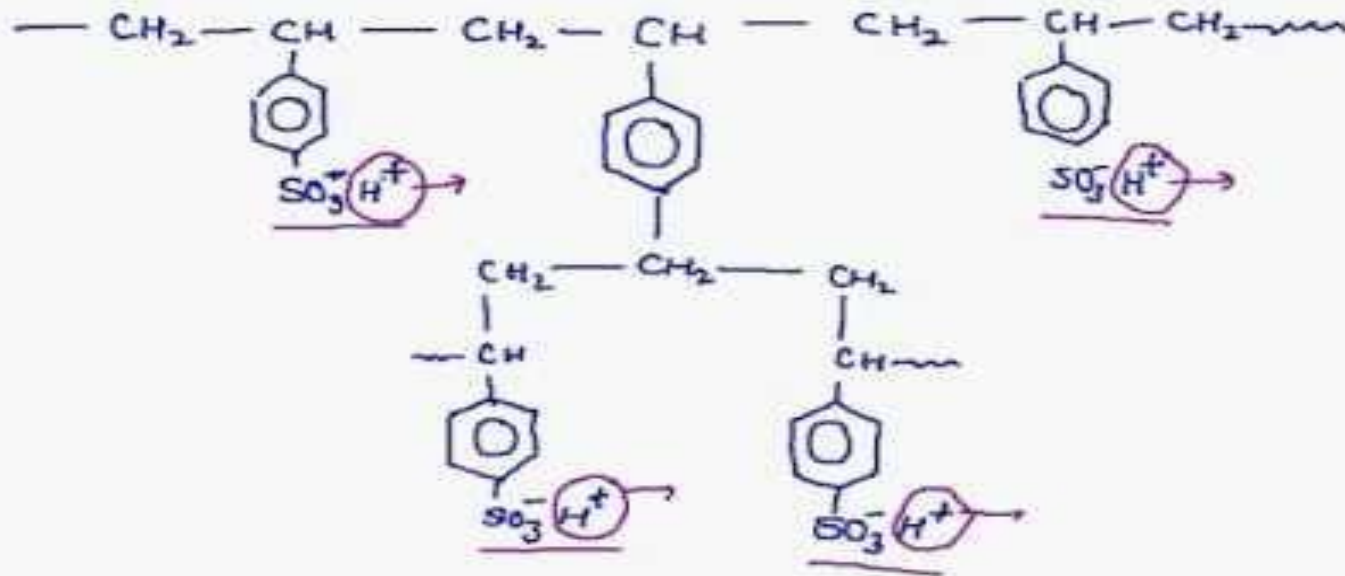
Cation exchange resin :→

Anion Exchange resin: Styrene-divinyl benzene copolymers which on further functionalization like formylation followed by Mannich reaction or nitration follo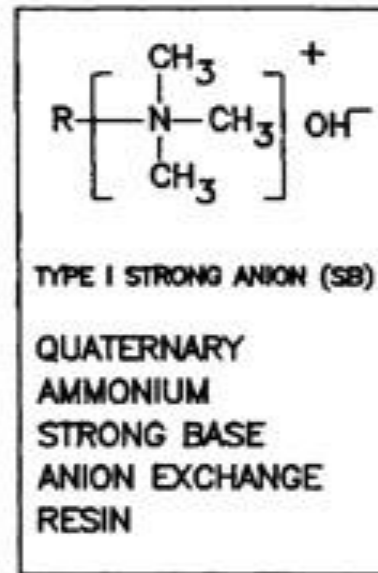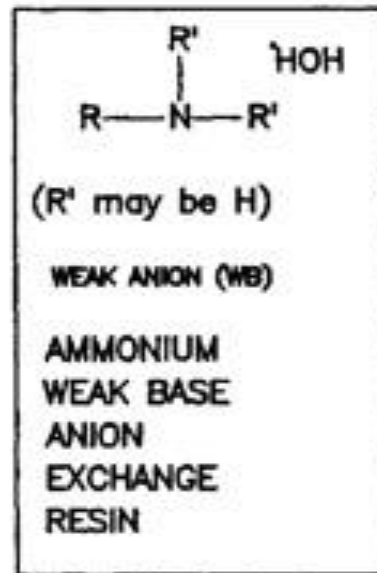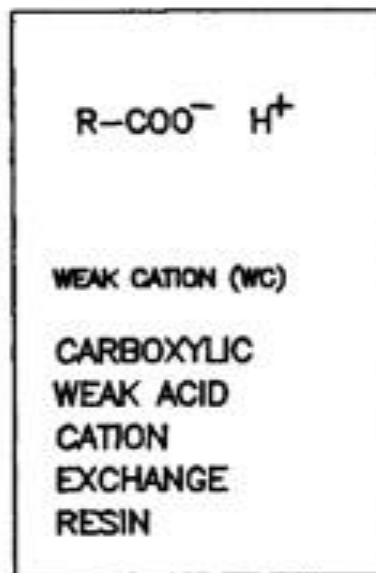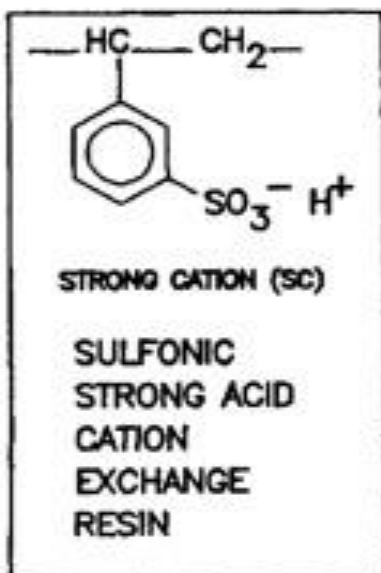wed by amination and alkylation gives quaternary ammonium groups as an integral part of the resin matrix. These after treatment with dil NaOH soln become capable of exchanging their OH- anions with anions of hard water.

