

APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 7

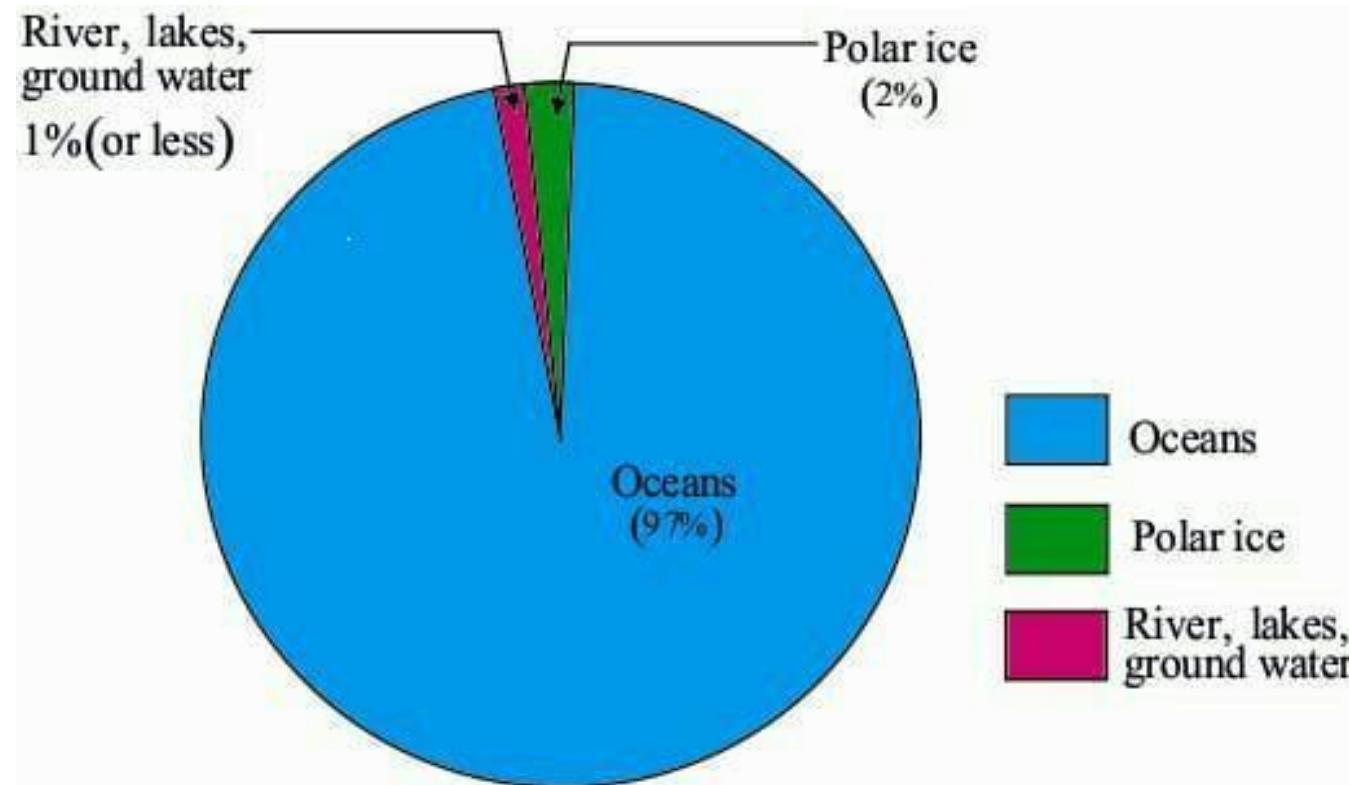


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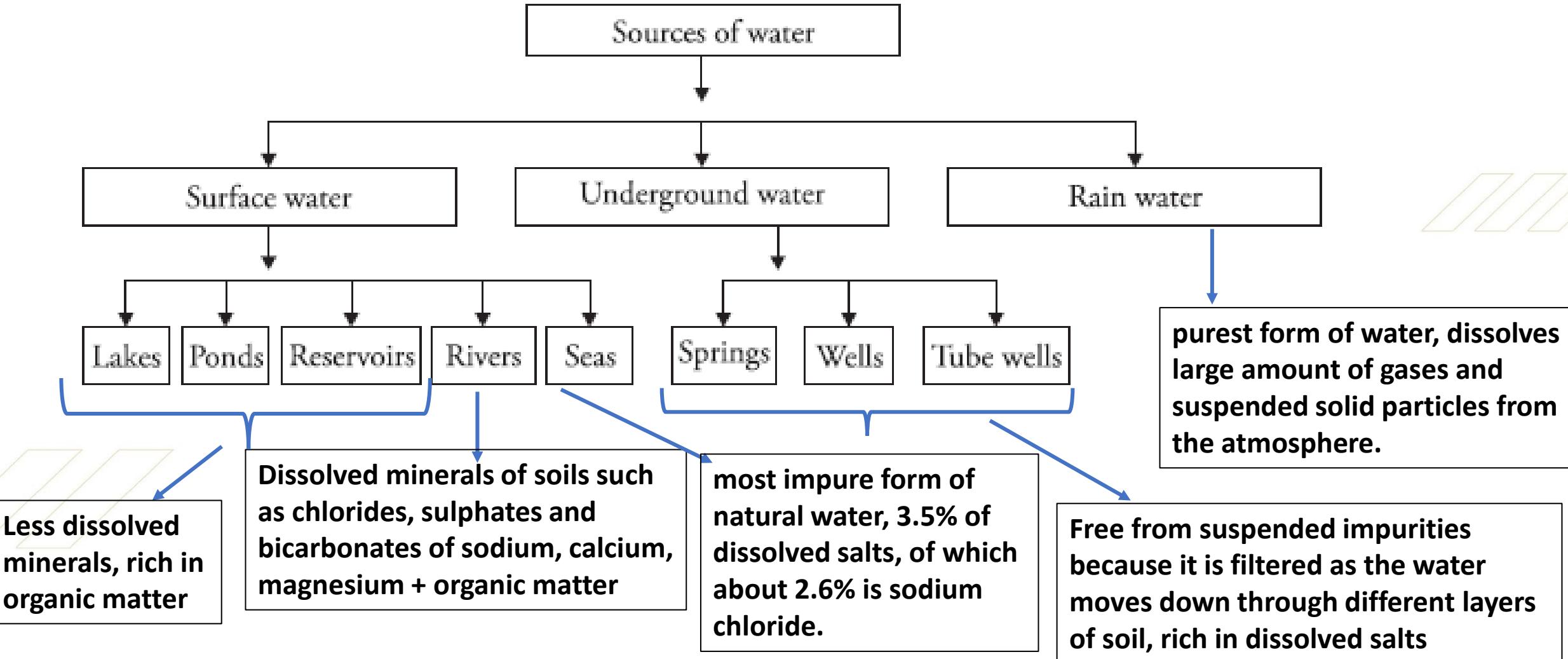


WATER

- Water is the most abundant and essential natural resource. It covers nearly 70% of the earth's surface.



Sources of water



Water Quality Standards

- **Importance of water quality standards**

- Help to identify the water quality, problems caused by improper treatment of waste water discharge, run off, addition of fertilisers, chemicals from agricultural areas
- For the purpose of safety of human beings, drinking characteristics and for the health of ecosystems.
- The **water quality parameters or characteristics for which analysis is carried out** generally fall into three groups:
 1. Physical characteristics
 2. Chemical characteristics
 3. Biological characteristics

1. Physical characteristics

(a) Color

- Clean water should be colorless.
- The presence of color in water indicates the presence of various minerals, decomposed organic matter like leaves, roots, organic and inorganic wastes, wastes from textile mill, paper pulp industries, foodprocessing industries,

(b) Taste and odor

- Water should be odorless and should have a fairly good taste.
- There are no specific units to measure these parameters, but generally decaying organic matter imparts odor and bad taste to water. The minimum odor that can be detected is called threshold odor number (TON).
- The value of TON is determined as follows:

$$TON = \frac{A+B}{A}$$

The greatest dilution of a sample with odor-free water that still yields a just-detectable odor.

