SOMAIYA
VIDYAVIHAR UNIVERSITY
K J Somaiya College of Engineering

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Engineering Chemistry

F. Y. B. Tech.

Lecture-1 (Introduction)

Dr. Jitendra Satam

Course Objectives

The objective of course is to appreciate the basic concepts of chemistry behind the development of futuristic materials and their applications in engineering and technology. The course objective is to understand chemical processes involved in development of sustainable energy sources. To analyze the knowledge of analytical techniques involved in the analysis and characterization of chemical compounds, nanomaterial.

Course Outcomes

After successful completion of the course, the student will able to-

CO1. Understand the importance of water in industry and methods to produce soft water and wastewater treatment.

CO2. Demonstrate and analyze the knowledge of polymeric for futuristic engineering applications.

CO3. Identify and compare the material best suited for the energy production in sustainable and efficient manner.

CO4. Apply the knowledge of green chemistry and nanotechnology for solving the problems of society in sustainable and greener way.

CO5. Understand and apply basic concepts of spectroscopy and electro-analytical technique in characterizing chemical compounds.

Water			
1.1	Introduction, Types of Hardness, Disadvantages of hardness Equivalence of $CaCO_3$, Experimental determination of hardness.	**10**	**CO1**
1.2	Softening of Hard water: Lime soda method Zeolite method, Ion Exchange process, Desalination of brackish water using Electro dialysis, Reverse osmosis		
1.3	Methods to determine extent of water pollution, BOD, COD, Treatment of industrial wastewater.		

Polymer Chemistry			
2.1	Introduction, Classifications, Characteristic properties, Concept of molecular mass, determination of molecular mass, Glass transition temperature Tg	**9**	**CO2**
2.2	Methods of polymerization, Compounding and fabrication of plastics, Structure and property relationship of polymer		
2.3	Synthesis, properties and Application of few commercially important polymers, Conducting polymer, Liquid crystal Polymer		

Energy			
3.1	Introduction, Classification, Renewable energy, production of electricity using solar energy, Photo voltaic cells, Fuel cell	**10**	**CO3**
3.2	Fuel: Definition, characteristic of good fuel, Calorific value of fuel, Solid fuel, Analysis of coal and its significance, Liquid fuel, refining of petroleum, cracking, characteristic of fuel for internal combustion engine (Knocking, anti-knocking agents, octane number, cetane number, unleaded petrol)		
3.3	Waste to energy conversion: Solid waste and its classification, need of energy production from waste, method of conversion of energy from solid waste		

Green Chemistry and Nanotechnology			
4.1	Green Chemistry: Introduction, Goals, 12 principles of green chemistry, Significance of 12 principles with industrial examples, Green synthesis of few important materials	7	CO4
4.2	Nanomaterial and Nanotechnology: Introduction, properties and synthesis of nanomaterial, Properties and applications of special nanomaterial structure carbon Clusters		

Spectroscopy and Instrumental methods of Analysis			
5.1	UV spectroscopy, Principle, Instrumentation and applications		
5.2	IR spectroscopy, Basic Principle, Instrumentation and applications		
5.3	1H NMR Spectroscopy: Principle, Instrumentation, Chemical Shift, Factors affecting chemical shift, Applications.	**9**	**CO5**
5.4	Electroanalytical techniques, pH metry, Conductometry, Potentiometry		

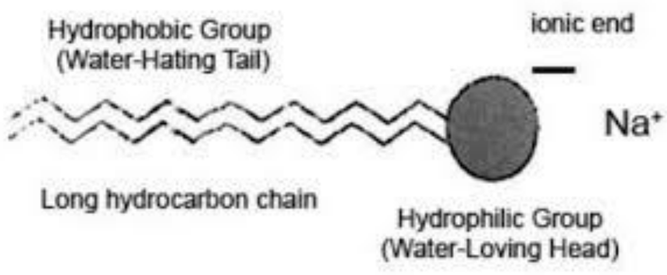
Hardness of Water

- 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



A detergent or soap molecule

$$2C_{17}H^{35}COONa + MgCl^{2} \rightarrow (C_{17}H^{35}COO)_2Mg\downarrow$$

Soap (Hardness of water) White ppt. + 2NaCl

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2\,Ca\downarrow$$

Soap (Hardness of water) White ppt, + 2NaCl

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 [$Ca\text{-}Mg(CO_3)_2$].

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 ($CaCO_3$)	Calcium sulphate ($CaSO_4$)
Magnesium carbonate ($MgCO_3$)	Magnesium sulphate ($MgSO_4$)
Calcium bicarbonate ($Ca(HCO_3)_2$)	Calcium chloride ($CaCl_2$)
Magnesium bicarbonate ($Mg(HCO_3)_2$)	Magnesium chloride ($MgCl_2$)
Calcium hydroxide ($Ca(OH)_2$)	
Magnesium hydroxide ($Mg(OH)_2$)	

Temporary Hardness (or) Carbonate Hardness (CH) (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 [$Ca(OH)_2$]
- Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon coving.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2$$

Permanent Hardness / Non – Carbonate Hardness (NCH) (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

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

Disadvantages of Hard water

1. Domestic :

- **Washing:** hard water lathers less and produce sticky scum of calcium and magnesium salts, this results in wastage of soap sometimes produces spots and stains on the fabric.
- **Bathing:** hard water reduces cleansing ability of soap also can cause skin disease.
- **Cooking:** Due to the presence of dissolved salts, boiling point elevation is seen, which results in excess fuel consumption and more time requirement while cooking.
- **Drinking:** Can effect digestive system, also can cause deposition of Calcium oxalate crystals in kidney or urinary tract.