DIVINYL-
BENZENE
MONOMER
FOR CROSS-
LINKING
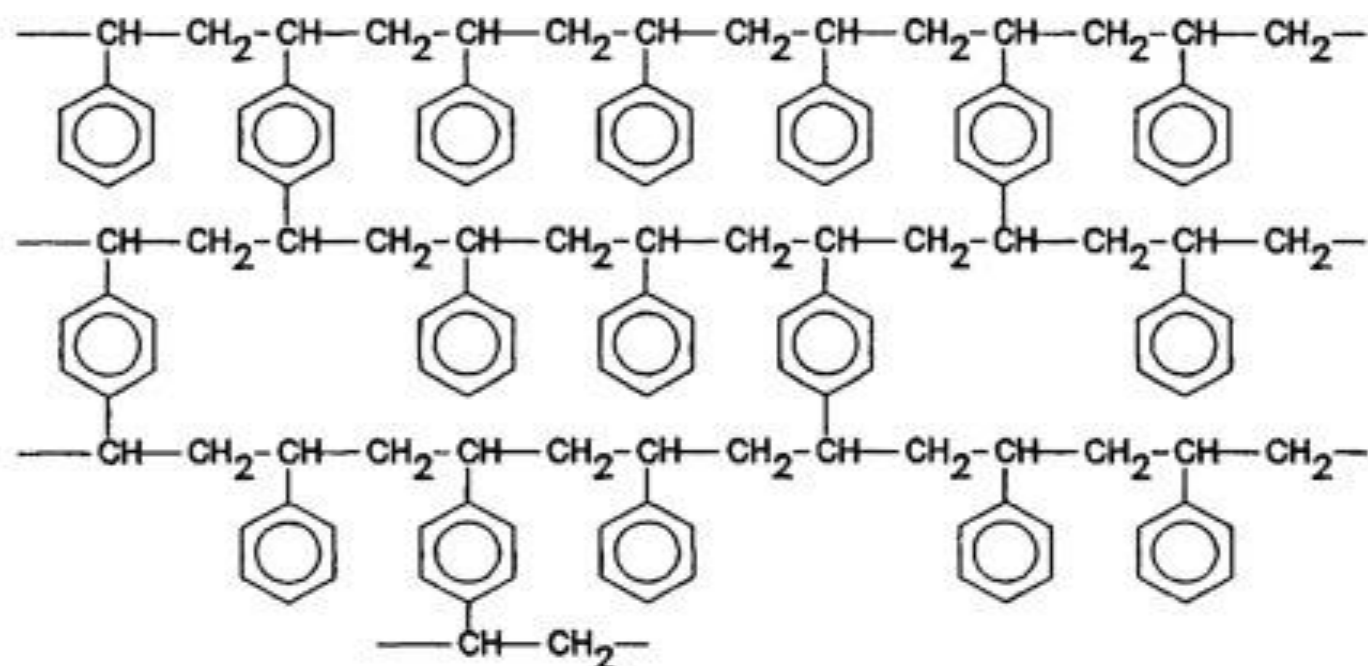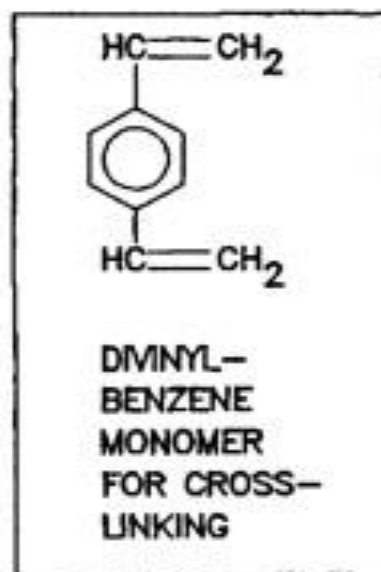
POLYSTYRENE DIVINYLBENZENE BACKBONE