A = Volume of sample in mL; B = Volume of distilled water (i.e., odor-free water in mL).

(c) *Temperature*

→ High temperature indicates thermal pollution and disturbs aquatic ecosystem by reducing the dissolved oxygen in water.

(d) *Electrical conductivity*

→ It gives an idea about the dissolved solids in water.

→ Greater the amount of dissolved solids, higher will be the conductivity.

→ It can be measured easily with the help of conductivity meter. The average value of conductivity for potable water should be less than $2 \mu\text{S}/\text{cm}$.

2. CHEMICAL CHARACTERISTICS

(a) **pH** → The pH of normal drinking water is 6.5–8.5.

→ It can be measured with the help of pH meter using a combined electrode (a glass electrode and a calomel electrode as reference electrode).

(b) **Hardness** → It expresses the concentration of calcium and magnesium ions in water in terms of equivalent of CaCO_3 . The maximum acceptance limit is 500 ppm.

(c) **Total dissolved solids (TDS)** → The maximum permissible limit is 500 mg/L. TDS includes both organic and inorganic dissolved impurities. It can be measured by evaporating a sample to dryness and then weighing the residue.

(d) **Total solids** → This includes both the dissolved solids as well as suspended impurities.

(e) **Dissolved oxygen** → Higher the amount of DO better is the quality of water. Normal water contains 4.7 mg/L of DO.

→ Lesser amount of DO in water indicates pollution in water.

→ Wrinkler or iodometric methods using membrane electrode is used for measuring DO in water.

(f) **Chlorides** → Its amount in water should be less than 250 ppm.

→ High percentage of chloride in water harms metallic pipes as well as agriculture crops.

(g) **Fluorides** → Maximum permissible limit is 1.5 ppm. The amount of fluoride in water sample can be determined using an ion meter.

→ Excess of fluoride causes discoloration of teeth, bone fluorosis and skeletal abnormalities.

(h) **Sulphates** → Permissible limit is 250 ppm. These are generally found associated with calcium, magnesium and sodium ions.

→ It leads to scale formation in boilers, causes boiler corrosion and imparts odor to water.

(i) **Nitrates** → Its concentration in drinking water should not exceed 45 mg/L.

→ Excessive nitrates in drinking water causes 'methemoglobinemia' or blue baby syndrome in infants.

→ Nitrates dissolve in water because of leaching of fertilisers from soil and nitrification of organic matter.

3. Biological characteristics

- Water should be free from all types of bacteria, viruses, protozoa and algae.
- The coliform count in any sample of 100 mL should be zero. (Coliform bacteria are defined as facultatively anaerobic, Gram-negative, non-spore-forming rods)



4. Bacteriological standards

(i) ***Water entering the distribution system*** → Coliform count in any sample of 100mL should be zero.

→ A sample of water entering the distribution system that does not confirm to this standard calls for an immediate investigation into both the efficacy of the purification process and the method of sampling.

(ii) ***Water in the distribution system*** → It shall satisfy these three criteria:

- (a) *E. coli* count in 100 mL of any sample should be zero.
- (b) Coliform organism should not be more than 10 per 100 mL of any sample.
- (c) Coliform organism should not be present in 100 mL of any two consecutive samples or more than 5% of the samples collected for the year.

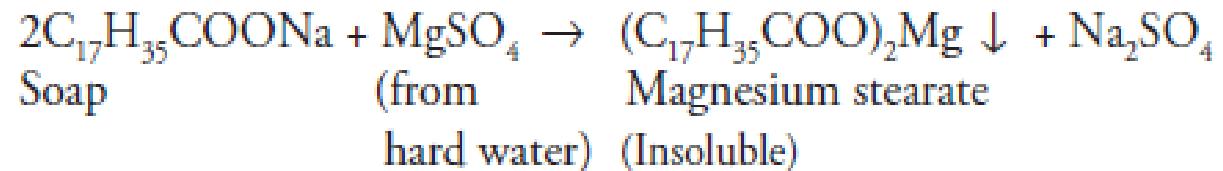
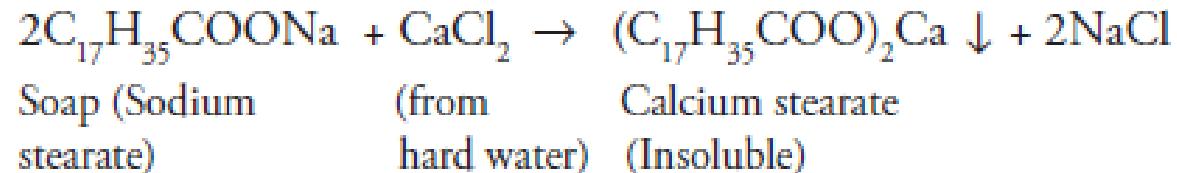
Hardness of water

- It is defined as the characteristic of water that prevents lathering of soap.

- Causes**

→ Hardness is due to the presence of certain soluble salts of calcium and magnesium in water.

→ A sample of hard water, when treated with soap (sodium or potassium salts of higher fatty acids like oleic, palmitic or stearic acid), does not form lather or foam but forms a white precipitate or scum instead.



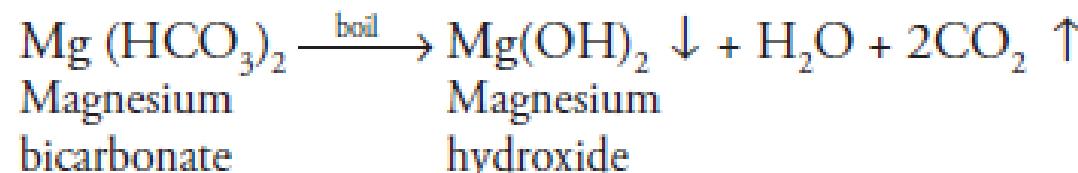
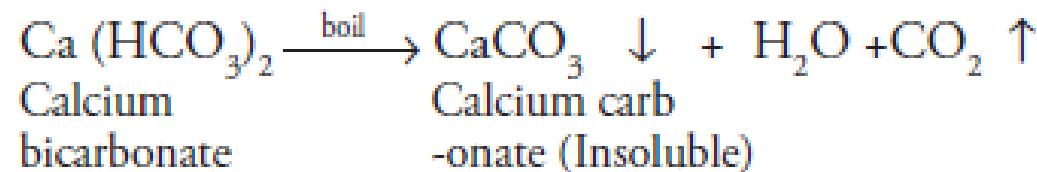
S.No	Hard water	Soft water
1	Water that does not form lather with soap but forms white precipitate	Water that produces lather or foam easily with soap is called 'soft water'
2	It contains soluble salts of calcium magnesium and other heavy metal ions like Al^{3+} , Fe^{3+} , and Mn^{2+} dissolved in it	It does not contain dissolved salts of calcium and magnesium
3	In hard water, the cleaning properties of soap is depressed and lot of soap is wasted in bathing and washing	The cleaning quality of soap is not depressed hence it is good for washing and cleaning
4	Owing to dissolved hardness, boiling point of water is elevated, therefore more fuel and time is required for cooking	Less fuel and time is required for cooking

Types of hardness

- **Temporary hardness/ carbonate hardness/ alkaline hardness**

→ It is called alkaline hardness because it is due to the presence of bicarbonate, carbonate and hydroxide and can be determined by titration with HCl using methyl orange as an indicator.

→ It can be removed by boiling of water. During boiling, the bicarbonates are decomposed forming insoluble carbonates or hydroxides that are deposited at the bottom of the vessel.



- **Permanent hardness / non-carbonate / non-alkaline hardness.**

- It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals.
- Salts mainly responsible for permanent hardness are CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, etc.
- It cannot be removed by simple boiling but can be removed by special chemical methods like lime-soda process, zeolite method, etc.

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Degree of hardness

- Hardness is always calculated in terms of equivalent of CaCO_3 .
- There are two basic reasons for choosing CaCO_3 as standard:
 - Calculations become easy as its molecular weight is exactly 100 (and equivalent weight is exactly 50).
 - It is the most insoluble salt that can be precipitated in water treatment.

• Calculation of equivalents of CaCO_3

To find out hardness in a given water sample, it is essential to convert hardness due to different salts (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4 , MgCl_2 , MgSO_4 , etc.) in terms of equivalent of CaCO_3 . This can be done by the formula:

$$\text{Equivalent of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

- Chemical equivalent of CaCO_3 is 50
- Chemical equivalent of salt =
$$\frac{\text{Molecular weight}}{\text{Valency}}$$
- Chemical equivalent of acid =
$$\frac{\text{Molecular weight}}{\text{Basicity}}$$

Basicity is the number of replaceable hydrogen ions in an acid.

- Chemical equivalent of base =
$$\frac{\text{Molecular weight}}{\text{Acidity}}$$

Acidity is the number of replaceable hydroxyl ions in a base.

Eg. For CaCO_3 , Molar mass = 100, Chemical equivalent of CaCO_3 = $100/2 = 50$

For H_2SO_4 , Molar mass = 98, Chemical equivalent of H_2SO_4 = $98/2 = 49$

For $\text{Al}_2(\text{SO}_4)_3$, Molar mass = 342, Chemical equivalent of $\text{Al}_2(\text{SO}_4)_3$ = $342/6 = 57$

Numericals

1. A water sample contains 248 mg CaSO₄ per liter. Calculate the hardness in terms of CaCO₃ equivalent.
2. How many grams of FeSO₄ dissolved per liter gives 300 ppm of hardness?

1. Solution

Weight of CaSO_4 per liter = 248 mg

Hardness in terms of CaCO_3 equivalent = ?

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

$$\frac{248 \times 100 / 2}{136 / 2} = 182.35 \text{ ppm.}$$

$$2. \quad \text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

Let mass of hardness producing substance, that is, $\text{FeSO}_4 = x$ mg

$$\text{Then } 300 = \frac{x \times 100 / 2}{152 / 2}$$

$$\text{or } 300 = \frac{x \times 100}{152} = 456 \text{ ppm} = 456 \text{ mg/L} = 0.456 \text{ g/L}$$

Disadvantages of Hard Water

• In Industries

- (a) **Steam generation in boilers** The use of hard water in boilers causes problems like scale and sludge formation, boiler corrosion, caustic embrittlement, priming and foaming, etc
- (b) **Sugar industries** Salts dissolved in hard water cause problems in crystallisation of sugar.
- (c) **Paper industries** The cations (Ca^{2+} , Mg^{2+} , Fe^{2+} etc) present in hard water react with the chemicals involved in different steps of paper manufacturing. This produces various unwanted side products and undesirable effects like loss of gloss and smoothness, change in color of paper, etc.
- (d) **Textile industries** During washing of the fabric or yarn with hard water the calcium and magnesium salts stick to the surface causing undesirable changes in color or texture of fabric.
- (e) **Dyeing industries** The salts dissolved in hard water react with the functional groups present in the dyes causing precipitation or change in shade.
- (f) **Pharmaceutical industry** Use of hard water in the preparation of drugs can lead to the production of undesirable products that may be harmful or even poisonous.

(2) *In domestic usage*

(a) Drinking : → Taste of soft water is better than hard water.

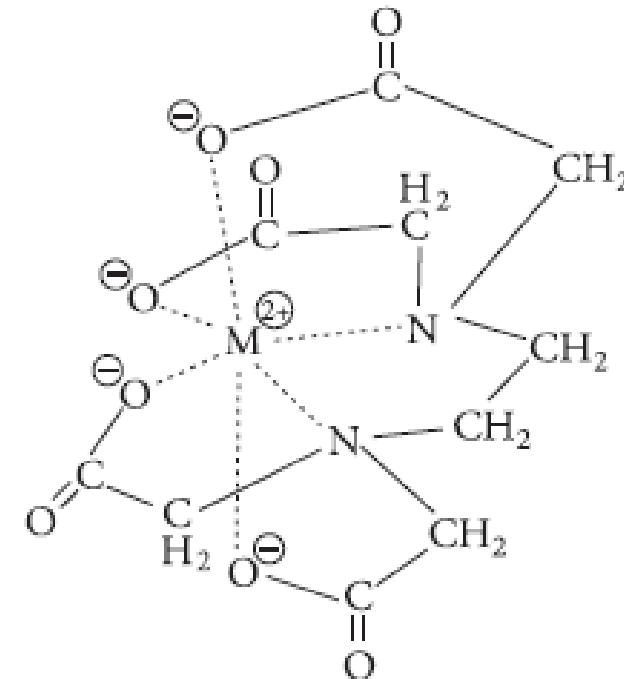
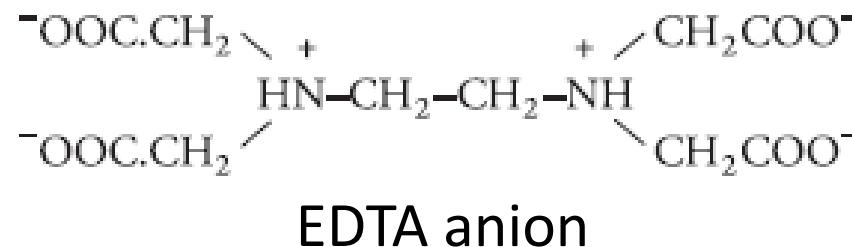
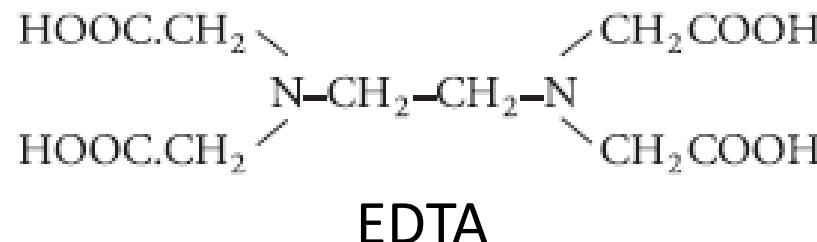
→ The dissolved calcium in hard water can help to produce strong teeth and healthy bones in children. However, hard water can have bad affect on our appetite and digestive system; sometimes it produces calcium oxalate that causes different urinary problems.

(b) Cooking The boiling point of hard water increases because of the presence of various salts; this causes wastage of time and fuel.

(c) Bathing and washing → As hard water does not form lather or foam with water, it adversely affects the cleaning properties of soap and a lot of it is wasted because of production of sticky precipitates of calcium and magnesium.

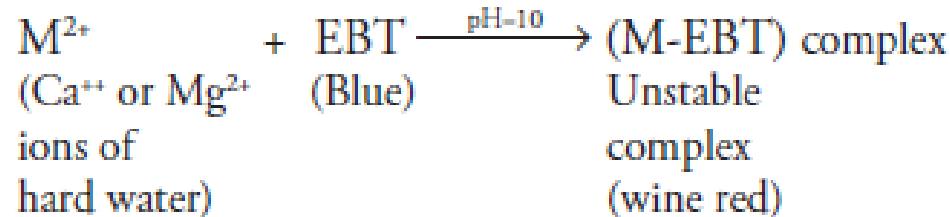
Estimation of hardness by EDTA Method

- This is a complexometric titration as ethylene diamine tetra-acetic acid (EDTA) forms a stable complex with Ca^{2+} and Mg^{2+} ions in the pH range 8–10.



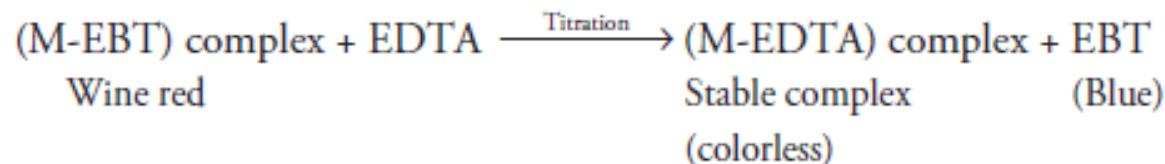
Structure of an M²⁺ -EDTA chelate

- Hard water is buffered to a pH value of 10 using NH₄OH-NH₄Cl buffer and a few drops of Eriochrome black-T indicator (EBT) are added.



where M = Ca and Mg ions.

- During the course of titration of water sample against EDTA, EDTA combines with free Ca²⁺ or Mg²⁺ ions to give very stable metal-EDTA complex which is colorless.



Thus at equivalent point, there is a change in color from wine red (due to M-EBT) to blue (due to free EBT).

- **Steps involved in this method:**

→ **Preparation of standard hard water** Dissolve 1.0 g of pure, dry CaCO_3 in minimum quantity of dilute HCl and evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 liter solution

→ Preparation of 0.01 M EDTA Solution, EBT indicator and buffer solutions

- **Procedure**

- **Standardisation of EDTA solution:** Titration of standard hard water with EDTA solution. Let the volume of EDTA consumed be V_1 mL.

→ **Determination of total hardness of water:** Titration of unknown hard water sample with EDTA solution. Let the volume of EDTA consumed this time be V_2 mL.

→ **Determination of permanent hardness of water:** Titration of unknown hard water sample (boiled initially to half volume) with EDTA solution. Let the volume of EDTA consumed this time be V_3 mL. (Boiling causes all the bicarbonates to decompose to CaCO_3 and Mg(OH)_2)

• Calculations

Step 1 Standardisation of EDTA solution

V_1 mL of EDTA = 50 mL of standard hard water

(Since each mL of standard hard water contains 1 mg of CaCO_3 equivalent hardness)

Therefore, V_1 mL of EDTA = 50 mg of CaCO_3 equivalent hardness

or $1 \text{ mL of EDTA} = \frac{50}{V_1} \text{ mg of } \text{CaCO}_3$ (1)

Step 2 Determination of total hardness

50 mL of unknown hard water = V_2 mL of EDTA

(Since 1 mL of EDTA has $\frac{50}{V_1}$ mg of CaCO_3 hardness – from Eq. (1)

= $V_2 \times \frac{50}{V_1}$ mg of CaCO_3 equivalent hardness (2)

The hardness given by Eq. (2) is the hardness in 50 mL water sample \therefore hardness in 1000 mL water sample

$$= V_2 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000$$

$$= 1000 \times \frac{V_2}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Hence total hardness of water} = 1000 \times \frac{V_2}{V_1} \text{ mg/L or ppm}$$

Step 3 Determination of permanent hardness of water

As 50 mL of boiled water = V_3 mL of EDTA

$$\text{Again as } 1 \text{ mL EDTA} = \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness} \quad [\text{from Eq. (1)}]$$

$$\therefore V_3 \text{ mL of EDTA} = V_3 \times \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent hardness} \quad (3)$$

hardness as given by Eq. (3) is the hardness in 50 mL boiled water

$$\therefore \text{hardness in } 1000 \text{ mL of boiled water} = V_3 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000 = 1000 \times \frac{V_3}{V_1} \text{ mg/L}$$

$$\text{Hence permanent hardness of water} = 1000 \times \frac{V_3}{V_1} \text{ mg/L or ppm}$$

Temporary hardness = Total hardness–Permanent hardness

$$= 1000 \times \frac{V_2}{V_1} - 1000 \times \frac{V_3}{V_1}$$

$$\text{or temporary hardness} = \frac{1000 (V_2 - V_3)}{V_1} \text{ ppm}$$

Volume of EDTA can be equated with CaCO_3 equivalent as follows

1000 mL of 1 M EDTA = 100 g of CaCO_3

1000 mL of 0.01 M EDTA = 1 g of CaCO_3

1 mL of 0.01 M EDTA = 1 mg of CaCO_3

1 mL of 0.02 N EDTA = 1 mg of CaCO_3

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Numericals based on EDTA method

1. 250 mL of a water sample on EDTA titration with Eriochrome Black –T consumed 13 mL of 0.022 M EDTA till end point is reached. Calculate the hardness of water ?
2. 25 mL of standard hard water consumes 12 mL of standard EDTA solution. 25 mL of hard water sample consumes 8 mL of EDTA solution. After boiling the sample, 25 mL of the boiled and cooled hard water consumes 6 mL of standard EDTA solution. Calculate the total, permanent and temporary hardness.
3. 0.28 g of CaCO_3 was dissolved in HCl and the solution was made to one liter with distilled water. A total of 100 mL of the above solution required 28 mL of EDTA solution on titration. 100 mL of the hard water sample required 35 mL of the same EDTA solution on titration. After boiling 100 mL of this water, cooling, filtering and then titration required 10 mL of EDTA solution. Calculate the temporary and permanent hardness of water.

Solution 1

1 mL of 0.01 M EDTA = 1 mg of CaCO_3 equivalents

$$13 \text{ mL of } 0.022 \text{ M EDTA} = \frac{1 \times 13 \times 0.022}{1 \times 0.01} = 28.6 \text{ mg of } \text{CaCO}_3$$

This amount of hardness is present in 250 mL of water sample.

$$\text{Hardness present in 1 liter} = \frac{28.6}{250} \times 1000 = 114.4 \text{ ppm}$$

Solution 2

It is assumed that 1 mL of standard hard water has 1 mg of CaCO_3 equivalent hardness.

Step (i) *Standardisation of EDTA*

25 mL of standard hard water = 12 mL of EDTA = 25 mg of CaCO_3 eq. hardness.

$$1 \text{ mL of EDTA} = \frac{25}{12} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness.} \quad (1)$$

Step (ii) *Total hardness*

$$25 \text{ mL of hard water sample} = 8 \text{ mL of EDTA} = 8 \times \frac{25}{12} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness.} \\ [\text{From Eq. (1)}]$$

$$1000 \text{ mL of hard water sample} = 8 \times \frac{25}{12} \times \frac{1000}{25} = 666.67 \text{ ppm}$$

Hence Total Hardness = 666.67 ppm

Step (iii) *Determination of permanent hardness of water*

$$\text{Given, } 25 \text{ mL of boiled water} = 6 \text{ mL of EDTA} = \frac{6 \times 25}{12} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1000 \text{ mL (or 1 liter) of unknown boiled water} = \frac{6 \times 25 \times 1000}{12 \times 25} = 500 \text{ ppm.}$$

Permanent Hardness = 500 ppm

Step (iv) *Determination of temporary hardness of water:*

Temporary Hardness = Total Hardness – Permanent Hardness

$$666.67 - 500 = 166.67 \text{ ppm}$$

Temporary Hardness = 166.67 ppm

Solution 3

According to eq (i) 1 mL of standard hard water has 0.28 mg of CaCO_3

\therefore 100 mL of standard hard water has 100×0.28 mg of CaCO_3

or, 28 mL EDTA solution = $100 \times 0.28 = 28$ mg of CaCO_3

$$1 \text{ mL EDTA solution} = \frac{28}{28} = 1 \text{ mg of } \text{CaCO}_3$$

Step (ii) Determination of total hardness of water

Given, 100 mL of unknown hard water sample \equiv 35 mL of EDTA \equiv 35 \times

= 35 mg of CaCO_3 equivalent hardness

$$\therefore 1000 \text{ mL (or 1 liter) of unknown hard water sample} = \frac{35}{100} \times 1000$$

= 350 mg of CaCO_3 equivalent hardness

Hence Total Hardness = 350 ppm

Step (iii) Determination of permanent hardness of water

Given, 100 mL of boiled water \equiv 10 mL of EDTA \equiv $10 \times 1 = 10$ mg of CaCO_3 eq. hardness.

$$\therefore 1000 \text{ mL (or 1 liter) of unknown boiled water} = \frac{10}{100} \times 1000 = 100 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness.}$$

Permanent Hardness = 100 ppm

Step (iv) Determination of temporary hardness of water

Temporary Hardness = Total Hardness – Permanent Hardness

$$350 - 100 = 250 \text{ ppm}$$

Temporary Hardness = 250 ppm

Homework questions

1. A standard hard water contains 15 g of CaCO₃ per liter. 20 mL of this water sample required 25 mL of EDTA solution, 100 mL of sample water required 18 mL of EDTA solution. The sample after boiling required 12 mL EDTA solution. Calculate total, permanent and temporary hardness of the given water sample in ppm.

(Ans. Total hardness = 2160 ppm; Permanent hardness = 1440 ppm; Temporary hardness = 720 ppm)

2. The EDTA was used to find out permanent and temporary types of hardness in a given hard water sample. Following observations were recorded:

(i) 22 mL of EDTA was consumed by 50 mL of standard hard water (containing 1 mg of CaCO₃ per mL).

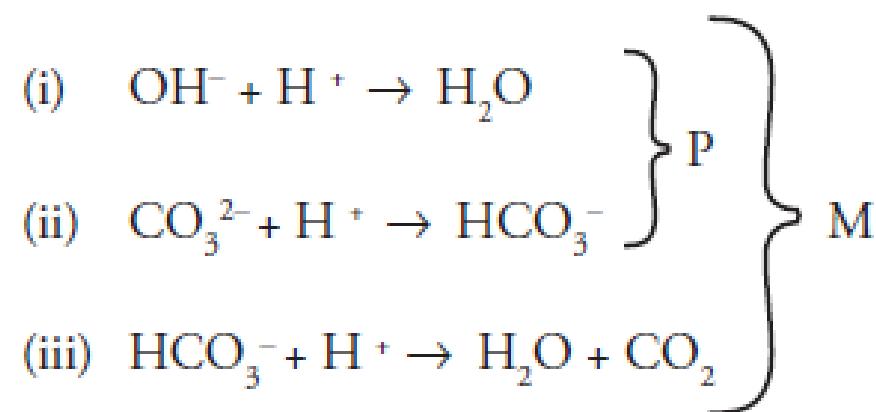
(ii) 50 mL water sample consumed 27 mL EDTA solution.

(iii) 50 mL water sample after boiling, filtering consumed 20 mL of EDTA solution.

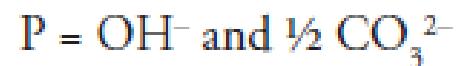
(Ans. Total hardness = 1227.27 ppm; permanent hardness = 909 ppm; temporary hardness = 318.2 ppm)

Alkalinity

- Alkalinity of water is a measure of total content of those substances which increase the hydroxide ions concentration (OH^-) upon dissociation or due to hydrolysis.
- **Alkalinity of water is attributed to the presence of**
 - (i) Caustic alkalinity (due to OH^- and CO_3^{2-} ions) and
 - (ii) Temporary hardness (due to HCO_3^- ions)
- These can be estimated separately by titration against standard acid, using phenolphthalein and, methyl orange as indicator.
- The determination is based on the following reactions



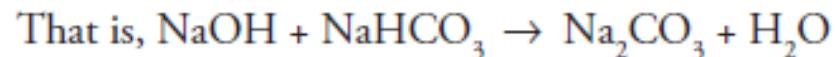
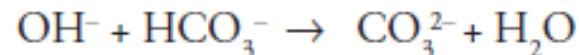
- The titration of the water sample against a standard acid up to phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one half of the normal carbonate present.
- Titration of the water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity



- Alkalinity in water may be due to the presence of the following combinations:

- (i) OH^- only
- (ii) CO_3^{2-} only
- (iii) HCO_3^- only
- (iv) OH^- and CO_3^{2-} together
- (v) CO_3^{2-} and HCO_3^- together

- The possibility of OH^- and HCO_3^- together is ruled out, because of the fact that they combine instantaneously to form CO_3^{2-} ions



Thus, OH^- and HCO_3^- ions cannot exist together in water

On similar analogy, OH^- , CO_3^{2-} and HCO_3^- ions also cannot exist together.

→Procedure

- Pipette out 100 mL of the water sample in a clean titration flask. Add 2–3 drops of phenolphthalein indicator.
- Run in N/50 H₂SO₄ (from a burette), till the pink color is just discharged. This is the first end point. Let the volume of acid used until phenolphthalein end point = V_1 mL.
- Then to the same solution, add 2 to 3 drops of methyl orange. Continue titration, till the pink color reappears. This is the second end point.
- Let *extra volume* of acid used to methyl orange end point = V_2 mL.

• CALCULATIONS

100 mL of water up to phenolphthalein end point = V_1 mL of N/50 H₂SO₄

$$\therefore 100 \text{ mL} \times N_p = V_1 \text{ mL} \times N/50$$

Water Acid

$$N_p = \frac{V_1 \text{ mL}}{100 \text{ mL}} \times \frac{N}{50} = \frac{V_1}{5000} \text{ N}$$

∴ Strength of alkalinity up to phenolphthalein end point in terms of CaCO₃ equivalent –
Strength = Normality × Eq. weight of CaCO₃

$$= \frac{V_1}{5000} \times 50 \text{ g/L}$$

$$= \frac{V_1}{5000} \times 50 \times 1000 \text{ mg/L}$$

$$P = 10 V_1 \text{ ppm}$$

Now 100 mL of water up to methyl orange end point

$$= (V_1 + V_2) \text{ mL of N/50 H}_2\text{SO}_4$$

$$\therefore 100 N_m = (V_1 + V_2) \text{ mL} \times N/50$$

$$\text{or Normality } N_m = \frac{(V_1 + V_2) \text{ mL}}{100 \text{ mL}} \times \frac{N}{50} = \frac{(V_1 + V_2)}{5000} \text{ N}$$

\therefore Strength of total alkalinity in terms of CaCO_3 equivalent

$$= \frac{(V_1 + V_2)}{5000} \times 50 \text{ g/L} = \frac{(V_1 + V_2)}{5000} \times 50 \times 1000 \text{ mg/L}$$

$$M = 10(V_1 + V_2) \text{ ppm}$$

Table 2.10 Calculation of alkalinity of water

S.No	Result of titration	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
1	$P=0$	Nil	Nil	M
2	$P=M$	P or M	Nil	Nil
3	$P=1/2M$ or $V_1 = V_2$	Nil	2P	Nil
4	$P>1/2M$ or $V_1 > V_2$	$2P-M$	$2(M-P)$	Nil
5	$P<1/2M$ or $V_1 < V_2$	Nil	2P	$M-2P$

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Numericals on alkalinity

1. 50 mL of a sample of water required 5 mL of N/50 H_2SO_4 using methyl orange as indicator but did not give any coloration with phenolphthalein. What type of alkalinity is present? Express the same in ppm.
2. A sample of water was alkaline to both phenolphthalein and methyl orange. 100 mL of this water sample required 30 mL of N/50 H_2SO_4 for phenolphthalein end point and another 20 mL for complete neutralisation. Determine the type and extent of alkalinity present.
3. A water sample is alkaline to both phenolphthalein as well as methyl orange. 200 mL of a this water sample on titration with N/50 HCl required 9.4 mL of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and titration is further continued, the yellow color of the solution just turned red after addition of another 21 mL of the acid solution. Elucidate on the type and extent of alkalinity present in the water sample.

Solution 1:

As the water sample does not give any coloration with phenolphthalein ($P = 0$), hence only HCO_3^- ions are present.

Now, 50 mL of water sample upto methyl orange end point = 5 mL of N/50 H_2SO_4

$$\therefore 50 \text{ mL} \times N_M = 5 \text{ mL} \times N/50$$

$$\text{or Normality} = 5 \text{ mL} \times N/50 \times 1/50 = \frac{1}{500} \text{ N}$$

Strength of alkalinity in terms of CaCO_3 equivalents

$$= N_M \times \text{Equivalent Weight of } \text{CaCO}_3 = \frac{1}{500} \times 50 \text{ g/L} = \frac{1}{500} \times 50 \times 1000 \text{ mg/L} = 100 \text{ mg/L}$$

Alkalinity due to HCO_3^- ions = 100 ppm.

Solution 2

100 mL of water upto phenolphthalein end point \equiv 30 mL of N/50 H₂SO₄

$$\therefore 100 \times N_p = 30 \times N/50$$

$$N_p = \frac{30}{100} \times \frac{N}{50}$$

Strength of alkalinity upto phenolphthalein end point in terms of CaCO₃

Strength = N_p × Equivalent weight of CaCO₃

$$\text{Strength} = \frac{30}{100} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{30}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 300 \text{ mg/L}$$

P = 300 ppm

Given 100 mL of water upto methyl orange end point \equiv 30+20 = 50 mL of N/50 H₂SO₄

$$\therefore 100 \times N_M = 50 \times N/50$$

$$N_M = \frac{50}{500} \times \frac{1}{50}$$

Strength = N_M × Equivalent Weight of CaCO₃

$$\text{Strength} = \frac{50}{100} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{50}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 500 \text{ mg/L}$$

$$M = 500 \text{ ppm}$$

Since P > $\frac{1}{2} M$ therefore both OH⁻ and CO₃²⁻ are present.

Alkalinity due to OH⁻ = 2P - M = 2 × 300 - 500 = 100 ppm

Alkalinity due to CO₃²⁻ = 2(M-P) = 2 (500 - 300) = 400 ppm

Solution 3

200 mL of water upto phenolphthalein end point \equiv 9.4 mL of N/50 HCl

$$\therefore 200 \times N_p = 9.4 \times N/50$$

$$N_p = \frac{9.4}{200} \times \frac{N}{50}$$

Strength of alkalinity upto phenolphthalein end point in terms of CaCO_3

Strength = $N_p \times$ Equivalent Weight of CaCO_3

$$\text{Strength} = \frac{9.4}{200} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{9.4}{200} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 47 \text{ mg/L}$$

P = 47 ppm.

As 200 mL of water upto methyl orange end point \equiv 9.4 + 21 = 30.4 mL of N/50 HCl

$$\therefore 200 \times N_M = 30.4 \times N/50$$

$$N_M = \frac{30.4}{200} \times \frac{1}{50}$$

Strength = $N_M \times$ Equivalent Weight of CaCO_3

$$\text{Strength} = \frac{30.4}{200} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{30.4}{200} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 152 \text{ mg/L}$$

M = 152 ppm

Since $P < \frac{1}{2} M$, hence CO_3^{2-} and HCO_3^- are present.

Alkalinity due to $\text{CO}_3^{2-} = 2P = 2 \times 47 = 94 \text{ ppm}$

Alkalinity due to $\text{HCO}_3^- = M - 2P = 152 - 94 = 58 \text{ ppm}$

\therefore the water sample contains

HCO_3^- alkalinity = 58 ppm

CO_3^{2-} alkalinity = 94 ppm



Homework questions

1. A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 mL of this water sample required 7.5 mL of N/50 HCl for neutralisation to phenolphthalein end point (P). At this stage a few drops of methyl orange were added. The acid required further was 14.5 mL of N/50 HCl for neutralisation to methyl orange end point(M). Calculate alkalinity of water as CaCO_3 due to the presence of carbonate and bicarbonate.
2. 100 mL of a raw water sample on titration with N/50 H_2SO_4 required 12.4 mL of the acid to phenolphthalein end point and 15.2 mL of the acid to methyl orange end point. Determine the type and extent of alkalinity present in the water sample.

Boiler Problems with Hard Water

- Boiler feed water should correspond with the following composition
 - (i) Its hardness should be below 0.2 ppm
 - (ii) Its caustic alkalinity (due to OH⁻) should lie in between 0.15 and 0.45 ppm
 - (iii) Its soda alkalinity (due to Na₂CO₃) should be 0.45–1 ppm

- Excess of impurities, if present, in boiler feed water generally cause the following problems
 - (i) Scale and sludge formation
 - (ii) Boiler corrosion
 - (iii) Caustic embrittlement
 - (iv) Priming and foaming

Problem -1 Scale and sludge formation

- Water evaporates continuously inside the boiler and the concentration of dissolved salts increases gradually. When the solution is saturated with respect to the salt concentration, the salts start precipitating out on the inner walls of the boiler.
- If the precipitate formed is soft, slimy and loose, it is called *sludge* and if the precipitate formed is hard and adhering on the inner walls of the boiler it is termed as *scale*.
- **SLUDGE** → It is soft, slimy and loose precipitate formed on the inner walls of the boiler.
- **Formation**
 - (a) Sludges are formed by substances which have greater solubility in hot water than in cold water like $MgSO_4$, $MgCl_2$, $MgCO_3$, $CaCl_2$ etc.
 - (b) They are formed at colder parts of the boiler and get collected at places where the flow rate is slow or at bends, plug opening, glass gauge connection, thereby causing even choking of the pipes.
 - (c) They are poor conductors of heat.
 - (d) They can be removed easily by scraping off with wire brush.

- **Prevention**

- (i) By using softened water.
- (ii) By frequently ‘**blow-down operation**’, that is, drawing off a portion of the concentrated water from the boiler and replacing it with fresh water.

- **Disadvantages of sludge formation**

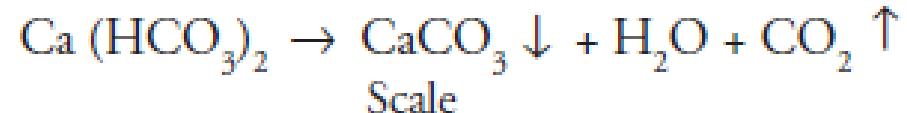
- (i) Being poor conductors of heat they tend to waste a portion of heat generated and thus decreases the efficiency of the boiler.
- (ii) Excessive sludge formation disturbs working of the boiler.
- (iii) When formed along with scale, they get entrapped in scale and both get deposited as scales.
- (iv) It settles in regions of poor water circulation such as pipe connection, plug opening, and glass gauge connection thereby choking the pipes.

- **SCALE** → They are deposits firmly sticking to the inner surface of the boiler which cannot be removed mechanically even with the help of hammer and chisel.

- **Formation of scale**

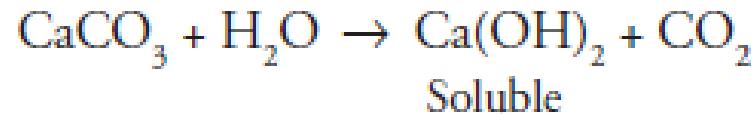
Scales are formed mainly due to four reasons:

- (i) **Decomposition of calcium bicarbonate**



→ CaCO_3 scale is soft and it is the main cause of scale formation in low-pressure boilers

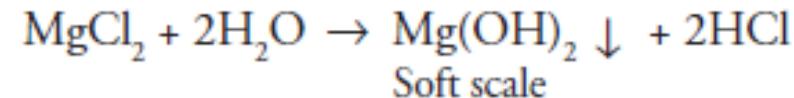
→ In higher pressure boilers CaCO_3 is soluble due to the formation of $\text{Ca}(\text{OH})_2$



- (ii) **Deposition of CaSO_4** → The solubility of CaSO_4 decreases as temperature increases.

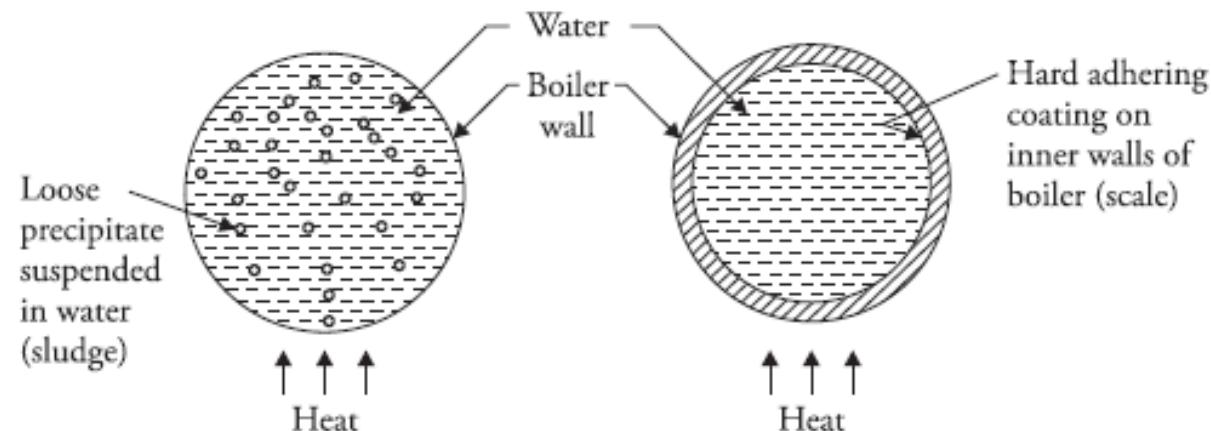
→ CaSO_4 is soluble in cold water and is completely insoluble in superheated water. Therefore, CaSO_4 gets precipitated as hard scale on the hot portion of the boiler.

(iii) **Hydrolysis of magnesium salts** At high temperature, dissolved magnesium salts undergo hydrolysis forming a soft scale of magnesium hydroxide.



(iv) **Formation of calcium and magnesium silicates**

- Very small quantities of SiO_2 present in hard water react with calcium and magnesium forming calcium silicate (CaSiO_3) and/or magnesium silicate (MgSiO_3).
- These are hard scales and are extremely difficult to remove.



• Disadvantages of scale formation

1. **Wastage of fuel** → Scales have poor thermal conductivity, therefore the rate of heat transfer from boiler to the water inside is greatly reduced. Hence extra heat is to be supplied to the boiler and this increases the fuel consumption.

→ Wastage of fuel depends upon the thickness of the scale. Greater the thickness of the scale larger is the wastage of fuel.

2. **Lowering boiler safety** → Due to scale formation which is poor conductor of heat, the boiler is to be over heated to provide steady supply of heat. Overheating makes the boiler material softer and weaker.

→ Therefore distortion of boiler tubes takes place and the boiler becomes unsafe to bear the pressure of the steam (in high-pressure boilers).

3. **Decrease in efficiency** → Deposition of scale in the valves and condensers of the boiler, chokes them partially. This results in decrease in efficiency.

4. **Danger of explosion** → Due to uneven expansion, the thick scales crack, as a result water comes in contact with the overheated inner walls of the boiler resulting in excessive steam formation which can lead to boiler explosion.

• Removal of scale

- (i) Loosely adhering scale can be removed either by **scraper** or wire brush or by blow-down operation.
- (ii) Brittle scales can be removed by thermal shocks (i.e heating the boiler and then suddenly cooling with cold water).
- (iii) Hard and adherent scales can be removed by dissolving in chemicals, for example, CaCO_3 scale can be dissolved by using 5–10% HCl. CaSO_4 scale can be removed by adding EDTA since the Ca-EDTA complex is highly soluble in water.

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APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 23



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Problem -2 Boiler Corrosion

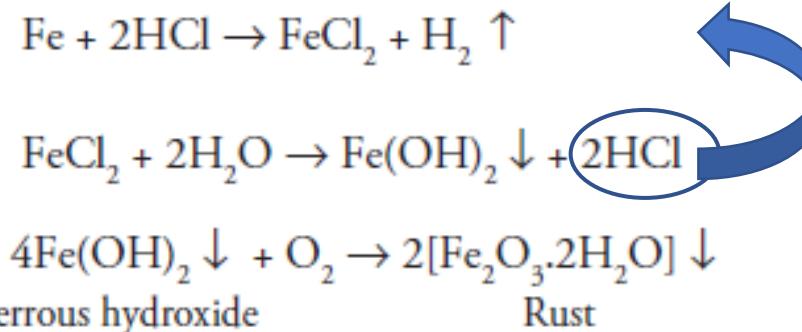
- The decay or disintegration of boiler material by chemical or electrochemical attack by its environment.
Boiler corrosion generally occurs due to three reasons.

1. Acid formation by dissolved salts
2. Dissolved carbon dioxide
3. Dissolved oxygen

(1) Acid formation by dissolved salts Magnesium chloride present in the boiler feed water undergoes hydrolysis producing hydrochloric acid

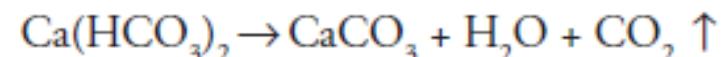


→ The acid thus liberated reacts with the boiler material (iron) to form ferrous hydroxide which is then converted to rust

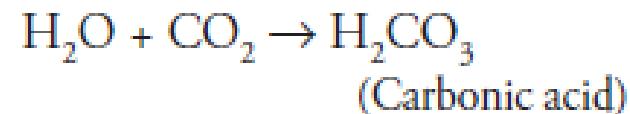


→ The HCl formed in step (2) again attacks boiler material.
→ A chain reaction is set up which causes extensive corrosion.

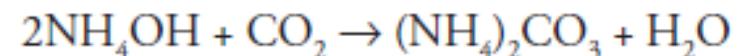
- **Prevention:** Boiler corrosion by acid formation can be prevented by adding calculated quantity of alkali which neutralises the acid thus formed.
- 2) **Dissolved carbon dioxide :** → The main source of CO_2 in boilers is by the decomposition of bicarbonates of calcium and magnesium.



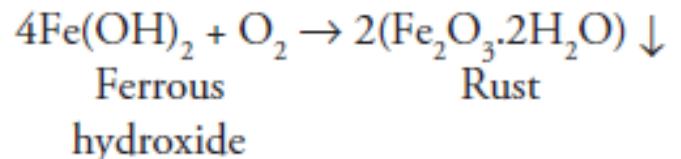
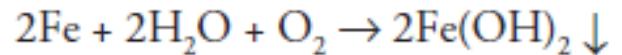
→ Carbon dioxide reacts with water forming carbonic acid



→ **Removal:** CO_2 can be removed either by adding ammonium hydroxide or by mechanical de aeration.



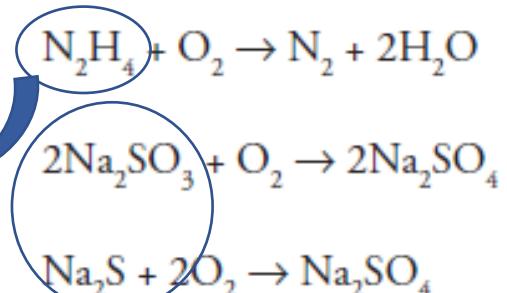
(3) Dissolved oxygen Water normally contains 8 ppm of oxygen dissolved at room temperature. At high temperature, the dissolved oxygen reacts with iron of the boiler to form ferric oxide (rust):



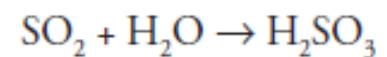
Removal

(i) **Addition of chemicals** Dissolved oxygen can be removed by adding a reducing agent like hydrazine, sodium sulphite or sodium sulphide.

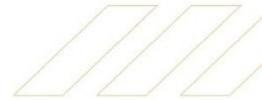
→ Aqueous hydrazine is an ideal chemical for removal of dissolved oxygen because it forms nitrogen which is harmless.



With Na_2SO_3 or Na_2S , Na_2SO_4 is formed, which decomposes at high temperature and produces SO_2 which reacts with water forming corrosive sulphurous acid.



(iii) Mechanical deaeration : The process consists of spraying water over preheated perforated plates stacked in tower. Removal of dissolved O₂ is ensured by applying high temperature and vacuum.



Problem 3 – Priming and Foaming

- **PRIMING**

- When water is heated rapidly inside the boiler or if there is a sudden increase in steam demand then water droplets are carried along the steam. This steam is termed as ‘wet steam’ and the formation of wet steam is called ‘priming’.

- **Causes**

1. Very high velocity of steam formation, when steam is formed at a great speed in the boiler, some droplets of water are carried along with steam.
2. Presence of considerable quantities of dissolved solids.
3. Sudden ebullition/boiling.
4. Faulty boiler design.

- **Minimisation of Priming**

1. Controlling rapid change in steam velocities.
2. Proper boiler design (by putting anti-priming plates or dash plates).
3. Maintaining low water level.
4. Use of water without suspended impurities.
5. By blowing off scales and sludges from time to time.

- **FOAMING →** Formation of small but persistent foam or bubbles which do not break easily.
- **Causes →** Presence of oil or alkalies in boiler feed water, which reduces the surface tension of water causing foaming.
- **Minimisation of foaming**
 1. By adding anti-foaming agents like castor oil or silicic acid.
 2. By adding compounds like sodium aluminates or aluminium sulphate, which removes oil from the boiler. These are hydrolysed to form Al(OH)_3 , which entraps oil drops.

Problem 4 – Caustic Embrittlement

- It is the phenomenon in which the boiler material becomes brittle due to the accumulation of excess alkali in the boiler.
- Particularly at those places which are under stress such as rivets, joints and bends with the result that the metal plates become brittle.
- When water is softened by lime – soda process, the excess sodium carbonate undergoes decomposition in high pressure boilers leading to the formation of NaOH.



- This NaOH makes the water alkaline. The alkaline water penetrates into the minute cracks and crevices between the rivets and joints by capillary action. Inside the cracks, the water evaporates and the concentration of NaOH increases on these sites due to poor circulation of water.

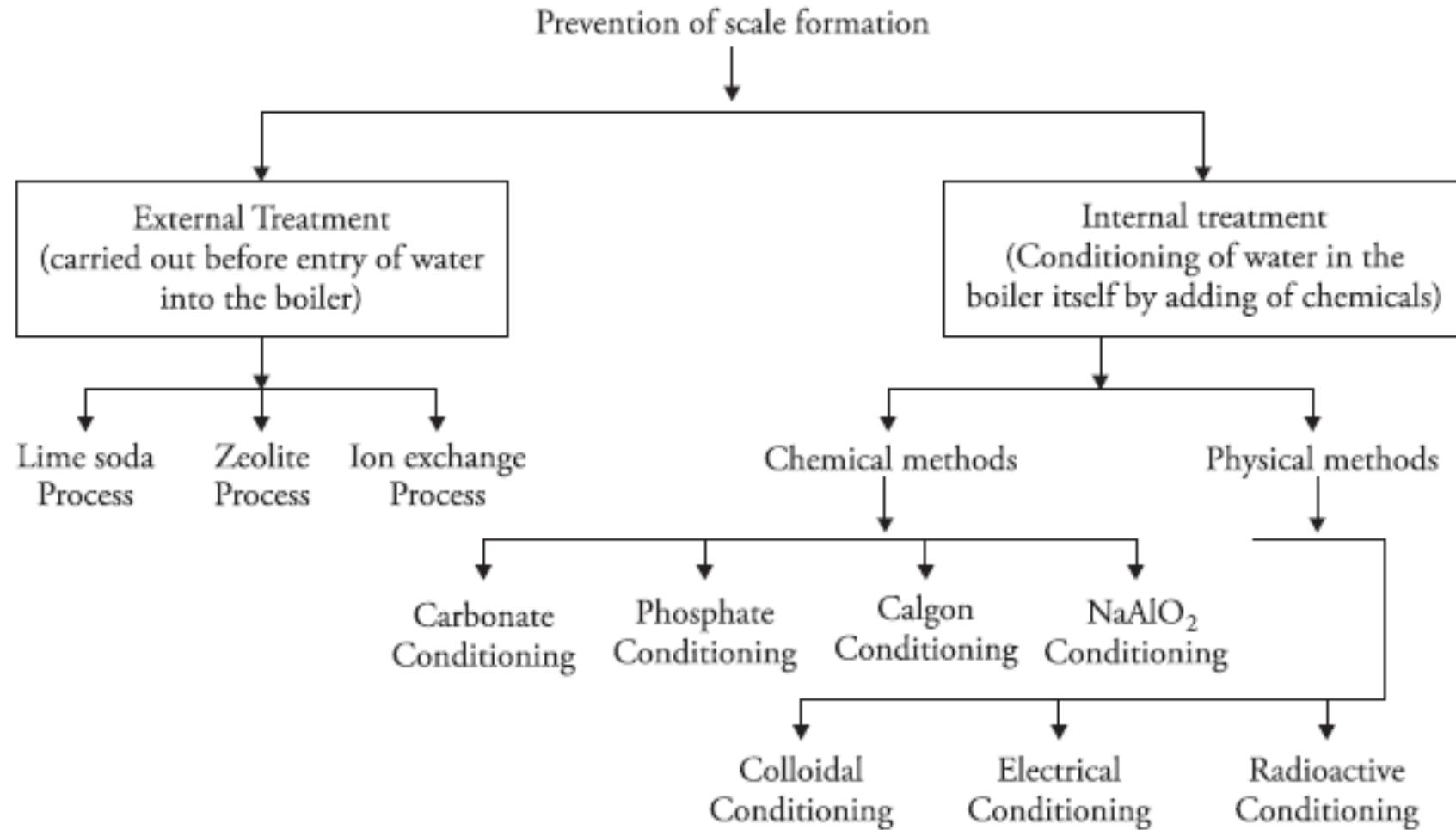


Prevention

1. By adding tannin or lignin to the boiler water. These block the minute cracks and prevent the infiltration of NaOH.
2. Caustic embrittlement can be prevented if Na_2SO_4 is added to the boiler water, because it is useful in blocking the hair cracks. $\text{Na}_2\text{SO}_4/\text{NaOH}$ should be used in the ratio 1:1, 2:1 and 3:1 for boilers working at pressure 10, 20 and above 20 atm, respectively.
3. By using sodium phosphate instead of sodium carbonate for softening water.
4. By adjusting the pH of boiler water between 8–9.
5. Use of excess Na_2CO_3 should be avoided in the lime-soda process.

Boiler water treatment

Prevention of scale formation



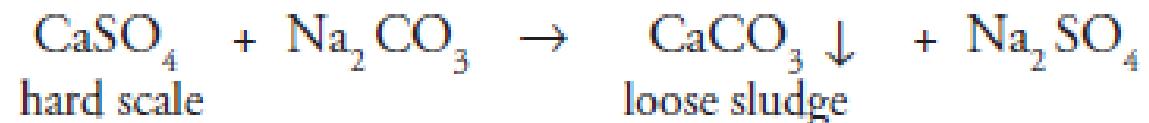
Internal Treatment

- **Sequestration or Conditioning.**

- It involves the treatment of boiler water inside the boiler by adding the suitable chemical which
 - a) Precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down operation **OR**
 - (b) convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

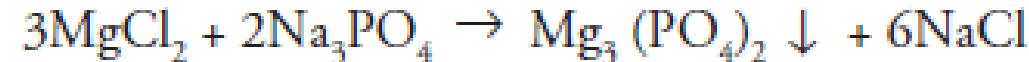
Chemical methods

1. **Carbonate conditioning :** → In low pressure boilers the scale formation can be avoided by adding sodium carbonate to boiler water, so that CaSO_4 is converted into calcium carbonate.
 → Consequently deposition of CaSO_4 as scale does not take place and calcium is precipitated as loose sludge of CaCO_3 , which can be removed by blow-down operation.



2. Phosphate conditioning → It is used equally in low- and high-pressure boilers. Magnesium chloride can be removed by adding appropriate sodium phosphate NaH_2PO_4 , Na_2HPO_4 , or Na_3PO_4 .

→ The phosphate reacts with calcium/magnesium salts forming loose sludge of calcium or magnesium phosphate which can be removed by blow-down operation



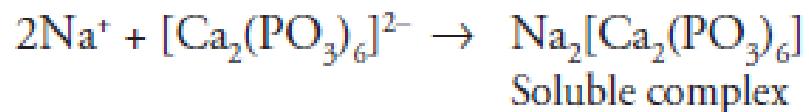
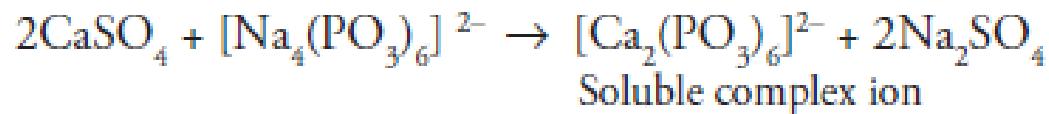
→ Imp. Requirement: The choice of phosphate salt depends upon the alkalinity of the boiler feed water (Eg. Calcium can be precipitated properly at a pH of 9.5)

3. Calgon conditioning → It involves adding sodium hexametaphosphate (also called calgon) to boiler water to prevent scale and sludge formation.

→ Calgon converts the scale forming impurities into highly soluble complexes.



Calgon



4. Colloidal conditioning → