



**SOMAIYA**  
VIDYAVIHAR UNIVERSITY

K J Somaiya College of Engineering



# Engineering Chemistry

## F. Y. B. Tech.

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# Hard water in industry



# Classification of Hardness

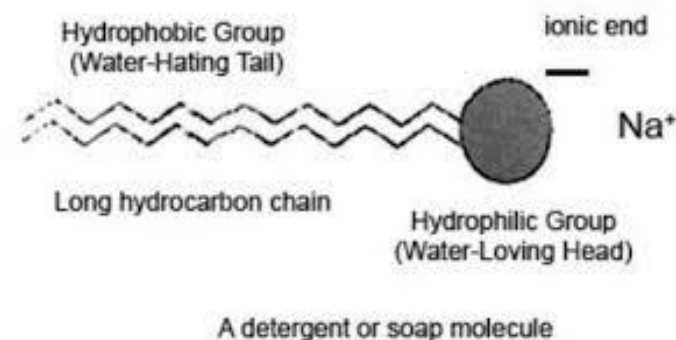
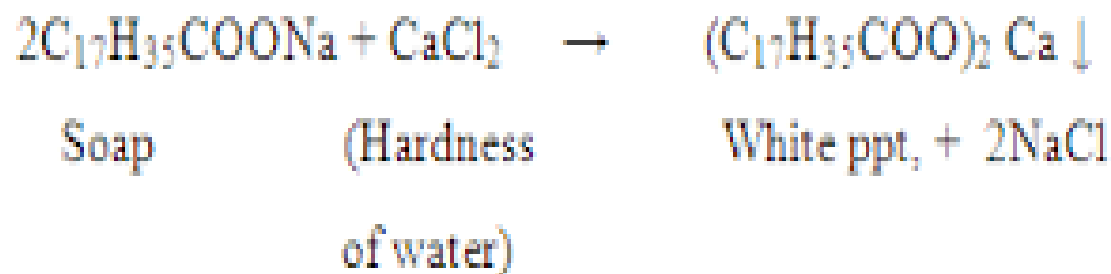
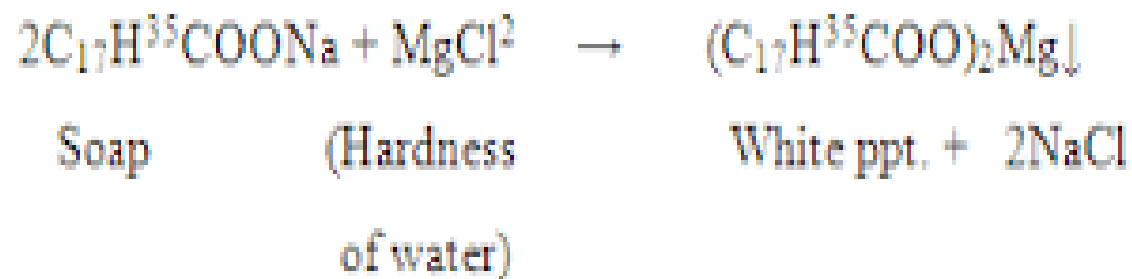
Hardness level (mg/l)	Classification
0-17	Soft Water
17-60	Slightly hard water
60-120	Moderately hard water
120-180	Hard water
>180	Very hard water

## HARDNESS OF WATER

- Hardness in Water is characteristic that prevents the ‘lathering of soap’ thus water which does not produce lather with soap solution readily, but forms a white curd is called hard water.
- Type of Hardness
  - Temporary or Carbonate Hardness
  - Permanent Hardness or non-carbonate Hardness.



# Reaction of Soap with Water



# How to detect hardness?

- When the water is treated with soap solution, if it prevents lathering and forms white scum, the water contains hardness. Or Water containing hardness, gives wine red colour with Eriochrome Black –T indicator.
- Although water hardness usually measures only the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminum and manganese may also be present at elevated levels in some geographical locations. The predominant source of magnesium is dolomite  $[\text{Ca-Mg}(\text{CO}_3)_2]$ .

## TYPES OF HARDNESS

Depending upon the types of dissolved salts present in water, hardness of water can be classified into two types:

- Temporary Hardness  
(Carbonate hardness or Alkaline hardness)
- Permanent Hardness  
(Non carbonate hardness or Non alkaline hardness)



# Types of Hardness

**TABLE 1**

**Water hardness salt types (source: Sengupta, 2013)**

Carbonate hardness compounds	Non-carbonate hardness compounds
Calcium carbonate ( $\text{CaCO}_3$ )	Calcium sulphate ( $\text{CaSO}_4$ )
Magnesium carbonate ( $\text{MgCO}_3$ )	Magnesium sulphate ( $\text{MgSO}_4$ )
Calcium bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ )	Calcium chloride ( $\text{CaCl}_2$ )
Magnesium bicarbonate ( $\text{Mg}(\text{HCO}_3)_2$ )	Magnesium chloride ( $\text{MgCl}_2$ )
Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )	
Magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ )	



## Temporary Hardness (or) Carbonate Hardness (or) Alkaline Hardness

- Temporary hardness is caused by carbonate, bicarbonate and hydroxide of calcium and magnesium ions in the water.
- It can be removed by boiling water or by the addition of lime  $[\text{Ca}(\text{OH})_2]$
- Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon filtration and removal of residue.



## **Permanent Hardness or Non – Carbonate Hardness (or) Non – alkaline Hardness**

Permanent hardness is hardness (mineral content) that cannot be removed by boiling.

It is usually caused by the presence of sulphates, chlorides, nitrates of calcium and magnesium and other metal ions which become more soluble on boiling.

