

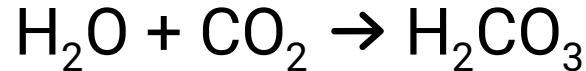
# Water

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# **Sources and Impurities in Water**

- Sources
- Impurities
  - i) Physical Impurities
  - ii) Chemical Impurities
  - iii) Biological Impurities

# **Acidity in water**



## **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

# TEXTILE INDUSTRY

- Hard water causes much of soap used in washing yarn, fabric etc. to go as waste because hard water cannot produce good quality of lather.
- Precipitates of **calcium** and **magnesium** soaps adhere to fabrics.
- These fabrics when dyed doesn't produce exact shades of color.
- If the water contains **Iron, manganese, color or turbidity**, it leaves stains on fabrics.
- Organic matter imparts foul smell.



# SUGAR INDUSTRY

- Water containing **sulphates, nitrates, alkali carbonated**, etc., if used in sugar refining causes difficulties in the crystallization of sugar.
- Moreover, the sugar so produced may be deliquescent.
- The color and taste of the sugar also changes.



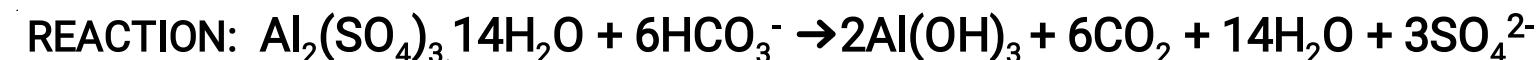
# DYEING INDUSTRY

- Hard water contains dissolved **calcium, magnesium** and **iron** salts. These salts present in hard water may react with costly dyes, forming undesirable precipitates, which yield impure shades.
- Uniform dyeing is not possible because
  1. Hard water decreases the solubility of dye or color. (PH increases)
  2. Basic dyes also precipitate out in hard water. (eg.  $\text{Ca}^{2+}$  ions react with  $(\text{HCO}_3^-)$  ions to form insoluble calcium carbonate ( $\text{CaCO}_3$ ))
- They also give spots on the fabrics being dyed.



# PAPER INDUSTRY

- Calcium and magnesium salts present in hard water tend to react with chemicals and other materials employed to provide a smooth and glossy (i.e. shining) finish to paper.
- It also produces in the cracks in paper.
- Alkalinity (consumes alum and increases the cost of production)



- Moreover, iron and manganese salts may even affect the brightness and color of paper being produced.
- Calcium and magnesium salts increase the ash content of paper.



# LAUNDRY INDUSTRY

- Laundries require soft water, free from color, **manganese** and **iron**
- Due to hard water, consumption of soaps increases.
- **Iron** and **manganese** salts impart a grey or yellow shade to the fabric
- Weakening of fibres causing tears and thus shortening the life of the
- Fabrics lose their soft and supple feel to become stiff and harsh.
- Extra detergent, extra rinse and wash cycles to clean the laundry.



# PHARMACEUTICAL INDUSTRY

- Pharmaceutical industries require ultra pure water which should be colorless, odourless, tasteless and free from pathogenic organisms.
- Hard water, if used for preparing pharmaceutical products like drugs, injection, ointments, etc. may produce undesirable products in them.
- According to the pharmaceutical guidelines stated by

## WORLD HEALTH ORGANISTION

If the pharmaceutical manufacturer's water supply is “hard” it needs to be “softened” which increases the cost of production.

## PHARMACEUTICAL INDUSTRY

### Application Scheme



# BEVERAGE INDUSTRY

- Water used in beverage industries is very sensitive.
- Water should be free from any contaminants and micro-organisms.
- Water required should not be alkaline, as it destroys or modifies the taste as it tends to neutralize the fruit acids.
- If hard water is used in this industry, it can change soft drink color, test and odor. Moreover a deposit can be developed here.
- So water must be treated before use for decreasing the effects of hard water in beverages industries. Otherwise it would lessen the product quality.

# RUST FORMATION

- The carbonate hardness salts cause deposition in tubes and pipes:  
**REACTION:**  $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$
- The calcium carbonate ( $\text{CaCO}_3$ ) thus formed is responsible for deposition in pipes.
- Similarly the  $\text{CO}_2$  which is released reacts with water to form carbonic acid which is corrosive and causes severe corrosion in pipes.
- This decreases the strength of the material making it unsafe to bear high temperature and pressure.



# SLUDGE AND SCALE FORMATION

- In boilers, conc. of salts increases due to continuous evaporation of water.
- When the conc. reaches saturation point it is thrown out of the water in form of ppt, which gets settled on the inner walls of the boiler.
- If the ppt takes place in form of loose and soft ppt it is called as **sludge**. It is formed at comparatively colder regions of boiler or at bends. Eg.  $\text{Mg(OH)}_2$
- If the ppt sticks firmly to the inner walls of the boiler it called as **scales**. Sometimes it is even difficult to remove with hammer or chisel. Eg.  $\text{MgSiO}_3$
- **DISADVANTAGES OF SLUDGE AND SCALE FORMATION**
  1. Wastage of fuel
  2. Lowering of boiler safety
  3. Decrease in efficiency
  4. Danger of explosion

# SLUDGE AND SCALE FORMATION

**SLUDGE**



**SCALE**



# CAUSTIC EMBRITTLEMENT

- In a boiler, some qty. of  $\text{Na}_2\text{CO}_3$  added to soften the water. But since high pressure and high temperature in the boiler converts  $\text{Na}_2\text{CO}_3$  to  $\text{NaOH}$ .



- Because of  $\text{NaOH}$ , boiler water becomes alkaline. This very dilute alkaline water flows through minute hair cracks.
- When water evaporates, this dilute alkali becomes concentrated.
- This concentrated alkali reacts with **iron** to form **sodium ferroate**.



- This sodium ferroate gets deposited in crevices and cracks.
  - This reaction is reversible i.e. where at high temperature sodium ferroate decomposes to form  $\text{NaOH}$  and  $\text{Fe}_3\text{O}_4$ . So reaction continues making use of iron metal of boiler.
- REACTION:**  $\text{Na}_2\text{FeO}_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{NaOH} + 2\text{Fe}_3\text{O}_4$



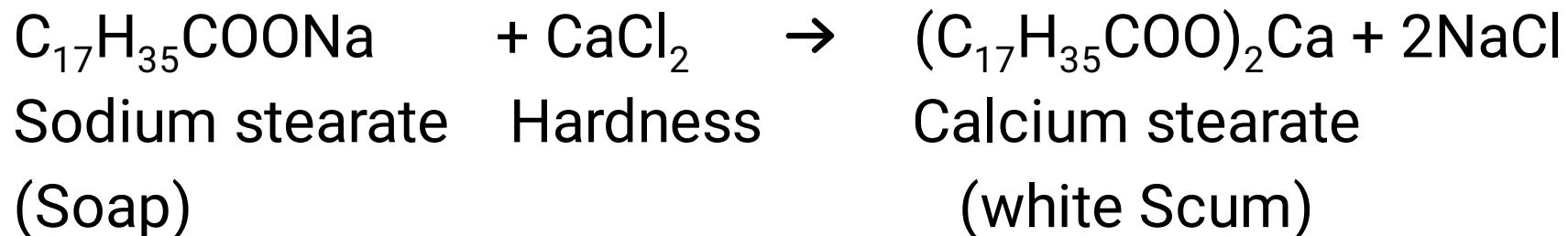
1. Engineering Chemistry Textbook by Chopra and Parmar
2. Engineering Chemistry by Pearson
3. <http://textilelearner.blogspot.com/>
4. <http://www.environmentalpollution.in/>
5. <https://www.chegg.com/homework-help/>
6. <http://web.deu.edu.tr/atiksu/ana52/>
7. <http://apps.who.int/medicinedocs/>

**THANK YOU!**

# 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



# 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.  $\text{CaCO}_3$ ,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{MgCO}_3$ ,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{FeCO}_3$

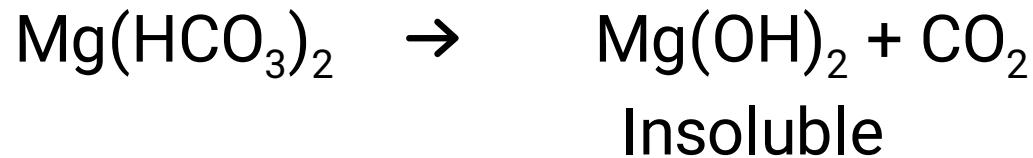
$\text{NaHCO}_3$ -non-hardness causing substance,  $\text{SiO}_2$ ,  $\text{NaCl}$ ,  $\text{KC}_3$ ,  $\text{KHCO}_3$

- **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.  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{CaBr}_2$ ,  $\text{CaSO}_4$ etc

$\text{KBr}$ -non-hardness causing substance.