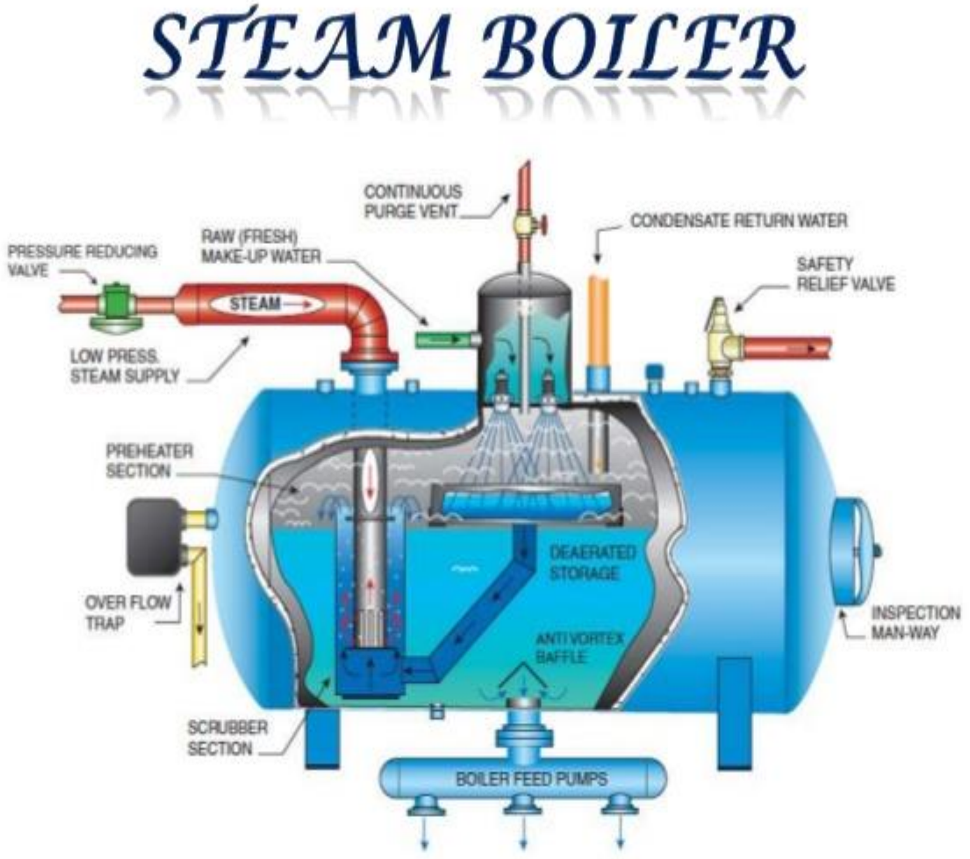
2. Industrial :

- **Textile/ Dyeing Industry:** Difficulty in producing exact shades of colour, can produce spots and stains on the fabric.
- **Sugar Industry:** Causes difficulty in crystallization of sugar due to the presence of sulphates, nitrates and chloride salts.
- **Paper Industry:** metal salts in hard water affects smoothness, glossy finish of paper
- **Cement Industry:** Affects hydration of cement and the final strength of concrete.
- **Pharmaceutical Industry:** Results in introduction of unwanted metal salts and affects the final purity of drugs.

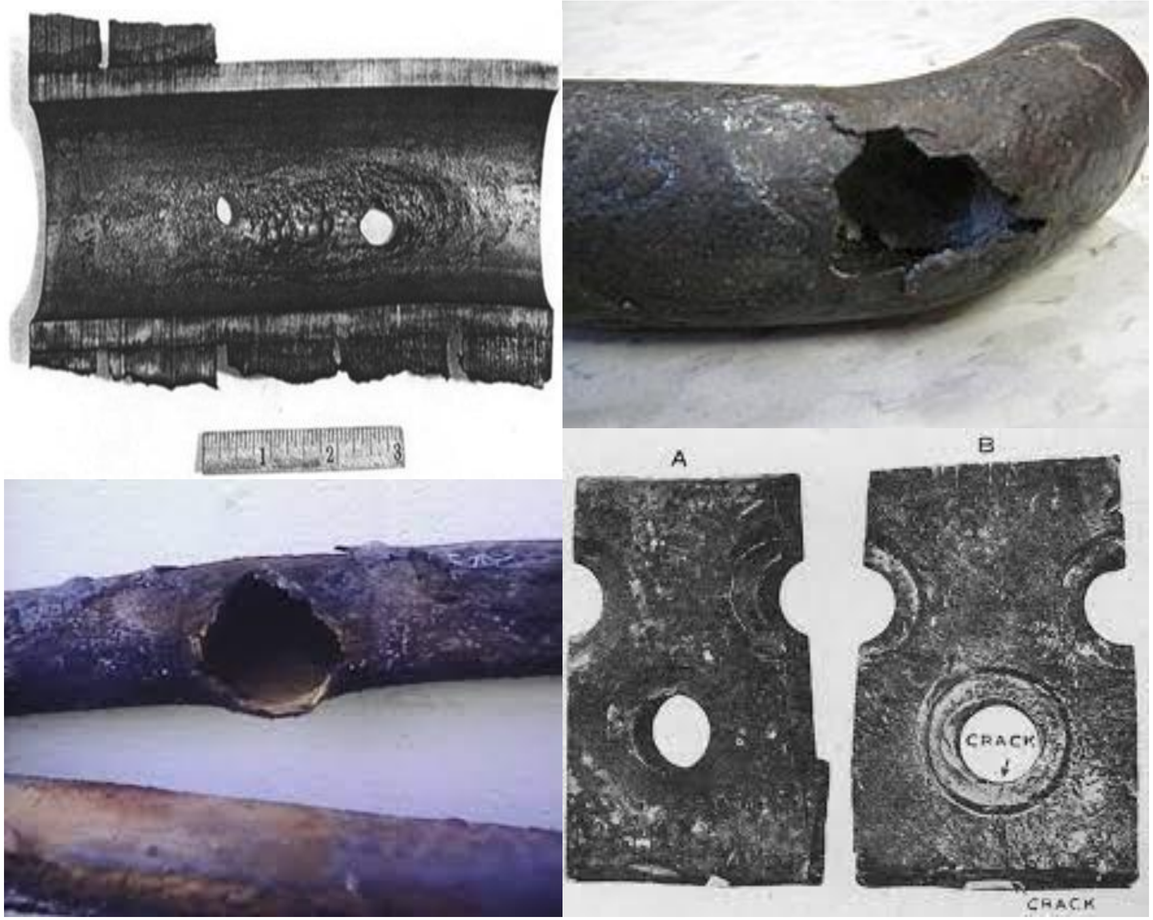
Disadvantages of Hard water

3. Steam Generators or Boilers

- Scale & Sludge Formation
- Caustic Embrittlement



Disadvantages of Hard water



Disadvantages of Hard water

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Sorry, Nothing Interesting Happens