Despite the name, permanent hardness can be removed using water – softener or ion-exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column. It can be removed by

- Lime – Soda process
- Zeolite process

## Expression of hardness in terms of equivalents of $\text{CaCO}_3$

- The concentrations of hardness producing salts are usually expressed in terms of equivalent amount of  $\text{CaCO}_3$ .
- $\text{CaCO}_3$  is chosen as a standard because, Its molecular weight (100) and equivalent weight (50) is a whole number, so the Calculations in water analysis can be simplified.
- It is the most insoluble salt, that can be precipitated in water treatment.
- If the concentration of hardness producing salt is **x mg/lit.**

$$\left. \begin{array}{l} \text{Amount} \\ \text{equivalent to } \text{CaCO}_3 \end{array} \right\} \frac{x \times 100}{\text{Molecular weight of hardness producing salt}}$$

## Expression of hardness in terms of equivalents of $\text{CaCO}_3$

$\text{CaCO}_3$  Equivalent Hardness (ppm) =

= Mass of Hardness Producing substance x Chemical equivalents of  $\text{CaCO}_3$  / Chemical equivalents of Hardness causing salt.

1. How many grams of  $\text{FeSO}_4$  dissolved per litre gives 210 ppm hardness?
2. Calculate temporary hardness and permanent hardness of water sample from the following data:

$\text{Mg}(\text{HCO}_3)_2 = 16 \text{ mg/L}$ ,  $\text{MgCl}_2 = 19 \text{ mg/L}$ ,  $\text{MgSO}_4 = 2.4 \text{ mg/L}$ ,  
 $\text{Mg}(\text{NO}_3)_2 = 2.96 \text{ mg/L}$ ,  $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/L}$ ,  $\text{SiO}_2 = 16 \text{ mg/L}$

# UNITS OF HARDNESS

- **Parts per million (ppm):**

It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per 1000000 parts of water.

- **Milligrams per litre (mg/lit):**

It is defined as the number of milligrams of  $\text{CaCO}_3$  equivalent hardness per 1 litre of water.

- **Clarke's degree ( $^{\circ}\text{Cl}$ )**

It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

- **French degree ( $^{\circ}\text{Fr}$ )**

It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per 105 parts of water.

- **Relationship between various units**

$$1 \text{ ppm} = 1 \text{ mg/lit} = 0.10 ^{\circ}\text{Fr} = 0.070 ^{\circ}\text{Cl}$$

# ESTIMATION OF TOTAL HARDNESS OF WATER BY EDTA METHOD

## Principle:

- The calcium and other metal ions present in the water are capable of forming complex with Indicator EBT and also with the EDTA in the pH range 8 - 10.
- To keep the solution at this pH range, a buffer [mixture of ammonium chloride and ammonium hydroxide] is used.
- The complex between Metal-EDTA is more stable than that of between the Metal-indicator (EBT).





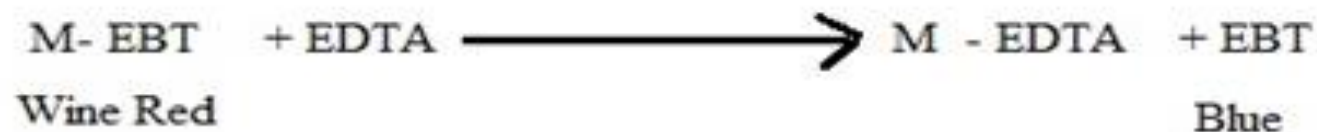
Less stable & Wine  
red Colour



(2) is more stable than (1)

More stable &  
Colourless

During the equivalence point



$$50 \text{ mL SHW} = V_1 \text{ mL EDTA}$$

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

$$\text{Hence, } 1 \text{ mL EDTA} = 50/V_1 \text{ mg CaCO}_3 \text{ eq.}$$

$$\text{Now } 50 \text{ mL of given hard water} = V_2 \text{ mL of EDTA}$$

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

$$1 \text{ L of given hard water} = 20 \times V_2 \times 50/V_1 \text{ mg CaCO}_3 \text{ eq.}$$

$$\text{Total Hardness of water} = 1000 V_2/V_1 \text{ ppm}$$

$$\text{Now, } 50 \text{ mL of boiled water} = V_3 \text{ mL of EDTA}$$

$$= V_3 \times 50/V_1 \text{ mg CaCO}_3 \text{ eq.}$$

$$1 \text{ L of boiled hard water} = 20 \times V_3 \times 50/V_1 \text{ mg CaCO}_3 \text{ eq.}$$

$$\text{Permanent Hardness} = 1000 V_3/V_1 \text{ ppm}$$

Sample A = 14.6 mg of  $\text{Mg}(\text{HCO}_3)_2$  per litre

Sample B = 820 mg of  $\text{Ca}(\text{NO}_3)_2$  and 2 mg  $\text{NaNO}_3$

Sample C = 20 g Silica and 16.2 mg  $\text{Ca}(\text{HCO}_3)_2$  per 500 ml

Determine the hardness of samples A, B, C ?

# Hardness Numerical

Sr. No.	Type of impurity	Amount of impurity	Molecular mass	M.F.	Equivalence of Ca CO <sub>3</sub> Hardness	Hardness Type
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	8.1 ppm	162	100/162	5 ppm	T
2	Mg(NO <sub>3</sub> ) <sub>2</sub>	14.8 ppm	148	100/ 148	10 ppm	P
3	MgSO <sub>4</sub>	3 ppm	120	100/120	2.5 ppm	P
4	CaCl <sub>2</sub>	2.22 ppm	111	100/111	2 ppm	P
5	KNO <sub>3</sub>	5 ppm	---	--	--	N.H.
6	FeSO <sub>4</sub> .7H <sub>2</sub> O	5.75 ppm	278	100/278	2.06 ppm	P
7	NaHCO <sub>3</sub>	3 ppm	--	--	--	N.H
	<b>Temporary Hardness = 5 ppm</b>					
	<b>Permanent Hardness = 16.56 ppm</b>					
	<b>Total Hardness = 21.56 ppm</b>					

# Numerical on EDTA method

a) 0.28 g of  $\text{CaCO}_3$  was dissolved in HCl and the solution is diluted to 1 litre.

100 mL of the above solution required 28 mL of EDTA solution.

100 mL of hard water sample required 33 mL of EDTA solution.

After boiling, cooling and filtration 100 mL of this solution on titration required 10 mL of EDTA solution. Calculate all types of hardness.

# Numerical on EDTA method

b) 55.5 mg of  $\text{CaCl}_2$  is dissolved in 750 ml of distilled water and 50 ml of this water on titration required 14 ml of EDTA.