- Temporary Hardness can be destroyed by boiling.
- boil



Permanent Hardness cannot be destroyed by boiling.

1. KHC03
  2. Mg(NO<sub>3</sub>)<sub>2</sub>= 10ppm      CaCO<sub>3</sub> eq. =3.5ppm
  3. FeSO<sub>4</sub>= 12ppm                CaCO<sub>3</sub>= 2.4ppm
  4. NaAlO<sub>2</sub>
  5. CaCl<sub>2</sub>= 7ppm                CaCO<sub>3</sub> = 1.1ppm
  6. Ca(NO<sub>3</sub>)<sub>2</sub> =60ppm    CaCO<sub>3</sub> eq. = 50ppm
- Hardness of water (CaCO<sub>3</sub> eq) = 3.5+2.4+1.1+50 =57ppm

CaCO<sub>3</sub> 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  $\text{CaCO}_3$
- Why to express hardness in terms of  $\text{CaCO}_3$ ?
- Ans: 1. the mol wt of  $\text{CaCO}_3$  is 100 and its equivalent wt is 50, which allows the multiplication and division in easy way when required.  
2.  $\text{CaCO}_3$  is the most insoluble salt which can be precipitated in water treatment.

# The Equivalent of CaCO<sub>3</sub>

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

Where Multiplication factor

= Chemical eq. of CaCO<sub>3</sub>

Chemical Eq. of hardness producing substance

= 50/ 74 {for Mg(NO<sub>3</sub>)<sub>2</sub>}

# Multiplication factors

Dissolved salt	Molar Mass	Chem. Eq.	M.F
1. Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	81	50/81 or 100/162
2. Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	73	50/73 or 100/146
3. CaSO <sub>4</sub>	136	68	50/68 or 100/136
4. FeCl <sub>2</sub>	127	63.5	50/63.5 or 100/127
5. CaCl <sub>2</sub>	111	55.5	50/55.5 or 100/111
6. MgSO <sub>4</sub>	120	60	50/60 or 100/120
7. MgCl <sub>2</sub>	95	47.5	50/47.5 or 100/95
8. CaCO <sub>3</sub>	100	50	1
9. MgCO <sub>3</sub>	84	42	50/42 or 100/84
10. CO <sub>2</sub>	44	22	50/22 or 100/44
11. Ca(NO <sub>3</sub> ) <sub>2</sub>	164	82	50/82 or 100/164
12. Mg(NO <sub>3</sub> ) <sub>2</sub>	148	74	50/74 or 100/148
13. HCO <sub>3</sub> <sup>-</sup>	61	61	50/61 or 100/122
14. OH <sup>-</sup>	17	17	50/17 or 100/34



# Units of hardness

1. Parts per millions(ppm): It is the parts of  $\text{CaCO}_3$  equivalent of hardness per  $10^6$  parts of water.
2. Milligram per Litre(mg/L): it is the number of milligram of  $\text{CaCO}_3$  equivalent of hardness present per litre of water.

$$\text{Mg/L} = \frac{1\text{g} \times 10^{-3}}{1000\text{mL}} = \frac{1\text{g}}{1000 \times 1000} = 1:10^6$$

3. Clarke's Degree ( ${}^\circ\text{Cl}$ ): It is the number of grains ( $1/70000$  lbs) of  $\text{CaCO}_3$  equivalent of hardness per gallon ( $10$  lbs) of water.  
OR It is parts of  $\text{CaCO}_3$  equivalent per  $70000$  parts of water.
4. Degree French ( ${}^\circ\text{Fr}$ ): It is the parts of  $\text{CaCO}_3$  equivalent per  $10^6$  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)  $20.23^{\circ}\text{Cl}$
- ii)  $31.3^{\circ}\text{Fr}$

**Numerical 2:** A sample of water has hardness 208ppm of  $\text{CaCO}_3$  equivalents. Find the hardness in terms of

- i) mg/L ii)  ${}^{\circ}\text{Fr}$  iii)  ${}^{\circ}\text{Cl}$  iv) meq/L

**Numerical 3:** How many grams of  $\text{FeSO}_4$  dissolved per litre gives 210.5ppm of hardness? (Fe = 56, S = 32, O = 16, Ca = 40, C = 12)

Soln: Mol. Wt of  $\text{CaCO}_3$  = 100g and mol. Wt of  $\text{FeSO}_4$  = 152g

100g of  $\text{CaCO}_3$  = 152g of  $\text{FeSO}_4$

100ppm of  $\text{CaCO}_3$  = 152ppm of  $\text{FeSO}_4$

Hence, 210.5ppm of hardness =  $152 \times 210.5 / 100$  ppm of  $\text{FeSO}_4$

$$= 319.96 \text{ mg/L}$$

$$= 0.320 \text{ g/L of } \text{FeSO}_4$$

**Numerical 4:** Calculate Temporary hardness and permanent hardness of water sample from the following data:  $Mg(HCO_3)_2 = 16.8\text{mg/L}$ ,  $MgCl_2 = 19\text{mg/L}$ ,  $MgSO_4 = 24\text{mg/L}$ ,  $Mg(NO_3)_2 = 29.6\text{mg/L}$ ,  $CaCO_3 = 4\text{mg/L}$ ,  $MgCO_3 = 10\text{mg/L}$ .

**Solution:**

Constituent (mg/L)	Multiplication Factor	CaCO <sub>3</sub> Eq.	Hardness
1. $Mg(HCO_3)_2 = 16.8$	$50/73$	11.5	T
2. $MgCl_2 = 19$	$50/47.5$	20	P
3. $MgSO_4 = 24$	$50/60$	20	P
4. $Mg(NO_3)_2 = 29.6$	$50/74$	20	P
5. $CaCO_3 = 4$	1	4	T
6. $MgCO_3 = 10$	$50/42$	11.9	T

$$\begin{aligned} \text{Temporary Hardness} &= \text{hardness due to } Mg(HCO_3)_2 + CaCO_3 + MgCO_3 \\ &= 11.5 + 4 + 11.9 = 27.4 \text{ ppm or } 27.4 \text{ mg/L} \end{aligned}$$

$$\begin{aligned} \text{Permanent Hardness} &= \text{hardness due to } MgCl_2 + MgSO_4 + Mg(NO_3)_2 \\ &= 20 + 20 + 20 = 60\text{mg/L} = 60\text{ppm} \end{aligned}$$

**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.

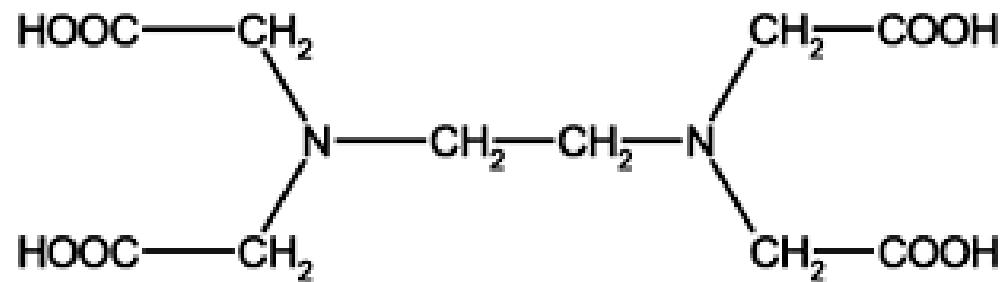
**Numerical 6:** How many grams of  $CaCl_2$  dissolved per litre gives 150ppm hardness?