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Disadvantages of Hard water

1. Domestic :

- **Washing:** hard water lathers less and produce sticky scum of calcium and magnesium salts, this results in wastage of soap sometimes produces spots and stains on the fabric.
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2. Industrial :

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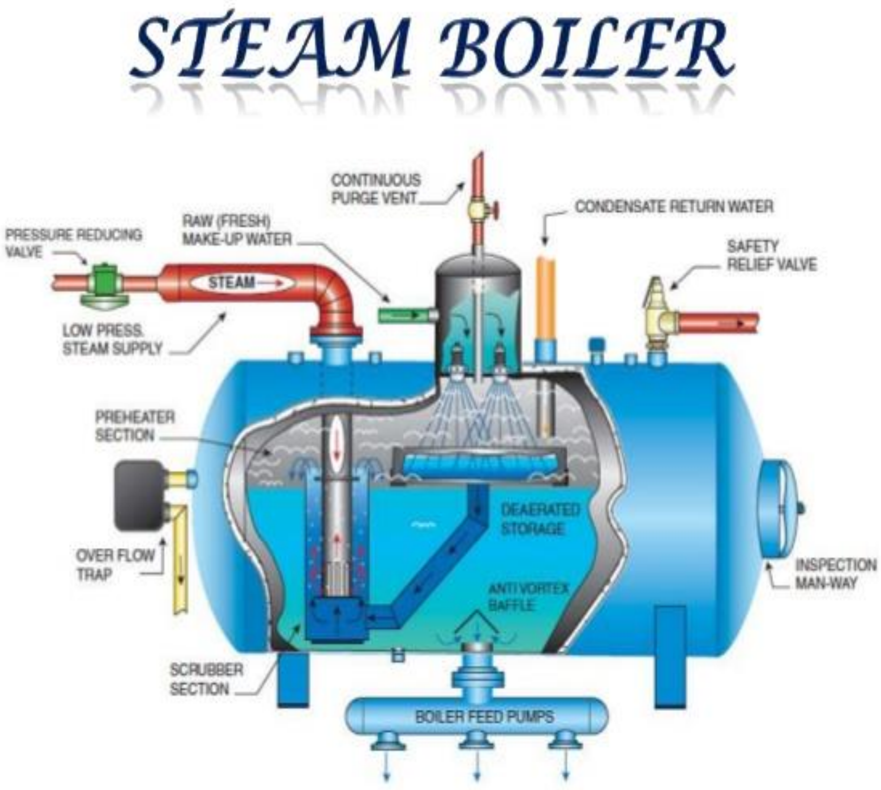
Disadvantages of Hard water

3. Steam Generators or Boilers:

This is used for generation of steam and is made of Mild steel. But usage of hard water in steam generation leads to the following problems. in boiler, water is continuously evaporated to steam and concentration of dissolved salts increases progressively.



- **Scale & Sludge Formation**
- **Caustic Embrittlement**

Scale & Sludge Formation

- If the precipitation takes place in the form of loose and slimy precipitate, it is called **sludge**.
- Sludge is a soft, loose and slimy precipitate formed within the comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow or at bends. Sludge's are formed by substances which have greater solubility in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, etc.

- On the other hand, if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called **scale.**
- Salts such as $CaSO_4$, $MgSO_4$, $CaSiO_3$, $MgSiO_3$ sticks firmly to the inner walls of the boiler vessel and are difficult to remove results in scale formation.

Disadvantages of Scale & Sludge Formation

- **Wastage of fuel:** Due to low thermal conductivity of scales and sludge, the rate of heat transfer decrease, so always need of excess heat to supply results in wastage of fuel.
- **Lowering of boiler safety:** Due to overheating makes the boiler vessel weaker lowers boiler safety
- **Decrease efficiency:** Sludge can deposit in the condenser and tubing of the boiler and choke them partially, results in Decrease efficiency.
- **Danger of explosion:** Continuous pressure generated by steam and choked condenser sometimes may result in explosion.

Caustic Embrittlement

- In steam generation boiler, some amount of Na_2CO_3 is added to soften the water. But the high pressure and temperature in the boiler converts Na_2CO_3 to NaOH

$$Na_2CO_3 + H_2O \longrightarrow 2\,NaOH + CO_2$$

- This makes boiler water alkaline as water starts converting into steam, eventually results in the formation of highly alkaline solution of NaOH that flows through the cracks.

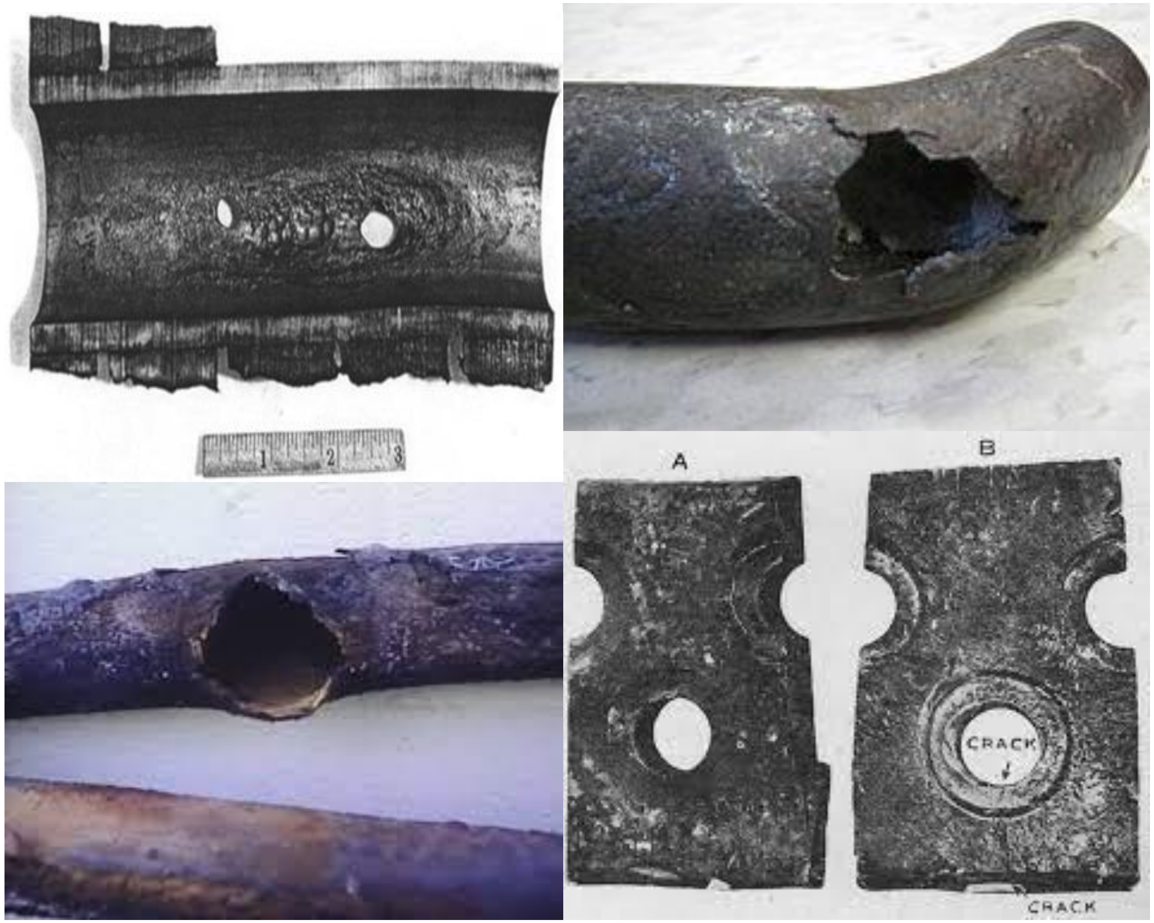
$$2\,NaOH + Fe \longrightarrow Na_2FeO_2 + H_2$$