100 ml of water sample on titration with same EDTA required 9.8 ml.

50 ml of boiled water sample on titration required 2.7 ml of same EDTA. Calculate the all types of hardness.

- 750 ml of SHW = 55.5 mg of  $\text{CaCl}_2$   
=  $(55.5 / 750) \times 100/111$  mg of  $\text{CaCO}_3$
- 1 ml of SHW = 0.067 mg of  $\text{CaCO}_3$
  
- 50 ml of SHW = 14 ml of EDTA
- 1 ml of EDTA =  $50 / 14$  ml of SHW  
=  $50 / 14 \times 0.067$  mg of  $\text{CaCO}_3$
- 1 ml of EDTA = 0.24 mg of  $\text{CaCO}_3$



## Total Hardness

100 ml of water sample = 9.8 ml of EDTA =  $9.8 \times 0.24$   
mg of  $\text{CaCO}_3$

- Total hardness =  $9.8 \times 0.24 \times 1000/100$  mg /L  
= 23.52 ppm or mg /l

c) 50 mL sample of water required 8.2 mL of M/20 Disodium EDTA solution for titration. After boiling and filtration the same volume required 4.5 mL of EDTA. Calculate all types of hardness.

M/20 EDTA = 0.05 M EDTA

1000 mL 1 M EDTA = 100 g  $\text{CaCO}_3$

1 mL, 1 M EDTA = 100 mg  $\text{CaCO}_3$

50 mL water sample = 8.2 mL of 0.05 M EDTA

1000 mL water sample = 20 x 8.2 M of 0.05 M EDTA  
= 164 mL of 0.05 M EDTA

1 mL, 1 M EDTA = 100 mg  $\text{CaCO}_3$

164 mL of 0.05 M EDTA = 164 x 0.05 x 100 = 820 ppm = **Total Hardness**

Now, 50 mL of boiled water = 4.5 mL of 0.05 M EDTA

1000 mL water sample = 20 x 4.5 M of 0.05 M EDTA

= 90 mL of 0.05 M EDTA

As, 1 mL, 1 M EDTA = 100 mg  $\text{CaCO}_3$

90 mL of 0.05 M EDTA =  $90 \times 0.05 \times 100 = 450 \text{ ppm}$  = **Permanent hardness**

**Temporary hardness =  $820 - 450 = 370 \text{ ppm}$**

d) 25 mL sample of water required 5.5 mL of M/10 Disodium EDTA solution for titration. After boiling and filtration 50 mL of water sample required 3.9 mL of EDTA. Calculate all types of hardness.

# Softening Methods

- **Lime-Soda Method**
- **Zeolite Softener method**
- **Ion Exchange Method**

# Lime-Soda Method

- In this method, calculated quantity of **Lime**  $[\text{Ca}(\text{OH})_2]$  and **Soda**  $[\text{Na}_2\text{CO}_3]$  **mixture** is added to hard water.
- Precipitates of  **$\text{CaCO}_3$**  and  **$\text{Mg}(\text{OH})_2$**  are formed due to reactions of hardness causing salts with lime and soda.
- These precipitates gets settled down in the form of **sludge**.
- This settling of precipitates is faster in **hot lime soda method** compared to cold Lime soda method.
- Hence for quick settling of particles of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ , **coagulants such as Alum**  $[\text{Al}_2(\text{SO}_4)_3]$ , **sodium meta aluminate**  $[\text{NaAlO}_2]$ , or  **$\text{FeSO}_4$**  could be used in cold lime soda method.

Constituent	Reaction	Need
$\text{Ca}^{2+}$ (Perm. Ca)	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	S
$\text{Mg}^{2+}$ (Perm. Mg)	$\text{Mg}^{2+} + \text{Ca(OH)}_2 \longrightarrow \text{Mg(OH)}_2 + \text{Ca}^{2+}$	
	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L+S
$\text{HCO}_3^-$ (e.g., $\text{NaHCO}_3$ )	$2\text{HCO}_3^- + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_3^{2-}$	L-S
$\text{Ca(HCO}_3)_2$ (Temp. Ca)	$\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \longrightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	L
$\text{Mg(HCO}_3)_2$ (Temp. Mg)	$\text{Mg(HCO}_3)_2 + 2\text{Ca(OH)}_2 \longrightarrow 2\text{CaCO}_3 + \text{Mg(OH)}_2 + 2\text{H}_2\text{O}$	2L
$\text{CO}_2$	$\text{CO}_2 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
$\text{H}^+$ (free acids HCl,	$2\text{H}^+ + \text{Ca(OH)}_2 \longrightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$	
	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L+S
Coagulants :	$\text{Fe}^{2+} + \text{Ca(OH)}_2 \longrightarrow \text{Fe(OH)}_2 + \text{Ca}^{2+}$	
$\text{FeSO}_4$	$2\text{Fe(OH)}_2 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Fe(OH)}_3$	
	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L+S
$\text{Al}_2(\text{SO}_4)_3$	$2\text{Al}^{3+} + 3\text{Ca(OH)}_2 \longrightarrow 2\text{Al(OH)}_3 + 3\text{Ca}^{2+}$	
	$3\text{Ca}^{2+} + 2\text{Na}_2\text{CO}_3 \longrightarrow 3\text{CaCO}_3 + 6\text{Na}^+$	L+S
$\text{NaAlO}_2$	$\text{NaAlO}_2 + \text{H}_2\text{O} \longrightarrow \text{Al(OH)}_3 + \text{NaOH}$	-L



From the above table it can be seen that 100 parts by mass of  $\text{CaCO}_3$  are equivalent to 74 parts of  $\text{Ca(OH)}_2$  and 106 parts of  $\text{Na}_2\text{CO}_3$ .