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

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

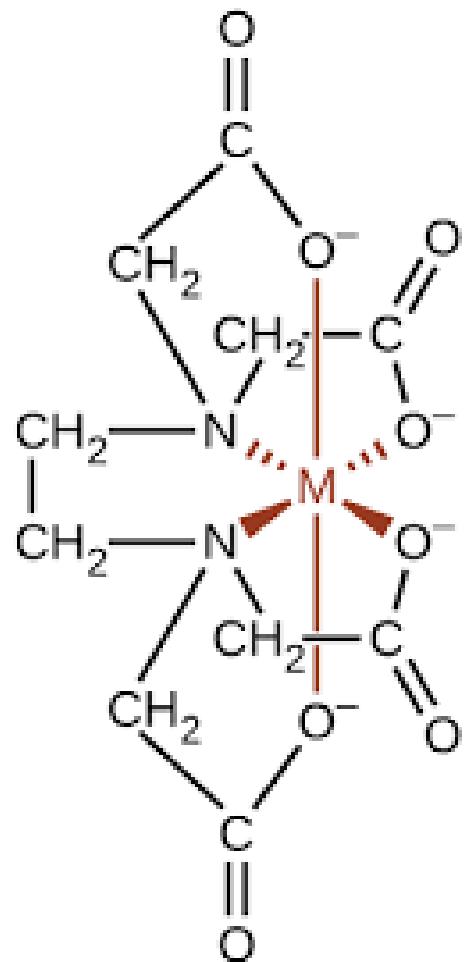
# Determination of hardness of water by EDTA method

- 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<sup>+</sup> ions on complete neutralization. Its formula is



*Figure 1. Molecular structure of EDTA*

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

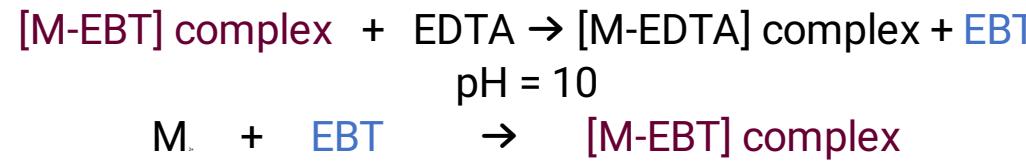


## Theory or Principle:

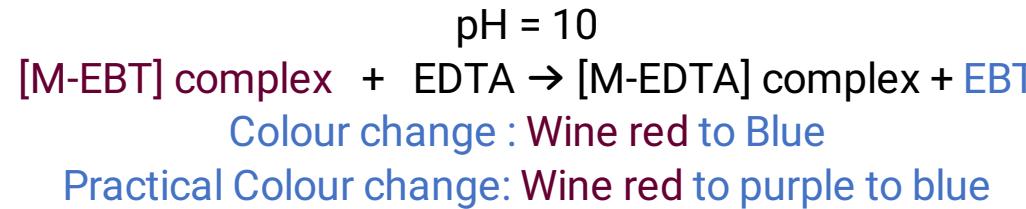
- The process involves the titration of metal ion solution with standardized EDTA soln. Indicator used is Eriochrome Black-T (EBT).
- EBT is alcoholic solution of blue eye. It forms an unstable wine-red complex with Ca<sup>2+</sup> & Mg<sup>2+</sup> at pH = 10. A buffer solution of NH<sub>4</sub>OH & NH<sub>4</sub>Cl 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.



**Titration Reaction:** During the course of titration with EDTA soln, EDTA combines with M<sup>2+</sup> ions to form stable complex M-EDTA & releases free EBT indicator, which immediately combines with remaining M<sup>2+</sup> ions present in solution. Thus wine red colour retained.



**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.



## **Experimental Procedure:**

### **A) Preparations of solutions**

#### **i) Preparation of Standard Hard water (SHW):**

Dissolve 1g of CaCO<sub>3</sub> 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<sub>3</sub> equivalent hardness.

1g of CaCO<sub>3</sub> in 1L of water = 1000mg of CaCO<sub>3</sub> in 1L = 1000ppm soln

1mL of SHW (CaCO<sub>3</sub>) soln = 1mg of CaCO<sub>3</sub>

100mL of SHW = 100 mg of CaCO<sub>3</sub>

1ppm = 1mg/L

**ii) Preparation of EDTA solution:** Dissolve 3.72g of pure EDTA + 0.1 mg MgCl<sub>2</sub> 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<sub>4</sub>Cl 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 V<sub>1</sub> mL.

50mL of SHW = V<sub>1</sub> mL of EDTA

1ml of EDTA = \_\_\_mg of CaCO<sub>3</sub>

**Step 2: Titration of unknown hard (bore well) water:** Titrate 50mL of sample water just same as given in step 1. Let the volume used be V<sub>2</sub> mL.

50mL of sample HW = V<sub>2</sub> 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 CaCO<sub>3</sub> and Mg(OH)<sub>2</sub>.) Filter the solution and titrate the filtrate as given in step 1. Let the volume used be V<sub>3</sub> mL.

50ml of boiled sample HW = V<sub>3</sub> mL of EDTA

**Permanent Hardness**

## **Calculations:**

50ml of SHW = V<sub>1</sub> mL of EDTA soln

Since 1 mL SHW contains 1mg of CaCO<sub>3</sub>,

50mg of CaCO<sub>3</sub> = V<sub>1</sub> mL of EDTA soln.

Hence,  $\frac{1\text{mL of EDTA}}{1\text{mL SHW}} = \frac{50}{1\text{mg of CaCO}_3}$  eq.

### **A) Total Hardness**

50mL of sample hard water = V<sub>2</sub> mL of EDTA soln

$$= V_2 \times \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ eq.}$$

Hence 1000mL of sample hard water =  $1000 \times V_2 \times \frac{50}{V_1} \times \frac{1}{50}$  mg of CaCO<sub>3</sub> eq.

there fore,  $\text{Total Hardness} = \frac{V_2}{V_1} \times 1000 \text{ ppm}$

### **B) Permanent Hardness:**

Now, 50ml of boiled sample water = V<sub>3</sub> mL of EDTA

$$= V_3 \times \frac{50}{V_1} \text{ mg of CaCO}_3$$

Hence 1000mL of Sample hard water =  $V_3 \times \frac{1000}{V_1} \text{ mg of CaCO}_3$

Therefore,  $\text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ ppm}$

**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<sub>3</sub>

50mL of SHW = 38 ml of EDTA soln.

There fore, 38mL of EDTA = 50mg of CaCO<sub>3</sub>

1mL of EDTA = \_50/38\_mg of CaCO<sub>3</sub>

**1mL of EDTA = 1.316mg of CaCO<sub>3</sub>**

**Total Hardness:**

100mL of sample HW =21 mL of EDTA solution

= 21 x 1.316 mg of CaCO<sub>3</sub>

= 27.636 mg of CaCO<sub>3</sub>

1000mL of sample HW = 27.636 x 1000/100

= 276.36mg of CaCO<sub>3</sub>/L = 276.36ppm

There fore **Total hardness = 276.36ppm**

**Permanent hardness:**

100mL of Boiled sample HW = 10mL of EDTA

= 13.16 mg of CaCO<sub>3</sub>

1000mL of boiled sample HW = 13.16 x 1000/100 = 131.6mg of CaCO<sub>3</sub> / L

**Permanent hardness = 131.6ppm**

**Temporary Hardness = Total hardness – permanent hardness**

= 276.36 – 131.6

= 144.76ppm

**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 CaCO<sub>3</sub>

50mL of SHW = 21mL of EDTA

There fore 21 mL of EDTA soln = 50mg of CaCO<sub>3</sub>

Hence      1mL of EDTA soln =  $50/21 = 2.381$ mg of CaCO<sub>3</sub> eq.