- This alkali reacts with iron metal of the vessel results in the formation of sodium ferroate Na_2FeO_2 and gets deposited in crevices or cracks.
- At high temperature Na_2FeO_2 decomposes reversibly forms NaOH and Fe_3O_4.

$$Na_2FeO_2 + H_2O + O_2 \longrightarrow NaOH + Fe_3O_4$$

- So the formation of Na_2FeO_2 and its reversible decomposition continues which further results in weakening (brittlement) of the boiler material and hence finally the boiler cracks.

Disadvantages of Hard water



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Disadvantages of Hard 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 $[Ca\text{-}Mg(CO_3)_2]$.

Expression of hardness in terms of equivalents of $CaCO_3$

- The concentrations of hardness producing salts are usually expressed in terms of equivalent amount of $CaCO_3$. $CaCO_3$ 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.

$$\left.\begin{array}{l}\text{Amount}\\ \text{equivalent to } CaCO_3\end{array}\right\} \frac{x \times 100}{\text{Molecular weight of hardness producing salt}}$$

Expression of hardness in terms of equivalents of $CaCO_3$

$CaCO_3$ Equivalent Hardness (ppm) =

= Mass of Hardness Producing substance x Chemical equivalents of $CaCO_3$ / Chemical equivalents of Hardness causing salt.

1. How many grams of $FeSO_4$ dissolved per litre gives 210 ppm hardness?
2. Calculate temporary hardness and permanent hardness of water sample from the following data:

$Mg(HCO_3)_2$ = 16 mg/L, $MgCl_2$ = 19 mg/L, $MgSO_4$ = 2.4 mg/L, $Mg(NO_3)_2$ = 2.96 mg/L, $Ca(HCO_3)_2$ = 8.1 mg/L, SiO_2 = 16 mg/L

UNITS OF HARDNESS

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

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 1000000 parts of water.

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

It is defined as the number of milligrams of $CaCO_3$ equivalent hardness per 1 litre of water.

- **<u>Clarke's degree (ºCl)</u>**

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

- **<u>French degree (ºFr)</u>**

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

- **<u>Relationship between various units</u>**

1ppm = 1 mg/lit = 0.10 ºFr = 0.070 ºCl

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 EDTA and indicator is more stable that of between the metal ion and indicator.

50 mL SHW = V_1 mL EDTA

50 x 1 mg of $CaCO_3$ = V1 mL EDTA

Hence, 1 mL EDTA = $50/V_1$ mg $CaCO_3$ eq.

Now 50 mL of given hard water = V_2 mL of EDTA

= $V_2 \times 50/V_1$ mg $CaCO_3$ eq.

1 L of given hard water = $20 \times V_2 \times 50/V_1$ mg $CaCO_3$ eq.

Total Hardness of water = 1000 V_2/V_1 ppm

Now, 50 mL of boiled water = V_3 mL of EDTA

= $V_3 \times 50/V_1$ mg $CaCO_3$ eq.

1 L of boiled hard water = $20 \times V_3 \times 50/V_1$ mg $CaCO_3$ eq.

Permanent Hardness = 1000 V_3/V_1 ppm

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Expression of hardness in terms of equivalents of $CaCO_3$

- The concentrations of hardness producing salts are usually expressed in terms of equivalent amount of $CaCO_3$. $CaCO_3$ 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.

$$\text{Amount equivalent to } CaCO_3 = \frac{x \times 100}{\text{Molecular weight of hardness producing salt}}$$

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 EDTA and indicator is more stable that of between the metal ion and indicator.

$$M + In \longrightarrow [M\text{–}In] \quad \text{--- (1)}$$

Less stable & Wine red Colour

$$M + EDTA \longrightarrow [M - EDTA] \quad \text{---- (2)}$$

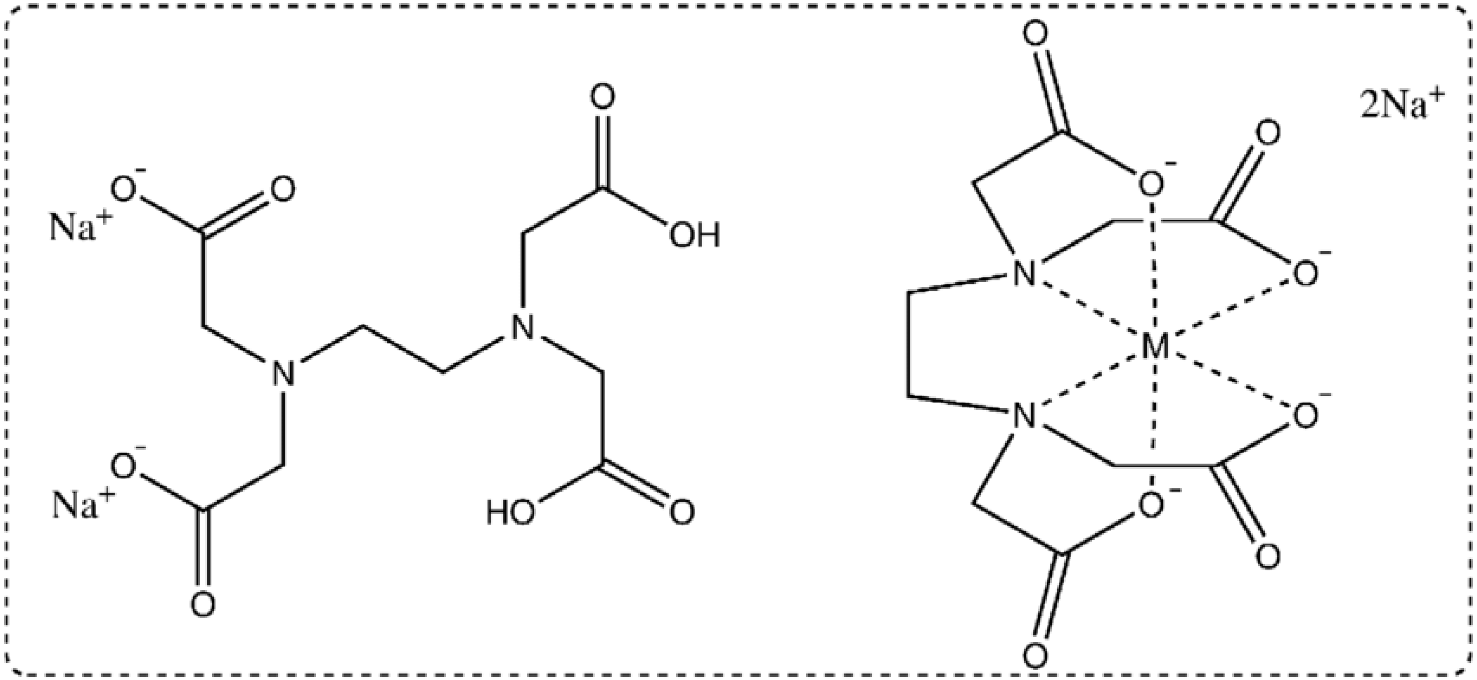
More stable & Coliurless

(2) is more stable than (1)

During the equivalnce point

$$\underset{\text{Wine Red}}{M\text{-}EBT} + EDTA \longrightarrow M - EDTA + \underset{\text{Blue}}{EBT}$$

Structure of Disodium salt of EDTA-Metal Complex



M^{2+} = Ca^{2+}, Mg^{2+}, Zn^{2+}

50 mL SHW = V_1 mL EDTA

50 x 1 mg of $CaCO_3$ = V1 mL EDTA

Hence, 1 mL EDTA = $50/V_1$ mg $CaCO_3$ eq.

Now 50 mL of given hard water = V_2 mL of EDTA

= $V_2 \times 50/V_1$ mg $CaCO_3$ eq.

1 L of given hard water = $20 \times V_2 \times 50/V_1$ mg $CaCO_3$ eq.

Total Hardness of water = 1000 V_2/V_1 ppm

Now, 50 mL of boiled water = V_3 mL of EDTA

= $V_3 \times 50/V_1$ mg $CaCO_3$ eq.

1 L of boiled hard water = $20 \times V_3 \times 50/V_1$ mg $CaCO_3$ eq.

Permanent Hardness = 1000 V_3/V_1 ppm

Temporary Hardness = [1000 V_2/V_1 ppm - 1000 V_3/V_1 ppm]

Numerical on EDTA method

a) 0.28 g of $CaCO_3$ 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.

- 1000 ml of SHW = 280 mg of $CaCo_3$

  1 ml of SHW = 0.280 mg of $CaCO_3$
- 100 ml of SHW = 28 ml of EDTA
- 1 ml of EDTA = 100 / 28 ml of SHW

  = 100 /28 x 0.280 mg of $CaCO_3$
- 1 ml of EDTA = 1 mg of $CaCO_3$

Total Hardness

100 ml of water sample = 33 ml of EDTA = 33 x 1 mg of $CaCO_3$

- Total hardness = 33 x 1000/100 mg /L = **330 ppm or mg /l**

Permanent Hardness

100 ml of boiled water sample = 10 ml of EDTA = 10 x 1 mg of $CaCO_3$

Permanent Hardness

= 10 x 10 mg /L = **100 ppm or mg /l**

Temporary Hardness = Total Hardness - Permanent Hardness

Temporary Hardness = 330 – 100 = 230 ppm or mg /l

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Numerical on EDTA method

a) 0.28 g of $CaCO_3$ 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.

- 1000 ml of SHW = 280 mg of $CaCo_3$

  1 ml of SHW = 0.280 mg of $CaCO_3$
- 100 ml of SHW = 28 ml of EDTA
- 1 ml of EDTA = 100 / 28 ml of SHW

  = 100 /28 x 0.280 mg of $CaCO_3$
- 1 ml of EDTA = 1 mg of $CaCO_3$

Total Hardness

100 ml of water sample = 33 ml of EDTA = 33 x 1 mg of $CaCO_3$

- Total hardness = 33 x 1000/100 mg /L = **330 ppm or mg /l**

Permanent Hardness

100 ml of boiled water sample = 10 ml of EDTA = 10 x 1 mg of $CaCO_3$

Permanent Hardness

= 10 x 10 mg /L = **100 ppm or mg /l**

Temporary Hardness = Total Hardness - Permanent Hardness

Temporary Hardness = 330 – 100 = 230 ppm or mg /l

b) 55.5 mg of $CaCl_2$ 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.

Solution:

750 ml of SHW = 55.5 mg of $CaCl_2$

= (55.5 / 750) x 100/111 mg of $CaCo_3$

1 ml of SHW = 0.067 mg of $CaCO_3$

- 50 ml of SHW = 14 ml of EDTA
- 1 ml of EDTA = 50 /14 ml of SHW

  = 50 /14 x 0.067 mg of $CaCO_3$
- 1 ml of EDTA = 0.24 mg of $CaCO_3$

Total Hardness

100 ml of water sample = 9.8 ml of EDTA = 9.8 x 0.24 mg of CaCO3

- Total hardness = 9.8 x 0.24 x 1000/100 mg /L = **23.52 ppm or mg /l**

Permanent Hardness

50 ml of water sample = 2.7 ml of EDTA = 2.7 x 0.24 mg of $CaCO_3$

Permanent Hardness

= 2.7 x 0.24 x 1000/50 mg /L = **12.96 ppm or mg /l**

Temporary Hardness = Total Hardness - Permanent Hardness

Temporary Hardness = 23.52 – 12.96 = ppm or mg /l

c) If the standard hard water contains 20 g/liter of $CaCO_3$. 25 mL of this standard hard water required 25 mL EDTA solution.
100 mL sample water required 18 mL EDTA solution.
The same sample after boiling and filtration required 12 mL of EDTA solution. Calculate the temporary hardness of sample water.

Solution:

1000 ml of SHW = 20 g of $CaCo_3$ = 20000 mg $CaCo_3$

1 ml of SHW = 20 mg of $CaCO_3$

25 ml of SHW = 25 ml of EDTA = 25 x 20 mg $CaCo_3$ = 500 mg $CaCo_3$

1 ml of EDTA = 25/25 x 20 ml of SHW

= 20 mg of $CaCO_3$

1 ml of EDTA = 20 mg of $CaCO_3$

Total Hardness

100 ml of water sample = 18 ml of EDTA = 18 x 20 mg of $CaCO_3$

Total hardness = 360 x 1000/100 mg /L = **3600 ppm or mg /l**

Permanent Hardness

100 ml of boiled water sample = 12 ml of EDTA = 12 x 20 mg of $CaCO_3$

Permanent Hardness

= 240 x 10 mg /L = 24**00 ppm or mg /l**

Temporary Hardness = Total Hardness - Permanent Hardness

Temporary Hardness = 3600 – 2400 = 1200 ppm or mg /l

d) 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 $CaCO_3$

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

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 $CaCO_3$

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 $CaCO_3$

90 mL of 0.05 M EDTA = 90 x 0.05 x 100 = 450 ppm = **Permanent hardness**

Temporary hardness = 820 – 450 = 370 ppm

e) 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.

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d) 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 $CaCO_3$

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

50 mL water sample = 8.2 mL of 0.05 M EDTA

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

= 164 mL of 0.05 M EDTA

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

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 mL of 0.05 M EDTA

= 90 mL of 0.05 M EDTA

As, 1 mL, 1 M EDTA = 100 mg $CaCO_3$

90 mL of 0.05 M EDTA = 90 x 0.05 x 100 = 450 ppm = **Permanent hardness**

Temporary hardness = 820 – 450 = 370 ppm

e) 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.

M/10 EDTA = 0.01 M EDTA

1000 mL 1 M EDTA = 100 g $CaCO_3$

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

25 mL water sample = 5.5 mL of 0.01 M EDTA

1000 mL water sample = 40 x 5.5 mL of 0.01 M EDTA

= 220 mL of 0.01 M EDTA

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

220 mL of 0.01 M EDTA = 220 x 0.1 x 100 = 2200 ppm = **Total Hardness**

Now, 50 mL of boiled water = 3.9 mL of 0.1 M EDTA

1000 mL water sample = 20 x 3.9 mL of 0.1 M EDTA

= 78 mL of 0.1 M EDTA

As, 1 mL, 1 M EDTA = 100 mg $CaCO_3$

78 mL of 0.01 M EDTA = 78 x 0.1 x 100 = 780 ppm = **Permanent hardness**

Temporary hardness = 2200 – 780 = ppm

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Lecture – 7, 8, 9

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Softening Methods

1. Lime-Soda Method
2. Zeolite Softener method
3. Ion Exchange Method

1. Lime-Soda Method

- In this method, calculated quantity of Lime [$Ca(OH)_2$] and Soda [Na_2CO_3] mixture is added to hard water.
- Precipitates of $CaCO_3$ and $Mg(OH)_2$ 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 $CaCO_3$ and $Mg(OH)_2$, coagulants such as Alum [$Al_2(SO_4)_3$], sodium meta aluminate [$NaAlO_2$], or $FeSO_4$ could be used in cold lime soda method.

Constituent	Reaction	Need
Ca^{2+} (Perm. Ca)	$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	S
Mg^{2+} (Perm. Mg)	$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
HCO_3^- (e.g., $NaHCO_3$)	$2HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + CO_3^{2-}$	L − S
$Ca(HCO_3)_2$ (Temp. Ca)	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$	L
$Mg(HCO_3)_2$ (Temp. Mg)	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$	2L
CO_2	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$	L
H^+ (free acids HCl,	$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
Coagulants : $FeSO_4$	$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2 + Ca^{2+}$ $2Fe(OH)_2 + H_2O + O_2 \longrightarrow 2Fe(OH)_3$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
$Al_2(SO_4)_3$	$2Al^{3+} + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3Ca^{2+}$ $3Ca^{2+} + 2Na_2CO_3 \longrightarrow 3CaCO_3 + 6Na^+$	L + S
$NaAlO_2$	$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$	− L

From the above table it can be seen that 100 parts by mass of $CaCO_3$ are equivalent to 74 parts of $Ca(OH)_2$ and 106 parts of Na_2CO_3.

Lime requirement for softening

$$= \frac{74}{100}\left[\begin{array}{c}\text{Temp. } Ca^{2+} + 2 \times \text{Temp. } Mg^{2+} + \text{Perm. } (Mg^{2+} + Fe^{2+} + Al^{3+}) \\ + CO_2 + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \\ \text{all in terms of } CaCO_3 \text{ eq.}\end{array}\right] \times \frac{\text{Volume of water}}{106} \times \frac{100}{\%\text{Purity}} \text{ kg}$$

And Soda requirement for softening

$$= \frac{106}{100}\left[\begin{array}{c}\text{Perm. } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+}) + H^+ (HCl \text{ or } H_2SO_4) - HCO_3^- \\ \text{all in terms of } CaCO_3 \text{ eq.}\end{array}\right] \times \frac{\text{volume of water}}{10^6} \times \frac{100}{\%\text{Purity}} \text{ kg}$$

There are two types of lime-soda process.

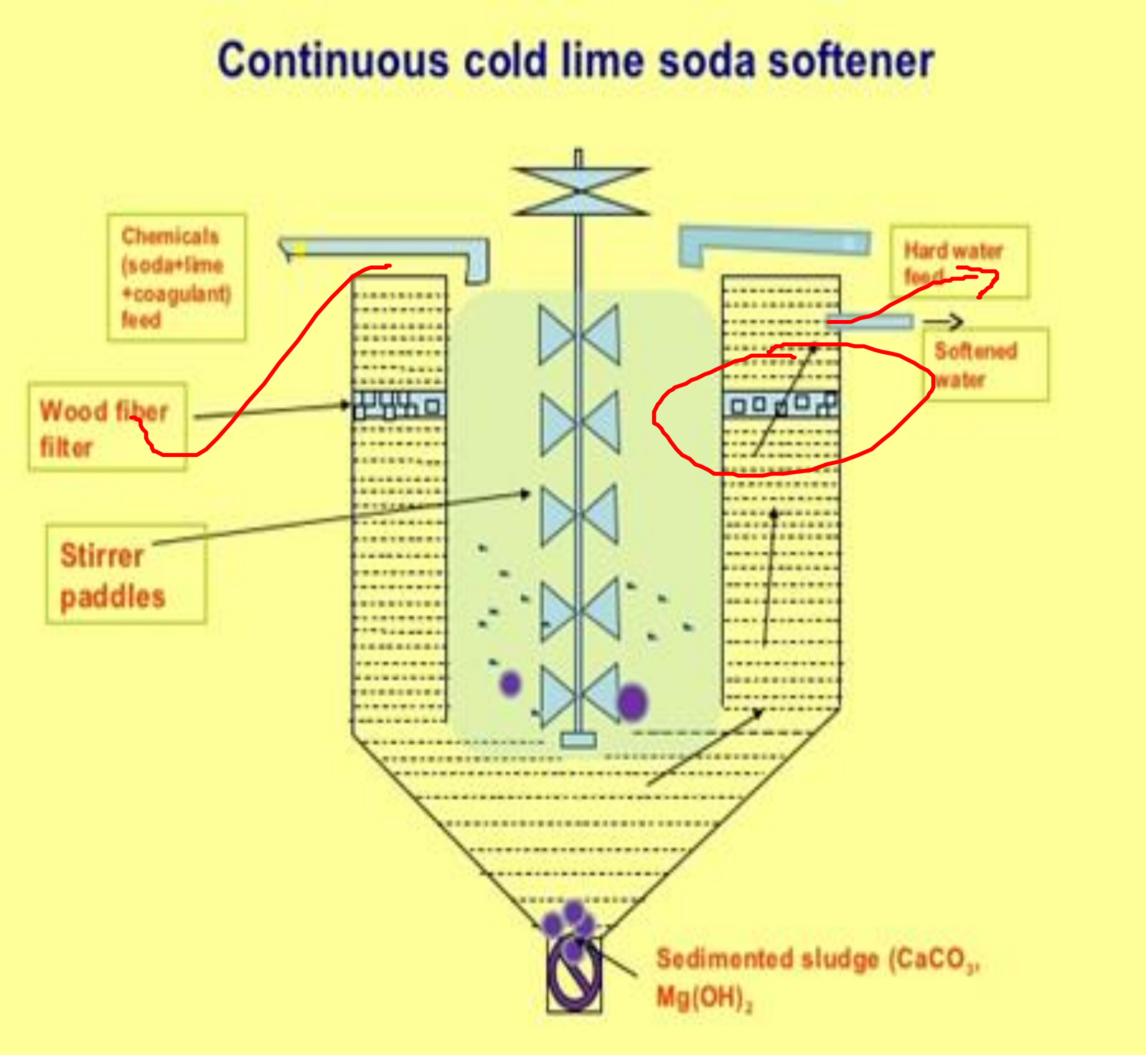
(1) Cold lime-soda process

and (2) Hot lime-soda process

A. 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 ^{0}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



1. Carried out at 25 ^{0}C to 30 ^{0}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

B. Hot Lime-Soda Method

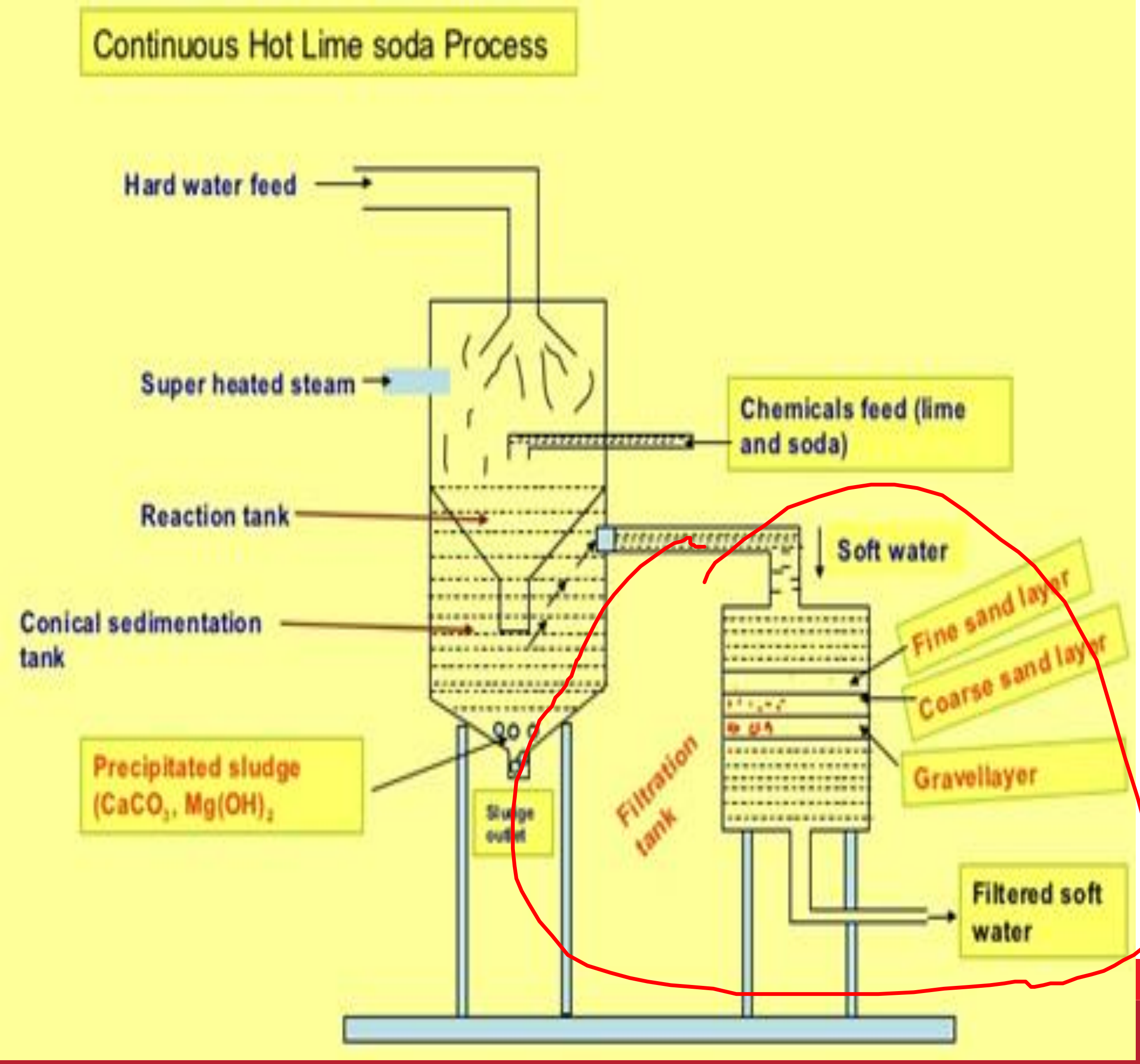
In Hot lime-soda process hard water is treated with soda and lime at 94-100℃
Hot lime-soda plant essentially consists of three parts

→ 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



1. Carried out at 95 ^{0}C to 100 ^{0}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

2. Zeolite softener method

- Sodium-Zeolites which are hydrated sodium alumino silicates, capable of exchanging their sodium ions with hardness producing ions are used.
- Chemically sodium zeolites are $Na_2O.Al_2O_3.xSiO_2.yH_2O$

  (Where, x= 2-10 & y= 2-6).

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

$2Na^+$ 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 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.

$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$

$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

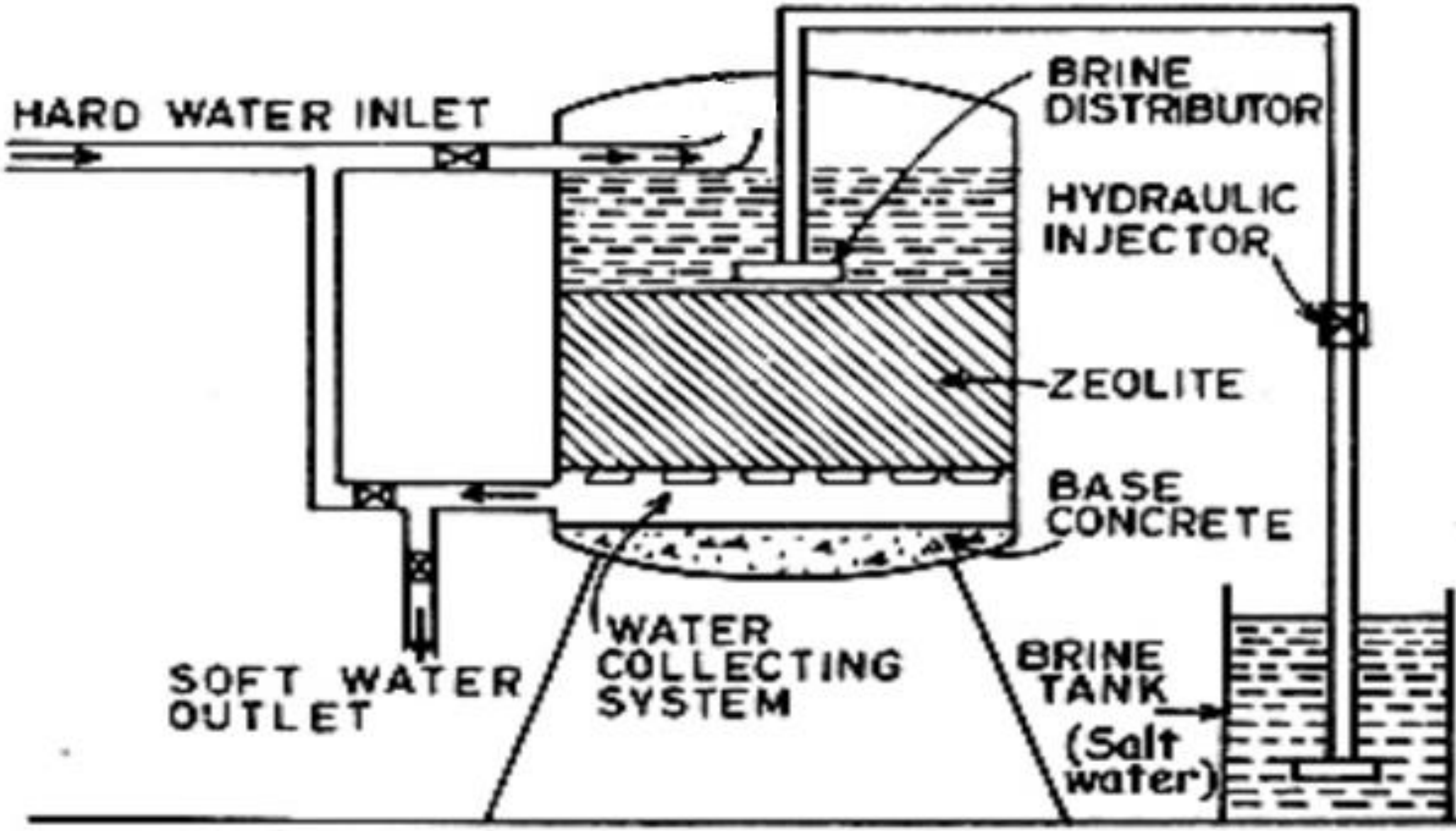
- **Regeneration:**

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

$$CaZe + 2NaCl \longrightarrow CaCl_2 + Na_2Ze$$

$$MgZe + 2NaCl \longrightarrow MgCl_2 + Na_2Ze$$

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 Fe^{3+} and 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