Lime requirement for softening

$$= \frac{74}{100} \left[ \begin{array}{l} \text{Temp. } \text{Ca}^{2+} + 2 \times \text{Temp. } \text{Mg}^{2+} + \text{Perm. } (\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) \\ + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \\ \text{all in terms of CaCO}_3 \text{ eq.} \end{array} \right]$$

And Soda requirement for softening  $\times \frac{\text{Volume of water}}{106} \times \frac{100}{\% \text{ Purity}} \text{ Kg}$

$$= \frac{106}{100} \left[ \begin{array}{l} \text{Perm. } (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- \\ \text{all in terms of CaCO}_3 \text{ eq.} \end{array} \right]$$

There are two types of lime-soda process.  $\times \frac{\text{Volume of water}}{106} \times \frac{100}{\% \text{ Purity}} \text{ Kg}$

(1) Cold lime-soda process

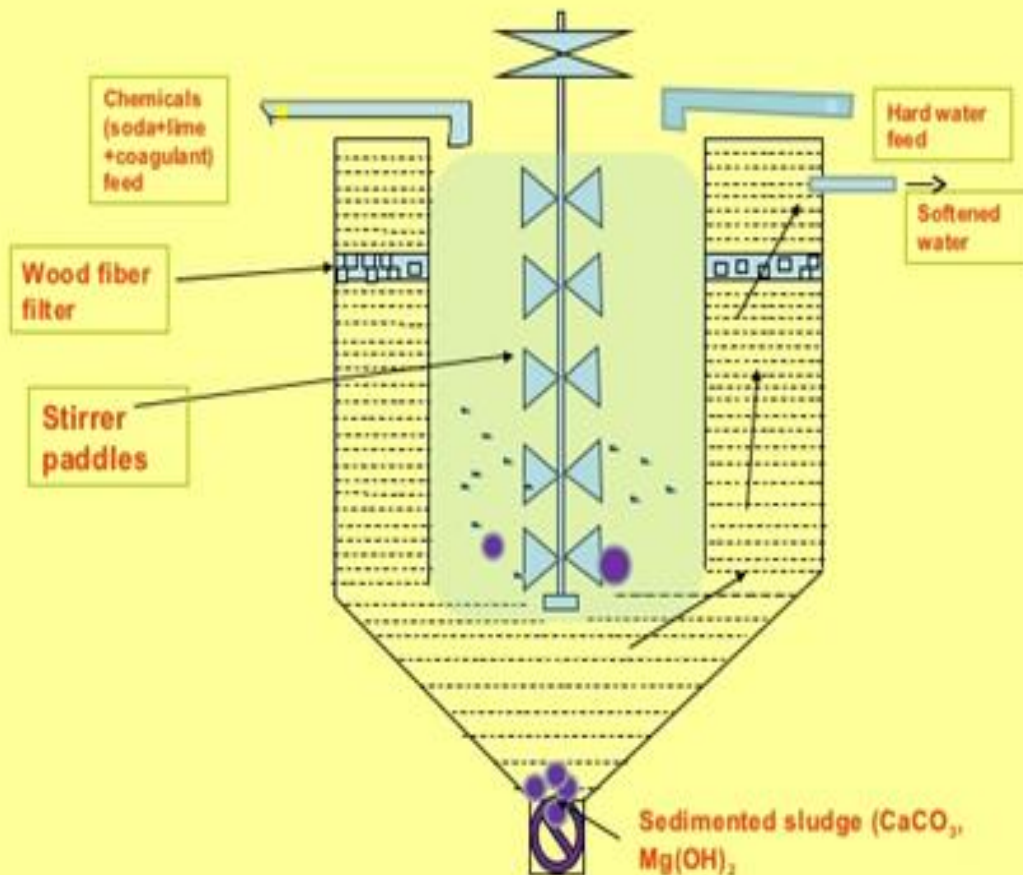
and (2) Hot lime-soda process

# Cold Lime-Soda Method

- In cold lime-soda method, hard water is treated with mixture of lime, soda and coagulants at room temperature about 25-30 °C
- **Inner cylindrical reaction tank** equipped with stirrer, which ensures complete mixing of lime, soda and coagulants with hard water
- In **outer conical sedimentation vessel**, sludge settles down
- **Wood fiber filters** ensures the complete removal of sludge particles from softened water

# Cold Lime-Soda Method

Continuous cold lime soda softener



1. Carried out at 25 °C to 30 °C
2. Coagulants required
3. Stirring is essential as the reaction is operated at low temperature
4. Slow process
5. Dissolved gases are not removed
6. Filtration is not easy
7. Residual hardness is 50-60 ppm
8. Low softening capacity