$SO_3^- H^+$

STRONG CATION (SC)

SULFONIC
STRONG ACID
CATION
EXCHANGE
RESIN

$R-COO^- \ H^+$

WEAK CATION (WC)

CARBOXYLIC
WEAK ACID
CATION
EXCHANGE
RESIN

$R-\overset{R'}{\underset{}{N}}-R'$ HOH

(R' may be H)

WEAK ANION (WB)

AMMONIUM
WEAK BASE
ANION
EXCHANGE
RESIN

$R-\left[\overset{CH_3}{\underset{CH_3}{N}}-CH_3\right]^+ OH^-$

TYPE I STRONG ANION (SB)

QUATERNARY
AMMONIUM
STRONG BASE
ANION EXCHANGE
RESIN

$R-\left[\overset{CH_3}{\underset{CH_2CH_2OH}{N}}-CH_3\right]^+ OH^-$

TYPE II STRONG ANION (SB)

QUATERNARY
AMMONIUM
STRONG BASE
ANION EXCHANGE
RESIN

Process: Ca(HCO3)2, CaCl2, MgCl2
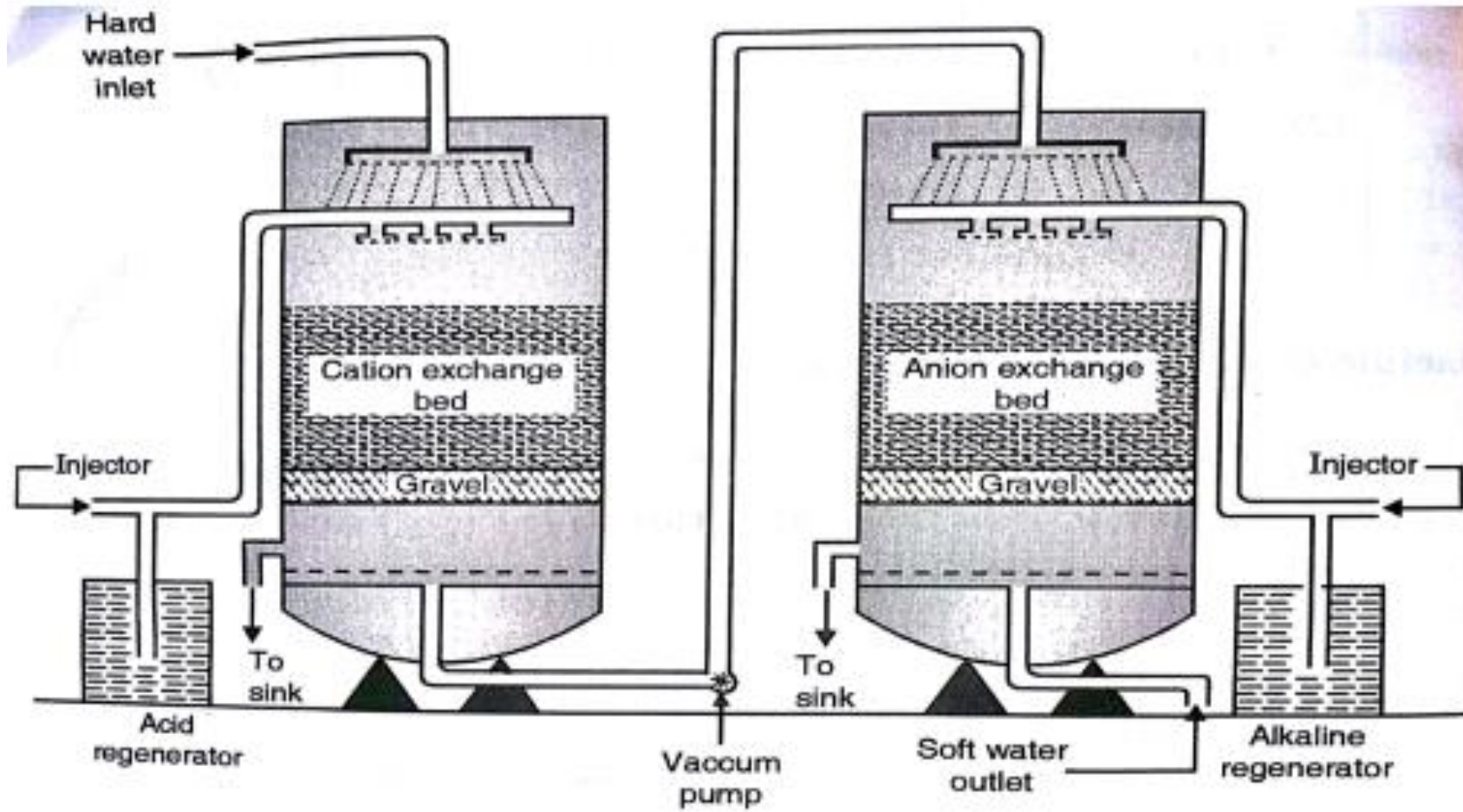
Demineralisation Diag. 2

Reactions with Cation Exchanger: RH+

RH+   + Ca^{2+} → R_2Ca + 2H+

Resin   Hardwater   Resin   Soften water

RH+   + Mg^{2+} →   R2Mg + 2H+
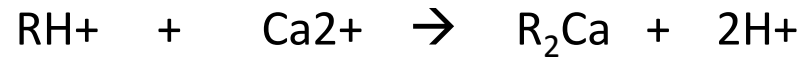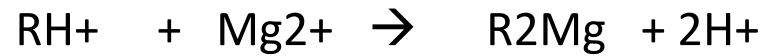
HCo_3^-, Cl^-, So_4^-

Reactions with Anion Exchanger: R'OH

R'OH   + Cl^- →   R'Cl + OH-

Resin   Hard Water   Resin   Soften water

2R'OH + SO_4^- →   R'2SO4 + 2OH-

Overall Reaction:

H+   +   OH-   → H2O
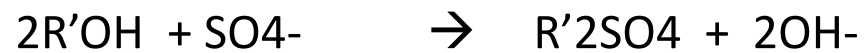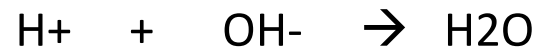
Regeneration Reactions

Cation Exchanger

R_2Ca + 2HCl   →   RH+   + CaCl2

                          Regenerated Resin   Washings

Anion Exchanger

R'_2SO_4 + 2NaOH   →   2 R'OH   + Na_2SO_4

Advantages

- The process can be used to soften highly acidic or alkaline water.

- It produces water of very low residual hardness (2ppm) so it is very good for treating water for use in high pressure boilers.

- Disadvantages:

The Equipment is costly and more expensive chemicals are needed.

If water contains turbidity then the output of the process is reduced. The turbidity must be below 10ppm. If it is more it has to be removed first by coagulation and filtration.

Numerical 1: After treating 10000 litres of water by ion exchanger the cationic resin required 200 litres of 0.1N HCl and anionic resin required 200 Litres of 0.1N NaOH soln. Find the hardness of water.

Soln:

Hardness of 10000L of water = 200 L of 0.1N HCl

$\qquad$ = 200L of 0.1 N NaOH

1 eq. of HCl = 1 Eq. of $CaCO_3$

0.1N of HCl = 0.1N of $CaCO_3$

Hence,

Hardness of 10000L of water = 200L of 0.1N $CaCO_3$ eq.

$\qquad$ = 20L of 1N $CaCO_3$ eq.

Std Statement: 1L of 1N $CaCO_3$ = Eq. wt = 50g

Hardness of 10000L of water = 20 x 1L of 1N $CaCO_3$

$\qquad$ = 20 x 50 g = 1000g

$\qquad$ = 1000000mg of $CaCO_3$ eq.

Hence,

Hardness of 1L of water = 1000000/10000 = 100mg/L = 100ppm

- Numerical 2: After treating 50000 litres of water by ion exchanger the cationic resin required 150 litres of 0.25N HCl and anionic resin required 150 Litres of 0.25N NaOH soln. Find the hardness of water.

BOD:

Biological oxygen demand of sewage is defined as the amount of free oxygen required for the biological oxidation of the organic matter under aerobic condition at 20°C for a period of 5days.

Unit of BOD = ppm or mg/L

Determination of BOD

A known volume of effluent sample is diluted with a known volume of water. Sample is diluted to ensure that sufficient oxygen is available for the complete aerobic oxidation of organic matter.

The diluted sample is divided into two parts and kept in two stoppered bottles. The dissolved oxygen content of one of the bottle is determined by Winkler's methodwhich is blank reading. It is denoted as DO_b .

Another bottle is incubated at 20°C for 5days. Then dissolved oxygen is determined. This is denoted as Doi.

The difference between Dob and Doi gives BOD.

BOD = (DOb-Doi) x dilution factor

= (Dob-DOi) x Volume of sample after dilution/volume of sample before dilution.

BOD test is susally influenced by the type of micro-organisms, presence of toxins, pH, Some reduced minerals;etc.

Reaction:

Organic Matter + O2 → CO2 + H2O

BOD is proportional to the amount of organic waste to be degraded.

An average sewage has BOD of 100-150ppm.

Drinking water should have BOD less than 1ppm.

Significance of BOD:

1. It indicates the amount of decomposable organic matter in sewage.

2. The higher is the BOD of a sample the higher the amount of decomposable organic matter in the sample and the higher is the pollution in water.

3. From BOD self purifying capacity of streams cans be determined. Thus it provides the degree of pollution at any time in the sewage stream.

COD

Chemical oxygen demand may be defined as the amount of oxygen required for the oxidation of chemically degradable organic matter in the hot conditions with the use of oxidants like acidified K2Cr2O7 in 2-3hrs.

Unit of COD = mg/L or ppm

Determination of COD:

A known volume of waste water sample is refluxed with a known excess of standard potassium dichromate soln and dilute sulphuric acid in presence of silver sulphate for 2-3hs. Silver sulfate is used as catalyst to promote oxidation of straight chain aliphatic compounds, aromatic compounds.
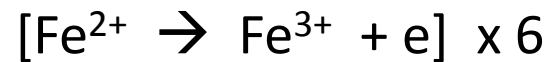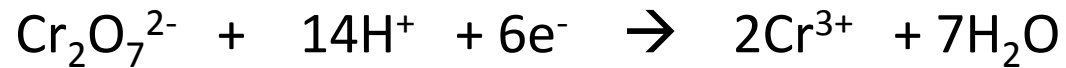
The organic matter of the sample is oxidized to ammonia, CO2 and H2O. The unreacted K2Cr2O7 is titrated against Ferrous ammonium sulphate[FeSo4.(NH4)2SO4.H2O]i.e. Mohr's Salt.

This experimentally measured amount of potassium dichromate is used to calculate the equivalent oxygen required by the waste water for degradation of the pollutants.

Reactions

$CxHyOz + (x + y/4 - z/2) O2 \rightarrow xCO2 + y/2 H2O$
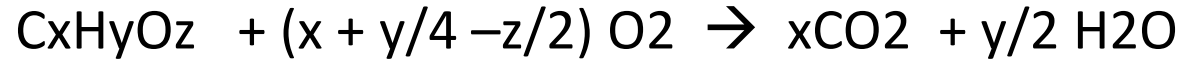
The unreacted dichromate solution is titrated against Mohrs salt using ferroin indicator.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$[Fe^{2+} \rightarrow Fe^{3+} + e] \times 6$

Overall reaction

$Cr_2O_7^{2-} + 14H^+ + 6 Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$
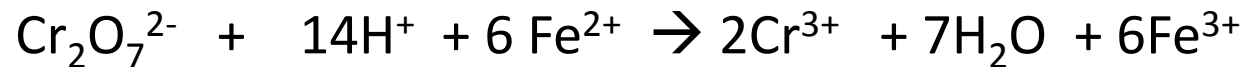
The COD is calculated as

$$COD = \frac{(V1-V2) \times N_{FAS} \times 8000}{Volume\ of\ sample}$$

V1 = vol. of FAS in blank titration

V2 = vol. of FAS in back titration

Significance of COD

The COD value is not affected by the presence of toxins and other unfavaourable conditions for the growth of microorganisms.

It is taken as basis for calculation of efficiency of treatment plant.

It help in designing the water treatment plant.

Numerical 1: A 50mL of sample contains 840ppm of dissolved oxygen. After 5days the dissolved oxygen value becomes 230 ppm, after the dilution of sample to 80mL. Calculate the BOD.

Soln: BOD = (Dob-Doi) x Volume of sample after dilution/ vol of sample before dilution

BOD = (840-230) x 80/50 = 976ppm

Numerical 2: A 25mL of sewage water sample was refluxed with 10mL of 0.25N K2Cr2O7 soln in presence of dil.H2SO4, Ag2SO4 and HgSO4. The unreacted dichromate required 6.5ml of 0.1N FAS. 10mL of same K2Cr2O7 required 27mL of 0.1N FAS. Calculate COD.

Given: Volume of sample = 25mL

Blank titration reading (V1) = 27mL

Back titration reading (V2) = 6.5mL

COD= (V1-V2) x N(FAS) x 8000/Vol. of Sample

= (27-6.5) x 0.1 x 8000/25 = 656ppm

Numerical 3: A 30mL of sewage water sample was refluxed with 15mL of 0.25N K2Cr2O7 soln in presence of dil.H2SO4, Ag2SO4 and HgSO4. The unreacted dichromate required 14 ml of 0.05N FAS. 10mL of same K2Cr2O7 required 20mL of 0.1N FAS. Calculate COD.

Note: Covert one statement in to fixed normality.

Volume of sample = 30mL

Blank Titration reading (V1) = 20ml of 0.1N FAS = **40 mL** of **0.05N** FAS

Back Titration reading (V2) = **14mL** of **0.05N** FAS

COD = 346.667ppm

Sewage Treatment

A sewage is the liquid waste which includes human and house hold waste water, industrial waste ground waste and street, storm waste.

Before disposing off the sewage to river or sea, it has to be treated.

To prevent –pollution of water

-- Offensive odour in water

- the destruction of fish and other aquatic life

Sewage treatment by activated sludge process.

Sewage contains minerals and inorganic matter in suspension and in solution. It contains sometimes harmful living organisms. Hence it is better to treat sewage before releasing into the river, lake and sea.

It involves four steps

1. Preliminary treatment
2. Primary treatment'
3. Secondary or biological treatment: activated sludge method
4. Tertiary treatment

1) Preliminary Treatment

The main objective of preliminary treatment is the removal of gross solid i.e. large floating and suspended matter, oil etc. For removing inorganic matter, sewage is allowed to pass through bar screens and mesh screens. It is also called as screening of sewage.

2) Primary Treatment

For removing suspended matter efficiently and economically, sedimentation process is carried out.

The sewage is treated with certain chemicals like(alum, hydrated lime etc.) which form a floc that absorbs and entrains the suspended and colloidal particles present.

3) Secondary treatment or Biological treatment

It is essentially an aerobic oxidation which includes filtration and activated sludge process.

i) Filtration: in this process, sewage water is filtered through specially designed sprinkling filters so that aerobic conditions are maintained.

During this process carbon of the organic matter is converted to CO_2 and nitrogen into NH_3 and finally onto nitrites and nitrates.

Trickling filters are used for the biological oxidation of sewage. Sewage is delivered to the filters by means of rotating distributors. As the trickled sewage starts flowing downwards, the aerobic bacteria grow on the surface. The bacteria bring about the biological oxidation of organic matter of sewage. The treated water comes out from bottom.

ii) Activated sludge process

The sludge formed from previous oxidation process is known as activated sludge.

This process consists if mixing of sedimented sewage with proper quantity of activated sludge and the mixture is then agitated for 4-6hrs by blowing air.

Suspended dissolved organic matter is oxidized by aerobic oxidation, then affluent is sent to sedimentation tank, where sludge is deposited and clean water drawn off.

A part of sludge deposited is used for next oxidation batch and the remainder is either spread on land as fertile matter or used for biogas or dumped in sea.

- 4) Tertiary Treatment

It is applied to decrease the load of nitrogen and phosphorous compounds present in effluents.

It involves treatment of effluent with lime which reacts with phosphorous to form calcium phosphate.

Nitrogen stripping is carried out to remove ammonia gas.

Chlorination was carried out to kill the disease causing microorganisms present in sewage water.

The so treated water is finally discharged into the rivers or lakes.