**Total Hardness**

50mL of sample HW = 21mL of EDTA soln

$$= 21 \times 2.381 = 50.001 \text{ mg of CaCO}_3 \text{ eq.}$$

1000mL of sample HW =  $50.001 \times 1000/50 = 50.001 \times 20$

$$= 1000.02 \text{ mg CaCO}_3/\text{L}$$

Hence Total hardness = 1000.02ppm

**Permanent Hardness**

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

$$= 7 \times 2.381 = 16.667 \text{ mg of CaCO}_3/\text{L}$$

1000mL of boiled sample HW =  $16.667 \times 1000/50 = 16.667 \times 20 = 333.34 \text{ mg of CaCO}_3$

Hence permanent hardness = 333.34ppm

Temporary Hardness = total hardness – permanent hardness =  $1000.02 - 333.34 = 666.68 \text{ ppm}$

**Numerical 3:** 0.38g of CaCO<sub>3</sub> was dissolved in HCl and the solution made up to 1 Litre 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 CaCO<sub>3</sub>~~

SHW = 0.38g of CaCO<sub>3</sub> / 1000mL = 380mg of CaCO<sub>3</sub> / 1000mL

~~1mL of SHW = 0.38mg of CaCO<sub>3</sub>.....using 1<sup>st</sup> statement of numerical~~

100mL of SHW = 25mL of EDTA

100mL of SHW = 38 mg of CaCO<sub>3</sub>

There fore 25mL of EDTA = 38mg of CaCO<sub>3</sub>

Hence 1mL of EDTA = 38/25 = 1.52mg of CaCO<sub>3</sub> .....using 2<sup>nd</sup> statement of numerical

**Total Hardness**

100mL of sample HW = 37mL of EDTA

$$= 37 \times 1.52 = 56.24 \text{ mg of CaCO}_3$$

1000ml of sample HW = 56.24 x 1000/100 = 562.4 mg of CaCO<sub>3</sub> /L

Hence Total hardness = 562.4ppm

**Permanent hardness**

100mL of Boiled sample HW = 10 ml of EDTA

$$= 10 \times 1.52 = 15.2 \text{ mg of CaCO}_3$$

1000mL of Boiled sample HW = 15.2 x 1000/100 = 152 mg of CaCO<sub>3</sub>

Hence permanent hardness = 152ppm

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

**Numerical 4:** 1.2g of CaCO<sub>3</sub> was dissolved in HCl and the solution made up to 1 Litre with distilled water. 50 mL of the above soln required 30 mL 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 CaCO<sub>3</sub> was dissolved in HCl and the solution made up to 1 Litre with distilled water. 20 mL of the above soln required 10 mL 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<sub>3</sub>

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

Std relationships says that,

1000mL of 1M EDTA = 100g of CaCO<sub>3</sub>.....due to Avogadro's numbers of molecules

1mL of 1M EDTA = 100mg of CaCO<sub>3</sub>

1mL of 0.05M EDTA =  $100 \times 0.05 = 5$ mg of CaCO<sub>3</sub>

Total Hardness:

50 mL of sample HW = 10.2mL of 0.05M EDTA soln  
=  $10.2 \times 5 = 51$ mg of CaCO<sub>3</sub> eq.

1000mL of sample HW =  $51 \times 1000/50 = 51 \times 20 = 1020$ mg of CaCO<sub>3</sub>

Hence Total Hardness = 1020ppm

Permanent Hardness:

50mL of Boiled sample HW = 6.5mL of 0.05M EDTA  
=  $6.5 \times 5 = 32.5$ mg of CaCO<sub>3</sub> eq.

1000mL of boiled Sample HW =  $32.5 \times 20 = 650$ mg of CaCO<sub>3</sub> eq

Hence Permanent Hardness = 650ppm

So, temporary hardness =  $1020 - 650 = 370$ ppm

**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

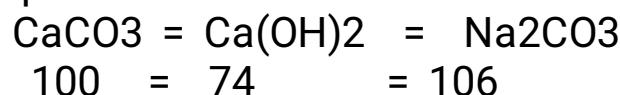
In this method hard water is treated with calculated amounts of slaked Lime[Ca(OH)<sub>2</sub>] and soda ash Na<sub>2</sub>CO<sub>3</sub> in reactions tanks. So as to convert hardness producing chemicals into insoluble compounds, which are then removed by settling and filtration.

Convert  $\text{Ca}^{2+}$  in  $\text{CaCO}_3$  and  $\text{Mg}^{2+}$  into  $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}^{2+} \rightarrow \text{Fe}(\text{OH})_2$

Constituent	Reactions Soda = $\text{Na}_2\text{CO}_3$ and Lime = $\text{Ca}(\text{OH})_2$	Requirement L or S
1) $\text{Ca}^{2+}$ (perm.) Eg. $\text{CaCl}_2$ , $\text{CaSO}_4$	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	S
2) $\text{Mg}^{2+}$ (perm.) Eg. $\text{MgCl}_2$ , $\text{MgSO}_4$	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$ ↓	L + S
3) $\text{HCO}_3^-$ Eg. $\text{NaHCO}_3$	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{CO}_3^{2-} = \text{Na}_2\text{CO}_3$	L - S
4) $\text{Ca}(\text{HCO}_3)_2$ Temp.	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	L
5) $\text{Mg}(\text{HCO}_3)_2$ Temp.	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	2L
6) $\text{CO}_2$	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
7) $\text{H}^+$	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \rightarrow 2\text{H}_2\text{O} + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
8) $\text{FeSO}_4$	$\text{FeSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 + \text{CaSO}_4$ $\text{Fe}(\text{OH})_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	L+S

Constituent	Reactions	Requirement t L or S
9) Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	$2\text{Al}^{3+} + 3 \text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{Ca}^{2+}$ $3\text{Ca}^{2+} + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 6\text{Na}^+$	L + S
10) NaAlO <sub>2</sub>	$\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NaOH}$	-L

Equivalence



$$\begin{aligned} \text{Lime required} &= 74/100 [\text{Mg}^{2+} \text{perm.} + \text{HCO}_3^- + \text{Ca}^{2+} \text{temp.} + 2 \text{Mg}^{2+} \text{temp.} + \text{CO}_2 + \text{H}^+ + \text{Fe}^{2+} + \text{Al}^{3+} - \text{NaAlO}_2] \text{ mg/L} \\ &= \underline{74 [\text{Mg}^{2+} \text{perm.} + \text{HCO}_3^- + \text{Ca}^{2+} \text{temp.} + 2 \text{Mg}^{2+} \text{temp.} + \text{CO}_2 + \text{H}^+ + \text{Fe}^{2+} + \text{Al}^{3+} - \text{NaAlO}_2]} \times \text{Volume of water} \times 100 \end{aligned}$$

$$\frac{100 \times 1000 \times \% \text{ Purity}}{_____}$$

$$= \text{g of Lime}$$

$$\begin{aligned} \text{Soda required} &= \underline{106 [\text{Ca}^{2+} \text{perm.} + \text{Mg}^{2+} \text{perm} - \text{HCO}_3^- + \text{H}^+ + \text{Fe}^{2+} + \text{Al}^{3+}]} \times \text{volume of water} \times 100 \\ &\quad \frac{100 \times 1000 \times \% \text{ purity}}{_____} \\ &= \underline{\underline{\text{g of Soda}}} \end{aligned}$$

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

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

Soln	Impurities	Multiplication Factor	CaCO <sub>3</sub> eq.	Requirement
1)	$Mg(HCO_3)_2 = 73\text{mg/L}$	$100/146 \text{ or } 50/73$	$= 73 \times 50/73 = 50$	2L
2)	$CaCl_2 = 222\text{mg/L}$	$100/111 \text{ or } 50/55.5$	$222 \times 100/111 = 200$	S
3)	$MgSO_4 = 120\text{mg/L}$	$100/120 \text{ or } 50/60$	$120 \times 100/120 = 100$	L + S
4)	$Ca(NO_3)_2 = 164\text{mg/L}$	$100/164 \text{ or } 50/82$	$164 \times 100/164 = 100$	S

$$\begin{aligned} \text{Lime required} &= \frac{74 \times [\text{CaCO}_3 \text{ eq of } 2 \times Mg(HCO_3)_2 + MgSO_4] \times \text{volume of water} \times 100}{100 \times 1000 \times \% \text{ purity}} \\ &= \frac{74 \times [2 \times 50 + 100] \times 6000 \times 100}{100 \times 1000 \times 74} = 200 \times 6 = 1200\text{g} = 1.2\text{Kg} \end{aligned}$$

$$\begin{aligned} \text{Soda Required} &= \frac{106 \times [\text{CaCO}_3 \text{ eq of } CaCl_2 + MgSO_4 + Ca(NO_3)_2] \times \text{vol. of water} \times 100}{100 \times 1000 \times \% \text{ purity}} \\ &= \frac{106 \times [200 + 100 + 100] \times 6000 \times 100}{100 \times 1000 \times 90} = 2826.67\text{g} = 2.827\text{Kg} \end{aligned}$$

Numerical 2: Calculate the quantity of soda and lime needed to soften 10000 litres of water containing following impurities.  $\text{Na}_2\text{SO}_4 = 7\text{mg/L}$ ,  $\text{SiO}_2 = 2\text{mg/L}$ ,  $\text{CaCl}_2 = 22.2\text{mg/L}$ ,  $\text{MgSO}_4 = 2.0\text{mg/L}$ ,  $\text{Mg}(\text{HCO}_3)_2 = 5.0\text{mg/L}$ .

Soln:

Impurities	Multiplication Factor	$\text{CaCO}_3 \text{ eq.}$	Requirement
1) $\text{Na}_2\text{SO}_4 = 7\text{mg/L}$	Non-hardness causing		
2) $\text{SiO}_2 = 2\text{mg/L}$	Non-hardness causing		
3) $\text{CaCl}_2 = 22.2\text{mg/L}$	$100/111 \text{ or } 50/55.5$	$= 22.2 \times 100/111$ $= 20$	<b>S</b>
4) $\text{MgSO}_4 = 2.0\text{mg/L}$	$100/120 \text{ or } 50/60$	$= 2 \times 100/120$ $= 1.67$	<b>L + S</b>
5) $\text{Mg}(\text{HCO}_3)_2 = 5.0\text{mg/L}$	$100/146 \text{ or } 50/73$	$= 5.0 \times 100/146 =$ $3.42$	<b>2L</b>

$$\begin{aligned}\text{Lime Required} &= \frac{74 \times [\text{CaCO}_3 \text{ eq. of MgSO}_4 + 2 \times \text{Mg}(\text{HCO}_3)_2 \times 10000]}{100 \times 1000} \\ &= \frac{74 \times [1.67 + 3.42 \times 2] \times 10000}{100 \times 1000} = 62.974\text{g}\end{aligned}$$

$$\begin{aligned}\text{Soda Required} &= \frac{106 \times [\text{CaCO}_3 \text{ eq. of CaCl}_2 + \text{MgSO}_4] \times \text{vol of water}}{100 \times 1000} \\ &= 229.702\text{g}\end{aligned}$$

Numerical 3: Calculate amount of lime (90% pure) and Soda (98% Pure) for the treatment of 1 million litres of water containing  $\text{Ca}(\text{HCO}_3)_2 = 8.1\text{ppm}$ ,  $\text{CaCl}_2 = 33.3\text{ppm}$ ,  $\text{HCO}_3^- = 91.5\text{ppm}$ ,  $\text{MgCl}_2 = 38\text{ppm}$ ,  $\text{Mg}(\text{HCO}_3)_2 = 14.6\text{ppm}$ . The coagulant  $\text{Al}_2(\text{SO}_4)_3$  was added at the rate of 17.1 ppm.

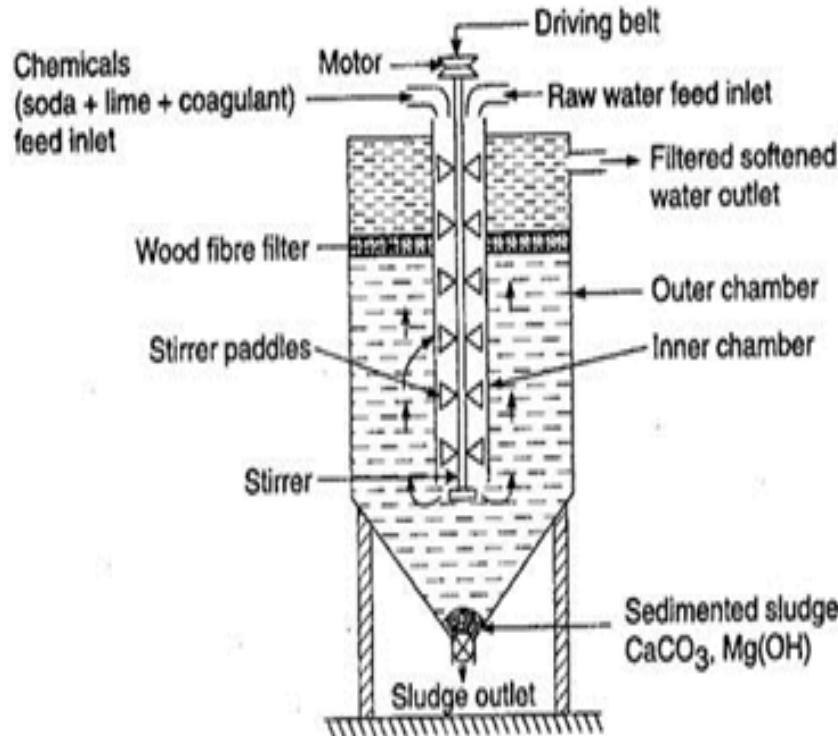
Impurities	Multiplication Factor	$\text{CaCO}_3$ eq.	Requirement
1) $\text{Ca}(\text{HCO}_3)_2 = 8.1\text{mg/L}$	= $100/162$ or $50/81$	5	L
2) $\text{CaCl}_2 = 33.3\text{mg/L}$	$100/111$ or $50/55.5$	30	S
3) $\text{HCO}_3^- = 91.5\text{mg/L}$	= $100/122$ or $50/61$	75	L - S
4) $\text{MgCl}_2 = 38.0\text{mg/L}$	$100/95$ or $50/47.5$	40	L + S
5) $\text{Mg}(\text{HCO}_3)_2 = 14.6\text{mg/L}$	$100/146$ or $50/73$	10	2L
6) $\text{Al}_2(\text{SO}_4)_3 = 17.1\text{mg/L}$	$100/114$ or $50/57$	15	L + S

Lime Required =  $127444.44\text{g} = 127.44\text{Kg}$   
 Soda required =  $10816.33\text{g} = 10.816\text{Kg}$

# Types of Lime Soda Processes

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

# Cold Lime Soda Method



## Principle:

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

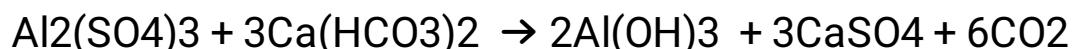
The precipitate formed are finely divided and therefore do not settle down easily and can't be filtered easily.

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

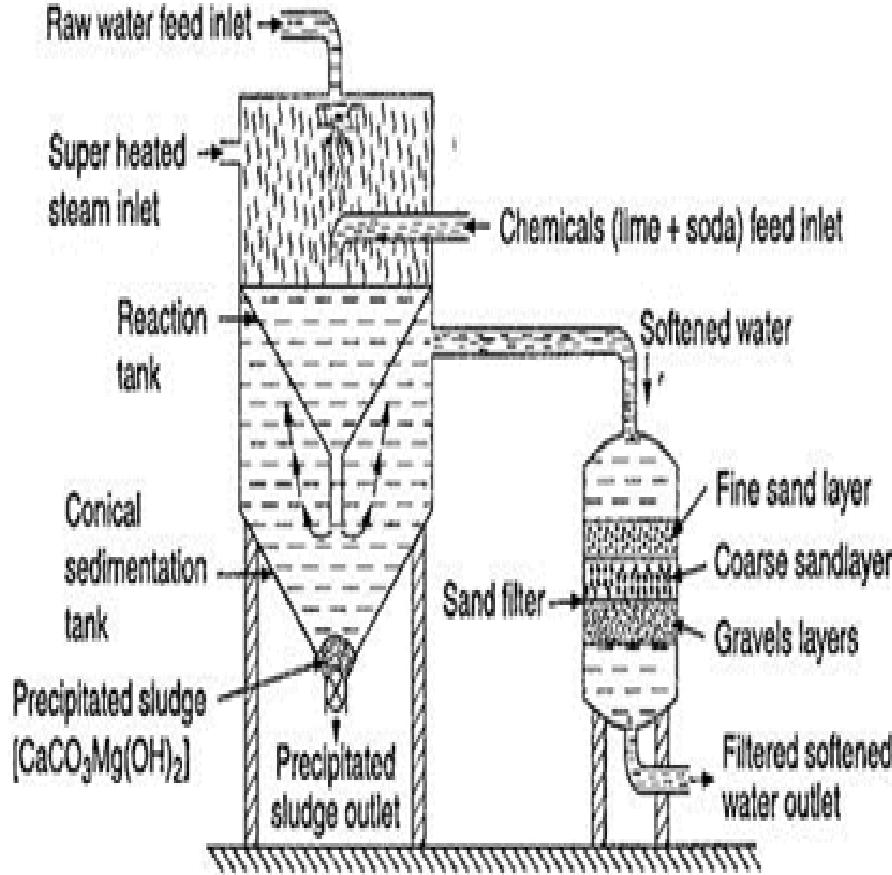
These hydrolyze to gelatinous ppt of aluminum hydroxide and entrap fine precipitate.

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.



# Hot Lime Soda Method



## Principle:

In this method water is treated with softening chemicals like soda and Lime at a temp. of  $80^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ . 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  $\text{CO}_2$  & 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

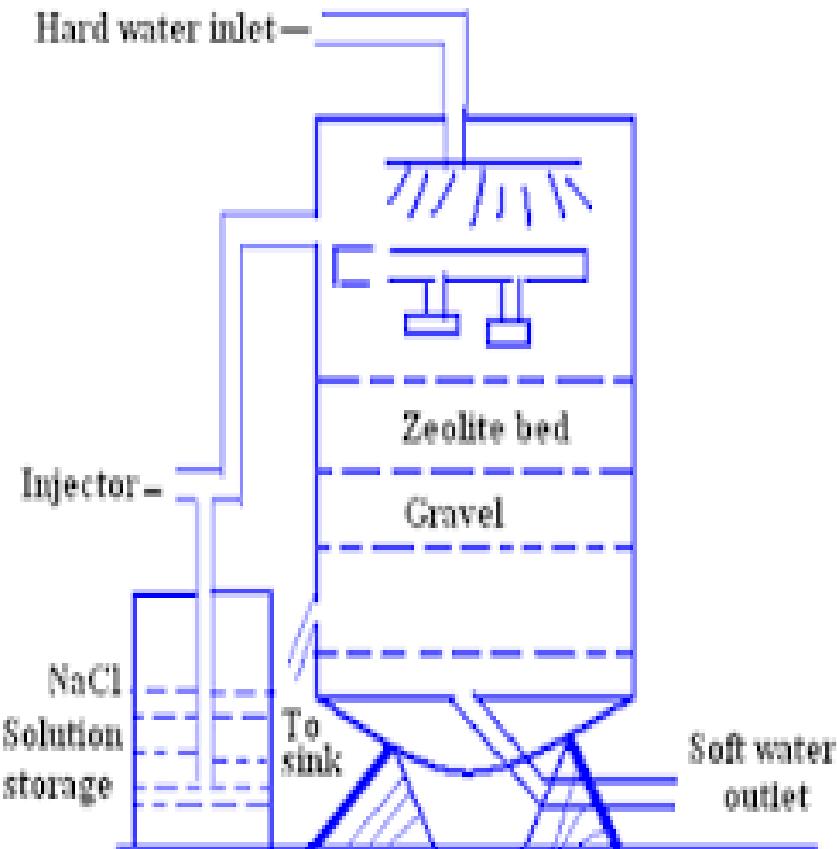
- It is very Economical
- If the process is combined with sedimentation & coagulation, lesser amounts of coagulants shall be needed.
- The process increases the pH value of the treated water, thereby corrosion of the distribution pipe is reduced.
- Besides the removal of hardness, the quantity of minerals 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:  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$
- Where  $x = 2-10$  and  $y = 2-6$
- 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  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- Synthetic Zeolite: are porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash.



Softening Process :



Regeneration :



## **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  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions by  $\text{Na}^+$  ions but leaves all the acidic ions like  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  as such in the softened water.
- When such soft water is used in boilers for steam generation, sodium carbonate decomposes producing  $\text{CO}_2$ , 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:

$$\begin{aligned} 5000 \text{ L of NaCl soln} &= 5000 \times 1170\text{mg of NaCl} \\ &= 5850000\text{mg of NaCl} \end{aligned}$$

$$1\text{eq of NaCl} = 1\text{eq of CaCO}_3$$

$$58.5\text{mg of NaCl} = 50\text{mg of CaCO}_3$$

$$5850000\text{mg of NaCl} = \underline{5000000} \text{ mg of CaCO}_3$$

There fore,

$$10000\text{L of Hard water} = 5000000\text{mg of CaCO}_3$$

$$1\text{L of Hard water} = 5000000/10000 = 500\text{mg of CaCO}_3$$

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  $1.6 \times 10^4$  hard water was passed through zeolite bed, what will be the hardness of water.

Soln:

$$\begin{aligned} 75\text{L of NaCl} &= 75 \times 75 \text{ g of NaCl} = 5625\text{g of NaCl} \\ &= 5625 \times 10^3 \text{ mg of NaCl} \end{aligned}$$

$$1\text{eq of NaCl} = 1\text{eq. Of CaCO}_3$$

$$58.5\text{mg of NaCl} = 50\text{mg of CaCO}_3$$

$$\begin{aligned} 5625 \times 10^3 \text{ mg of NaCl} &= 5625 \times 10^3 \times 50/58.5 \text{ mg of CaCO}_3 \\ &= 4.81 \times 10^6 \text{ mg of CaCO}_3 \end{aligned}$$

$$1.6 \times 10^4 \text{ L of hard water} = 4.81 \times 10^6 \text{ mg of CaCO}_3$$

$$\begin{aligned} 1\text{L of hard water} &= 4.81 \times 10^6 / 1.6 \times 10^4 \\ &= 300\text{ppm} \end{aligned}$$

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:

$$\begin{aligned}125\text{L of NaCl} &= 125 \times 50\text{g of NaCl} \\&= 6250\text{g} = 6250000\text{mg of NaCl}\end{aligned}$$

$$58.5\text{mg of NaCl} = 50\text{mg of CaCO}_3$$

$$\begin{aligned}6250000\text{mg of NaCl} &= 6250000 \times 50 / 58.5 \\&= 5341880\text{mg of CaCO}_3\end{aligned}$$

$$1\text{L of hard water} = 350\text{mg of CaCO}_3$$

Therefore,

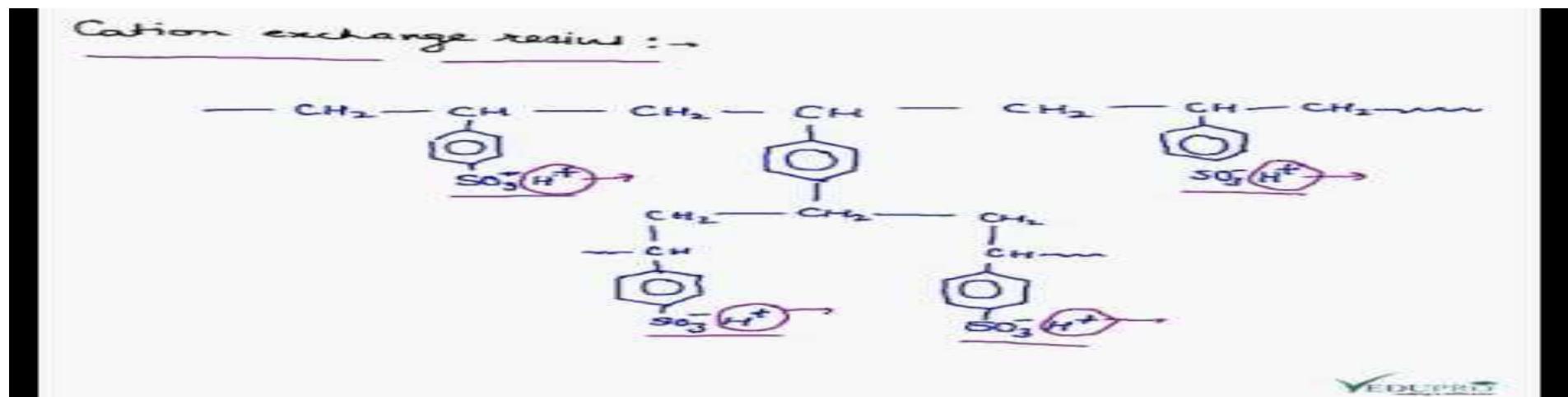
$$x \text{ L of Hard water} = 5341880\text{mg of CaCO}_3$$

$$\begin{aligned}\text{Hence volume of hard water} &= 5341880 / 350 \\&= 15262.5\text{L}\end{aligned}$$

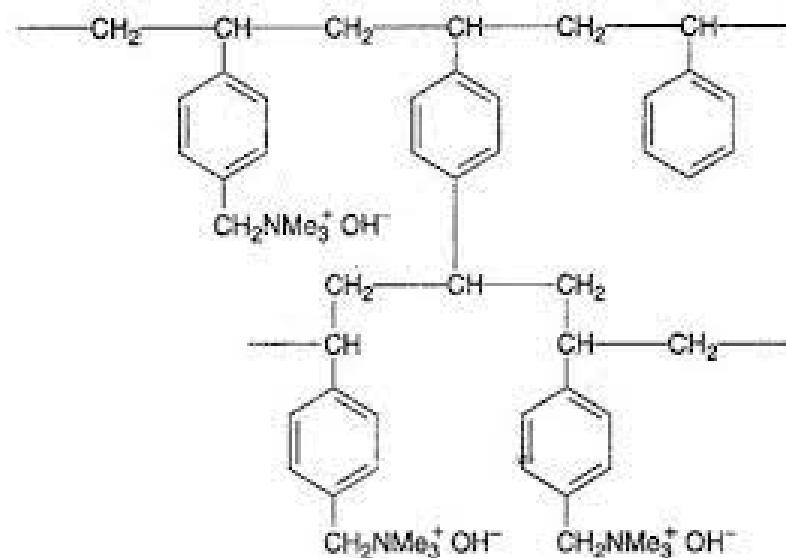
- Numerical4: Calculate the volume of NaCl (12.5g/L) in L for regeneration of zeolite, the 200ppm of 10000L of hardwater was passed through it to get zeolite exhausted.

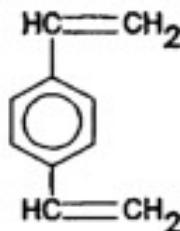
# Softening of Water by Ion-Exchange Process Or Demineralization process

- Ion exchange resins are insoluble cross linked long-chained organic polymers with a microporous structure.
- **Cation Exchange resin:** Styrene-divinyl benzene copolymers which on sulphonation or carboxylation become capable of exchanging their hydrogen ions with the cations in hard water.

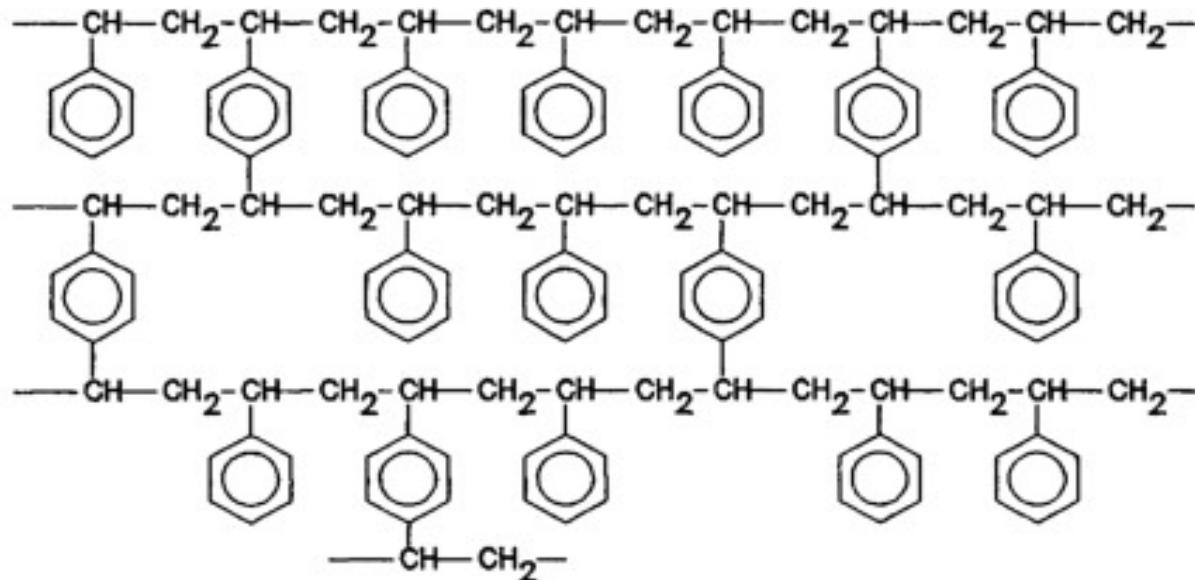


**Anion Exchange resin:** Styrene-divinyl benzene copolymers which on further functionalization like formylation followed by Mannich reaction or nitration followed by amination and alkylation gives quaternary ammonium groups as an integral part of the resin matrix. These after treatment with dil NaOH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

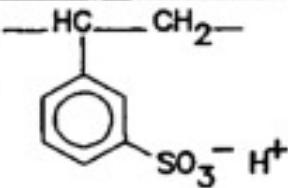




DIMINYL-BENZENE MONOMER FOR CROSS-LINKING



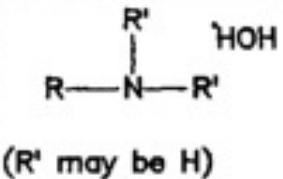
POLYSTYRENE DIMINYLBENZENE BACKBONE



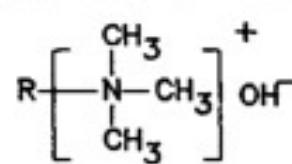
STRONG CATION (SC)  
SULFONIC  
STRONG ACID  
CATION  
EXCHANGE  
RESIN



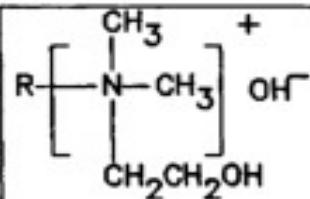
WEAK CATION (WC)  
CARBOXYLIC  
WEAK ACID  
CATION  
EXCHANGE  
RESIN



WEAK ANION (WA)  
AMMONIUM  
WEAK BASE  
ANION  
EXCHANGE  
RESIN

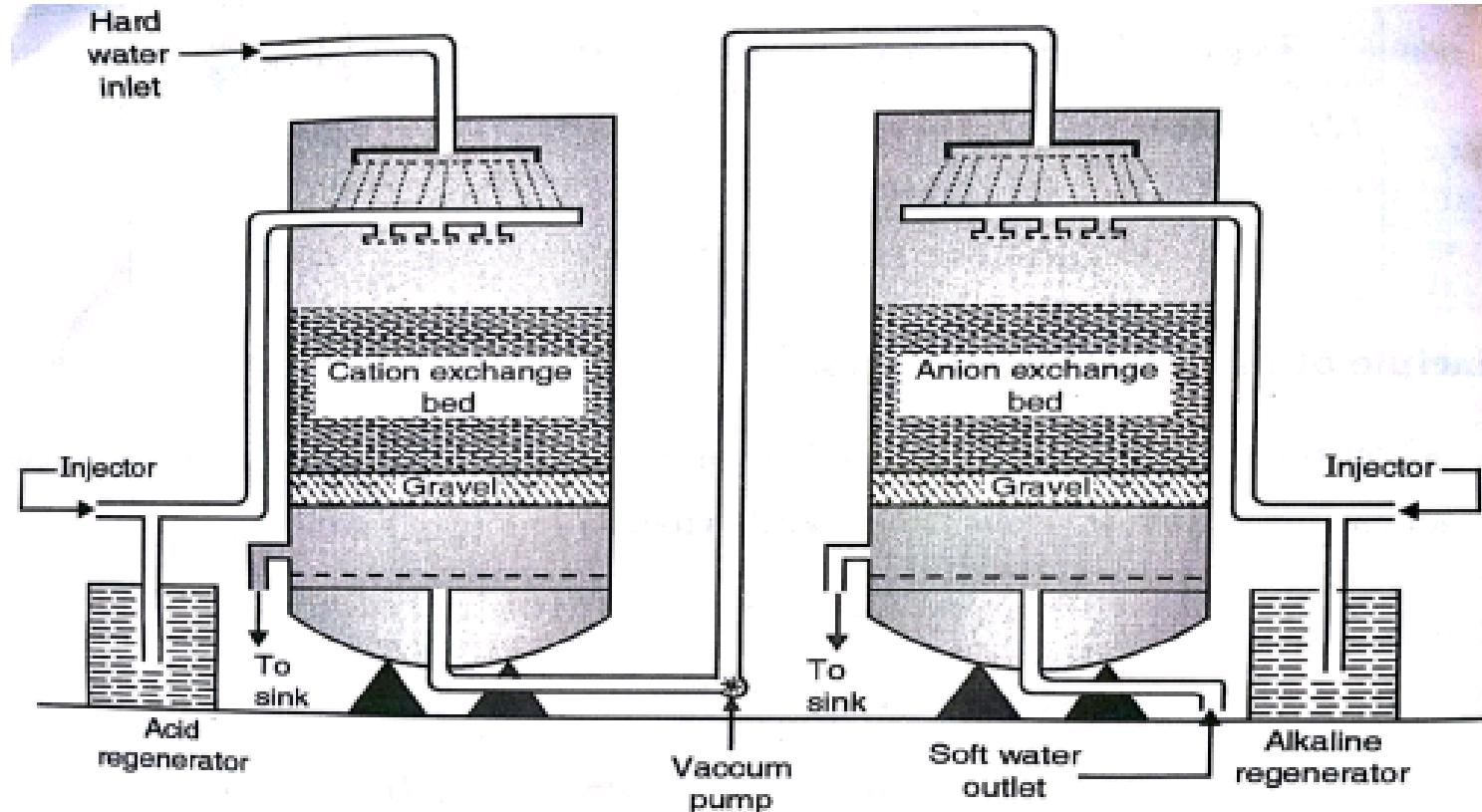


TYPE I STRONG ANION (SB)  
QUATERNARY  
AMMONIUM  
STRONG BASE  
ANION EXCHANGE  
RESIN



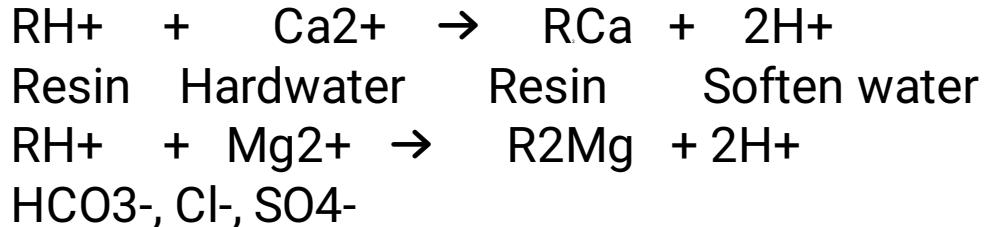
TYPE II STRONG ANION (SB)  
QUATERNARY  
AMMONIUM  
STRONG BASE  
ANION EXCHANGE  
RESIN

Process: Ca(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>

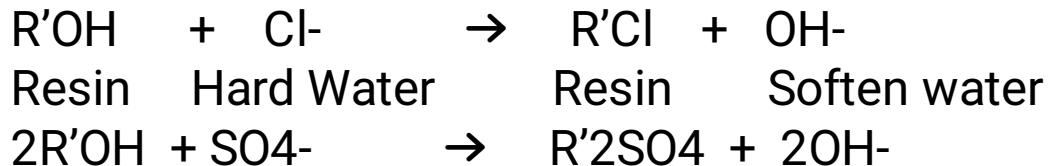


Demineralisation Diag. 2

## **Reactions with Cation Exchanger: RH+**



## **Reactions with Anion Exchanger: R'OH**



## **Overall Reaction:**



## **Regeneration Reactions**

### **Cation Exchanger**



### **Anion Exchanger**



# 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:

$$\begin{aligned}\text{Hardness of 10000L of water} &= 200 \text{ L of 0.1N HCl} \\ &= 200 \text{L of 0.1 N NaOH}\end{aligned}$$

$$1 \text{ eq. of HCl} = 1 \text{ Eq. of CaCO}_3$$

$$0.1\text{N of HCl} = 0.1\text{N of CaCO}_3$$

Hence,

$$\begin{aligned}\text{Hardness of 10000L of water} &= 200 \text{L of 0.1N CaCO}_3 \text{ eq.} \\ &= 20 \text{L of 1N CaCO}_3 \text{ eq.}\end{aligned}$$

$$\text{Std Statement: 1L of 1N CaCO}_3 = \text{Eq. wt} = 50\text{g}$$

$$\begin{aligned}\text{Hardness of 10000L of water} &= 20 \times 1\text{L of 1N CaCO}_3 \\ &= 20 \times 50 \text{ g} = 1000\text{g} \\ &= 1000000\text{mg of CaCO}_3 \text{ eq.}\end{aligned}$$

Hence,

$$\text{Hardness of 1L of water} = 1000000/10000 = 100\text{mg/L} = 100\text{ppm}$$

- 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 method, which is blank reading. It is denoted as DOb

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.

$BOD = (DOb - DOI) \times \text{dilution factor}$

$= (DOb - DOI) \times \text{Volume of sample after dilution} / \text{volume of sample before dilution.}$

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

Reaction:



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 can 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 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 2-3hrs.

Unit of COD = mg/L or ppm

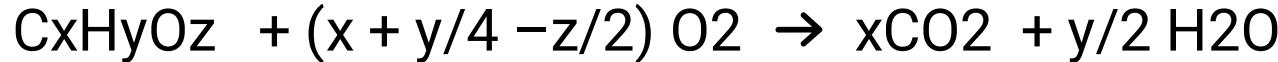
Determination of COD:

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, CO<sub>2</sub> and H<sub>2</sub>O. The unreacted K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is titrated against Ferrous ammonium sulphate [FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.H<sub>2</sub>O] 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



The unreacted dichromate solution is titrated against Mohrs salt using ferroin indicator.



Overall reaction



The COD is calculated as

$$COD = \frac{(V_1 - V_2) \times N}{\text{Volume of sample}} \times 8000$$

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 unfavourable 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:  $BOD = (Dob-Doi) \times \text{Volume of sample after dilution} / \text{vol of sample before dilution}$

$$BOD = (840-230) \times 80/50 = 976\text{ppm}$$

Numerical 2: A 25mL of sewage water sample was refluxed with 10mL of 0.25N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> soln in presence of dil.H<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub>. The unreacted dichromate required 6.5ml of 0.1N FAS. 10mL of same K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> required 27mL of 0.1N FAS. Calculate COD.

Given: Volume of sample = 25mL

Blank titration reading (V<sub>1</sub>) = 27mL

Back titration reading (V<sub>2</sub>) = 6.5mL

$$\begin{aligned} COD &= (V_1 - V_2) \times N(\text{FAS}) \times 8000 / \text{Vol. of Sample} \\ &= (27 - 6.5) \times 0.1 \times 8000 / 25 = 656\text{ppm} \end{aligned}$$

Numerical 3: A 30mL of sewage water sample was refluxed with 15mL of 0.25N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> soln in presence of dil.H<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub>. The unreacted dichromate required 14 ml of 0.05N FAS. 15mL of same K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> required 20mL of 0.1N FAS. Calculate COD.

Note: Covert one statement in to fixed normality.

Volume of sample = 30mL

Blank Titration reading (V<sub>1</sub>) = 20ml of 0.1N FAS = **40 mL of 0.05N FAS**

Back Titration reading (V<sub>2</sub>) = **14mL of 0.05N FAS**

$$COD = 346.667\text{ppm}$$