# Hot Lime-Soda Method

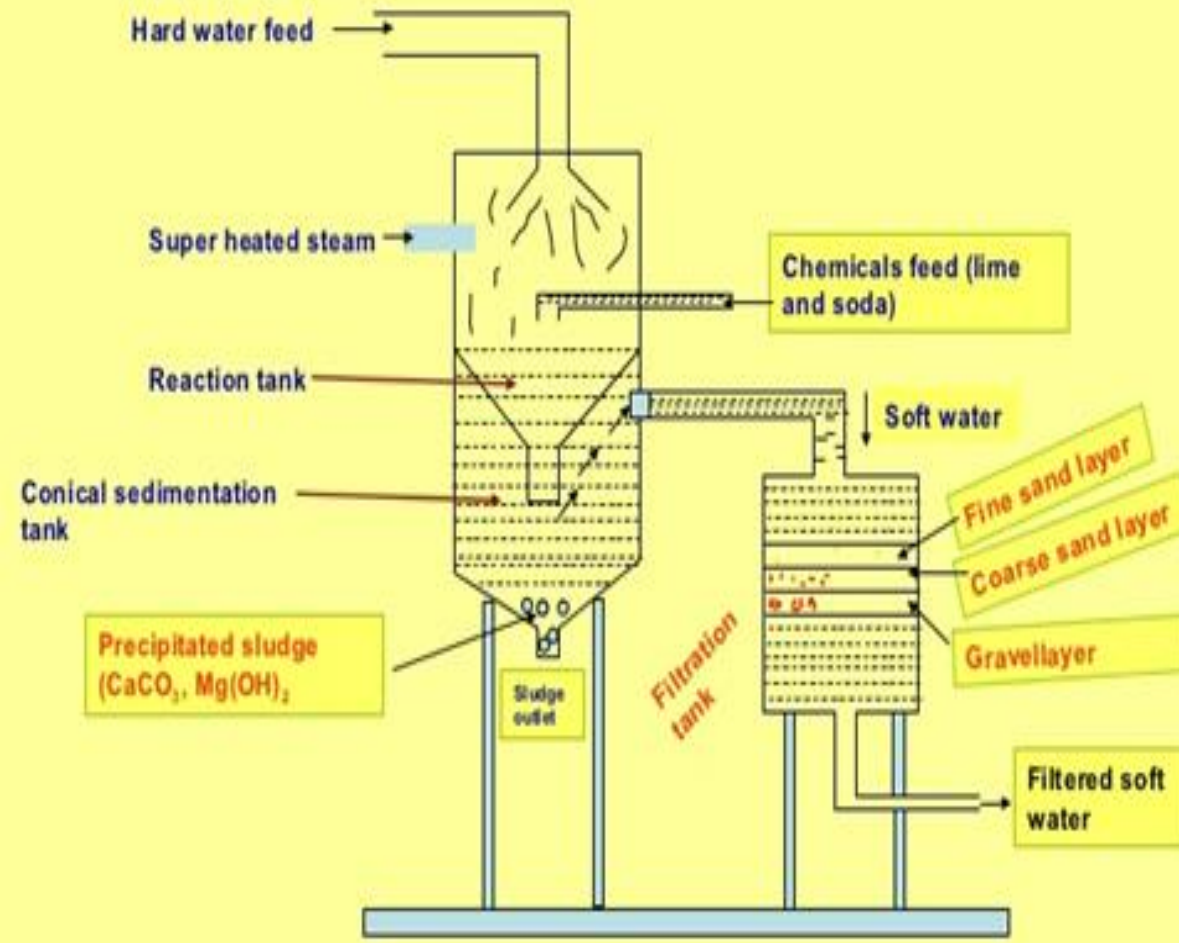
In Hot lime-soda process hard water is treated with soda and lime at **94-100°C**

Hot lime-soda plant essentially consists of three parts

- A '**Reaction tank**' in which raw water, chemicals and steam are thoroughly mixed.
- A '**Conical sedimentation vessel**' in which sludge settles down, and
- A '**sand filter**' which ensures complete removal of sludge from the softened water.

# Hot Lime-Soda Method

## Continuous Hot Lime soda Process



1. Carried out at  $95^\circ\text{C}$  to  $100^\circ\text{C}$
2. Coagulants are not required
3. Stirring is not essential as the reaction is operated at high temperature
4. Fast process
5. Dissolved gases gets removed due to high temperature
6. Filtration is easy, hence sand filter is sufficient
7. Residual hardness is 15-30 ppm
8. High softening capacity



## **Advantages of hot lime-soda method over cold lime-soda method**

- Economical process
- pH value of softened water is high (Decrease corrosion)
- Alkaline nature of treated water reduces pathogens, bacteria in water
- Fe (II) and Mn (II) can also be removed to certain extent

# Disadvantages of Lime-soda method

- Softened water is 50 ppm hardness in cold lime-soda method and 15-30 ppm hardness in hot lime-soda method.
- Such water can not be used in high pressure boilers
- Disposal of large quantity of sludge is a big problem



# Zeolite Softener Method

- Sodium-Zeolites which are **hydrated sodium aluminosilicates**, capable of exchanging their sodium ions with hardness producing ions are used.
- Chemically sodium zeolites are  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$   
(Where,  $x = 2-10$  &  $y = 2-6$ ).

**Principle:** hard water passed over zeolite, it exchanges its own sodium ions with hardness causing ions.

$2\text{Na}^+$  ions are generally exchanged with each bivalent hardness producing ions.

# Process

- For **softening**, hard water is passed over zeolite bed at specific rate
- The hardness causing ions will be retained on zeolite and they are exchanged with equivalent sodium ions
- After certain usage zeolite gets exhausted as all the sodium ions got exchanged
- Such exhausted zeolite is **regenerated by passing 10 % brine** solution over it
- This regenerates the zeolite by replacing hardness causing ions with  $\text{Na}^+$  ions to become Na-zeolite
- **Hence softening and regeneration are exactly opposite reactions**

# Reactions

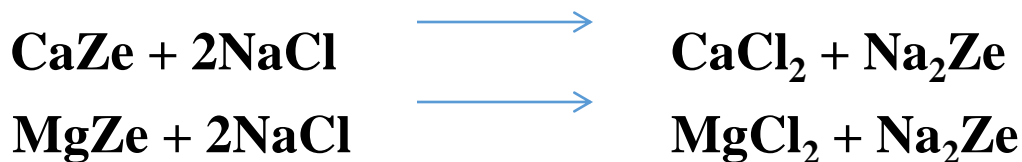
- **Softening:**

For softening of hard water, it is passed over sodium zeolite bed. Exchange of hardness causing ions takes place with sodium ions present on zeolite. The following reactions takes place.

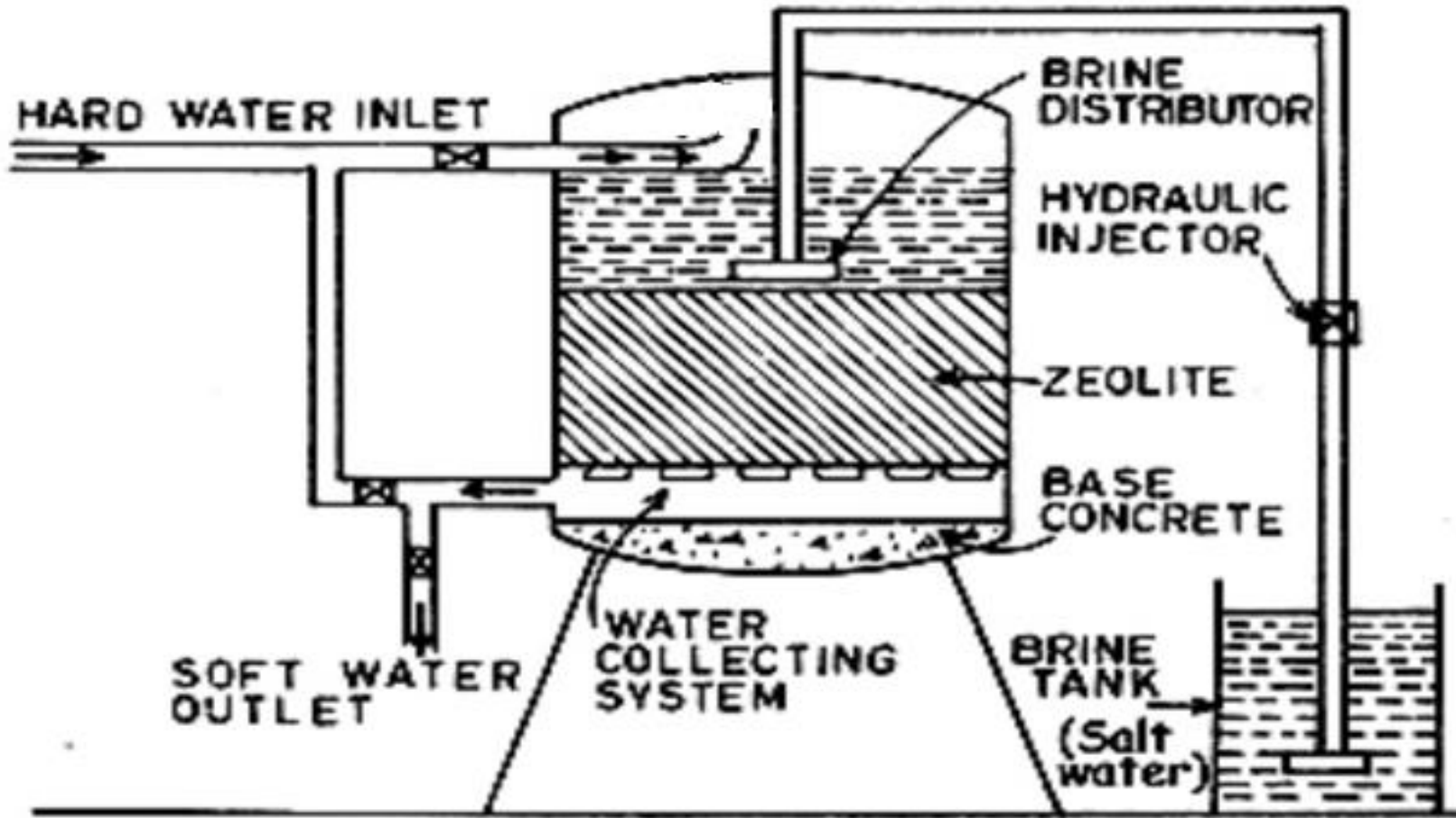


- **Regeneration:**

For regeneration of exhausted zeolite, 10 % brine solution is passed over used zeolite.



## Zeolite water softener



## Advantages

- Water obtained after treatment is about 10 ppm hardness
- No sludge formation is taking place
- Equipment is compact and easy in operation
- Equipment occupies less space and low in maintenance

# Limitations and Disadvantages of Zeolite softener method

## Limitations

- Suspended impurities blocks the pores of zeolite
- Colored ions such as  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  forms strong bonds with zeolite hence can not be removed while regeneration from zeolite
- Mineral acids can destroy zeolite

## Disadvantages

- The treated water is high in sodium salts
- Only cations could be removed leaving behind anions in water

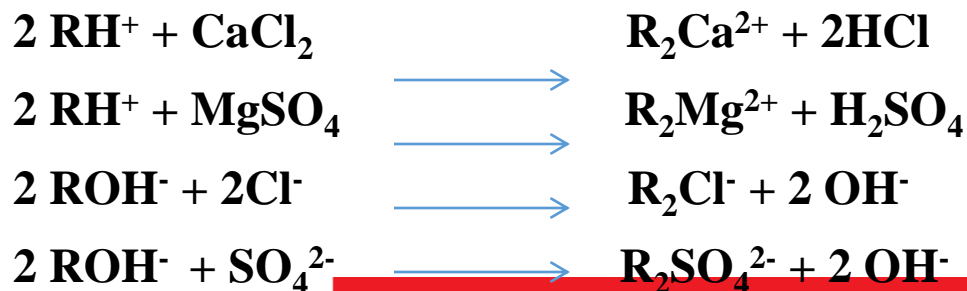
## **Ion Exchange softener method (De-mineralization process)**

- Ion exchange resins are insoluble, cross-linked, long chain organic polymers with micro-porous structure. The functional groups attached to the chains are responsible for ion exchanging property.
- **Cation Exchanger resins ( $RH^+$ ) :**  
Resins containing acidic functional groups ( $-COOH$ ,  $-SO_3H$  etc.) are capable of exchanging their  $H^+$  ions with other cations in hard water.
- **Anion Exchanger resins ( $ROH^-$ ) :**  
Resins containing basic functional groups ( $-NH_2-OH$ ,  $=NH-OH$ ,  $-NMe_2-OH$  etc.) are capable of exchanging their  $OH^-$  with other anions in hard water.

# Process - Softening

- For **softening**, hard water is first passed over cations exchanger resin column at specific rate, which removes cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  etc. from hard water.
- The hardness causing ions will be retained on cation exchanger resin and they are exchanged with equivalent amount of  $\text{H}^+$  ions
- Further, the softened water from cation exchanger column is passed through anion exchanger column, which removes anions like,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  etc. with equivalent amount of  $\text{OH}^-$  ions from the resin.
- $\text{H}^+$  and  $\text{OH}^-$  ions from resin columns combines to form water.

## Softening

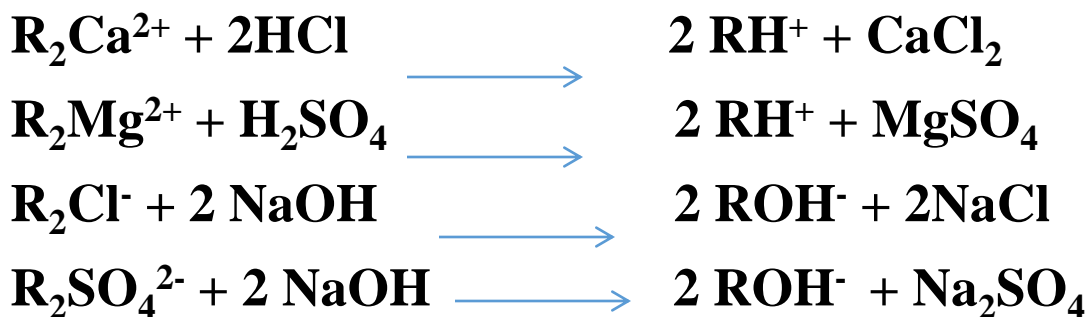




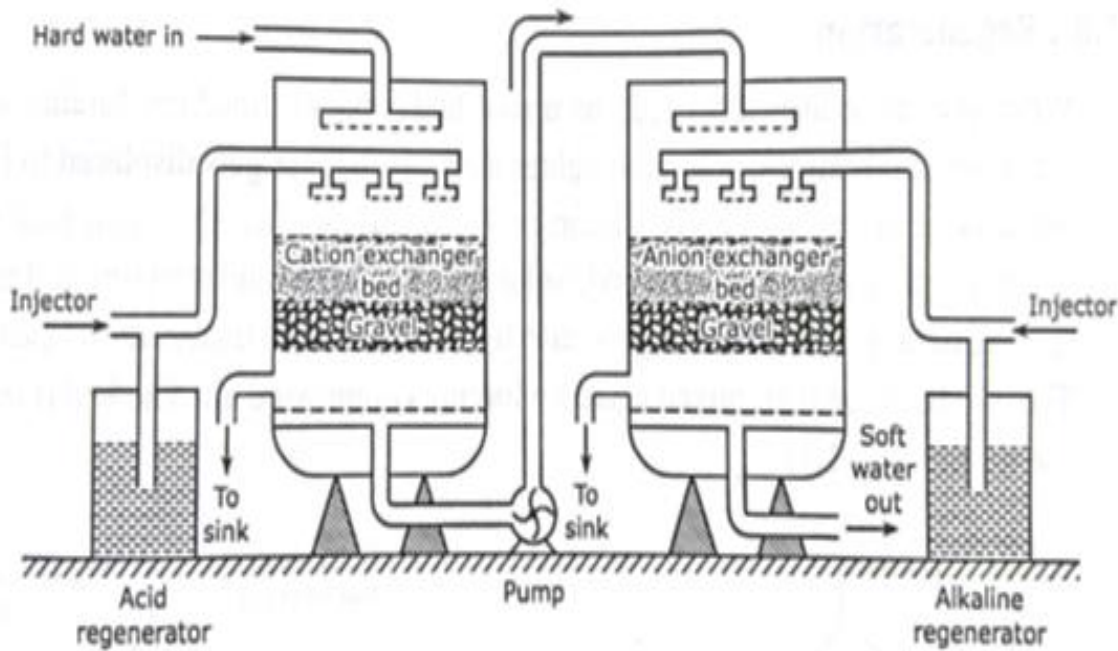
# Process - Regeneration

- After certain usage both cation and anion exchanger resins gets exhausted and they can not exchange any more cations or anions.
- Exhausted cation exchanger resin is regenerated by passing dil. HCl solution
- Exhausted anion exchanger resin is regenerated by passing dil. NaOH solution
- This regenerates both the resins making the method reusable.

## Regeneration



# Ion Exchange Softener



(Commercial plant)



## Advantages

- The process can be used for highly acidic or alkaline water.
- It produces water of very low hardness (less than 2 ppm).
- Softened water can be used in steam generation boiler.

## Disadvantages

- The equipment is costly and expensive resins are required.
- Turbid water could decrease the efficiency of the method. Hence turbidity need to be removed first by coagulation and then water could be passed over the resin.

# BOD (Biological Oxygen Demand)

- It is a measure of amount of oxygen required for the biological oxidation of organic matter under aerobic conditions at 20<sup>0</sup> C for a period of 5 days.



- BOD is the direct measurement of extent of pollution in waste water & industrial effluent.
- **Only applicable for bio-degradable pollutants.**
- Higher the BOD, higher will be the level of pollutants in water.
- **Drinking water should have BOD less than 1 ppm.**

# Principle

- Dissolved oxygen content of diluted waste-water is determined at the beginning of the reaction by **Winkler's method or by DO meter**.
- Same sample of water is kept for incubation in the presence of micro-organisms for 5 days at 20<sup>0</sup> C and decrease in the dissolved oxygen content is determined by **Winkler's method or by DO meter**.

$$\text{BOD} = [(\text{DO})_{\text{Blank}} - (\text{DO})_{\text{Incubated}}] \times \text{Dilution Factor}$$

$(\text{DO})_{\text{Blank}}$  = Dissolved oxygen of diluted sample in the beginning of the reaction

$(\text{DO})_{\text{Incubated}}$  = Dissolved oxygen of diluted sample after incubation for 5 days at 20<sup>0</sup> C.

$$\text{Dilution Factor} = \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

# BOD Meter

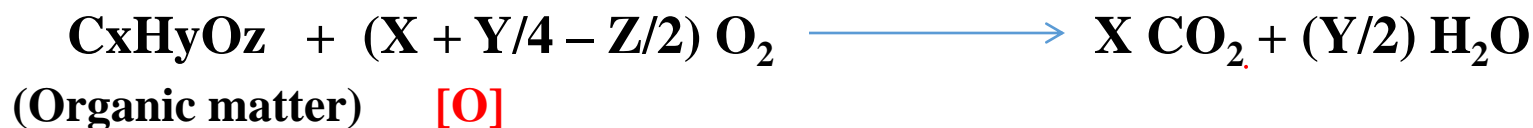


# Significance of BOD

1. BOD gives the extent of bio-degradable pollutants in wastewater sample
2. It also helps in pollution control in water
3. It also express self-purification capacity of any water body.

# COD (Chemical Oxygen Demand)

- It is a measure of amount of oxygen required for the chemical oxidation of organic matter when refluxed in acidified potassium dichromate in the presence of  $\text{Ag}_2\text{SO}_4$  or  $\text{HgSO}_4$  catalyst for 3 hours.



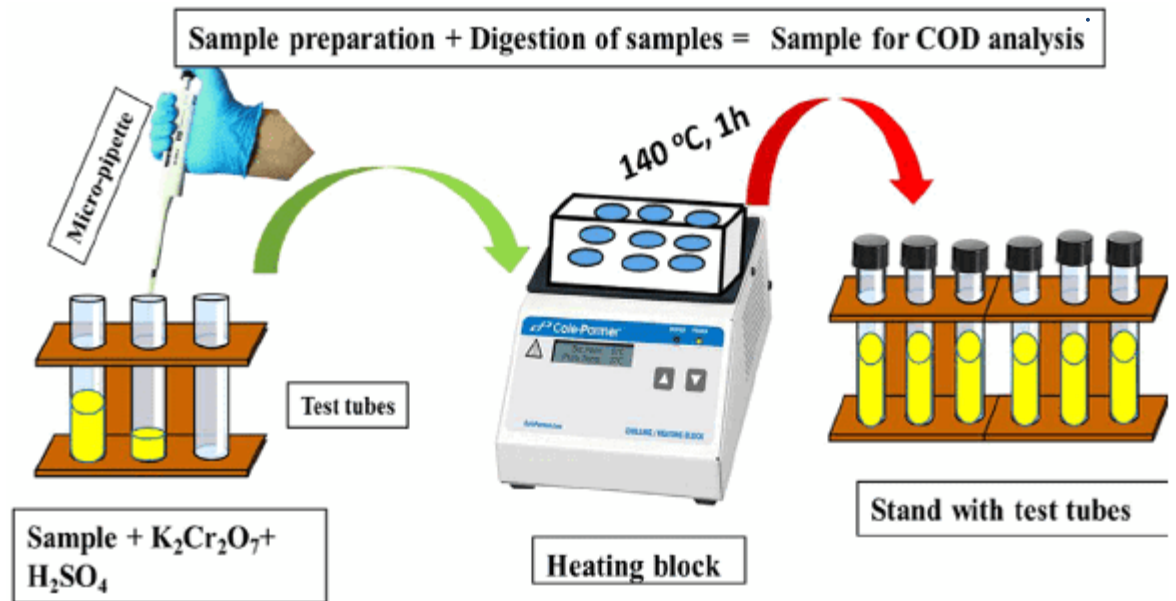
- COD is the direct measurement of extent of pollution in waste water & industrial effluent.
- Applicable for both bio-degradable and non bio-degradable pollutants.
- Higher the COD, higher will be the level of pollutants in water.
- Drinking water should have COD less than 1 ppm.**



# Principle

- A known volume of waste water sample (say 250 ml) is refluxed with a known excess of standard potassium dichromate (1 N) and dilute/conc. sulfuric acid mixture in the presence of silver sulphate catalyst for about 3 hours.
- This oxidases organic matter to  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .
- The unreacted potassium dichromate is titrated against **Ferrous ammonium sulphate (Mohr's salt) with ferroin indicator till blue colour changes to wine red, the reading is ( $V_t$ )**.
- This gives the amount of potassium dichromate consumed (in terms of equivalent oxygen) required for degradation of organic pollutants.
- Blank titration is performed initially with known volume of waste water sample and added acidified standard potassium dichromate titrated against Ferrous ammonium sulphate (Mohr's salt) with ferroin indicator till blue colour changes to wine red, the reading is ( $V_b$ ) (zero minute reading)

# COD Meter



# Principle

$$\text{COD} = \frac{(V_b - V_t) \times N_{\text{FAS}} \times 8 \times 1000}{Y} \text{ mg/L or ppm}$$

**$V_b$  = Volume of FAS required for blank titration (Zero time)**

**$V_t$  = Volume of FAS required for reaction mass after time (t)**

**$Y$  = Volume of waste water sample taken**

# Significance of COD

1. COD gives the extent of pollution caused by bio-degradable and non bio-degradable pollutants in wastewater sample
2. It helps in rapid determination of pollutants level in water compared to BOD
3. It is taken as a basis for calculation of efficiency and designing of water treatment plants.

# Comparison between BOD and COD

BOD	COD
It measures oxygen demand of bio-degradable organic pollutants only	It measures oxygen demand of bio-degradable and non biodegradable organic pollutants
Less stable measurement technique as micro-organisms are susceptible to variables such as pH and temperature	More stable measurement technique as no micro-organisms are used and potassium dichromate oxidizes any type of organic pollutants in water
Slow process, takes 5 days	Fast process , takes 3 hours
BOD values are generally less than COD values	COD values are generally greater than BOD values

# Formulae

**1.  $BOD = [(DO)_{Blank} - (DO)_{Incubated}] \times \text{Dilution Factor}$**

$(DO)_{Blank}$  = Dissolved oxygen of diluted sample in the beginning of the reaction

$(DO)_{Incubated}$  = Dissolved oxygen of diluted sample after incubation for 5 days at 20 ° C.

$$\text{Dilution Factor} = \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

**2.**

$$COD = \frac{(V_b - V_t) \times N_{FAS} \times 8 \times 1000}{Y} \text{ mg/L or ppm}$$

$V_b$  = Volume of FAS required for blank titration (Zero time)

$V_t$  = Volume of FAS required for reaction mass after time (t)

$Y$  = Volume of waste water sample taken

A 50 ml of sample contains 840 ppm dissolved oxygen. After 5 days the dissolved oxygen value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.



A 25 ml of Sewage water sample was refluxed with 10 ml of 0.25 N  $K_2Cr_2O_7$  solution of dil.  $H_2SO_4$ ,  $Ag_2SO_4$  &  $HgSO_4$ . The unreacted dichromate required 6.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same  $K_2Cr_2O_7$  solution and 25 ml of distilled water under the same conditions

as the sample required 27 ml of 0.1 N FAS. Calculate the COD of sewage sample.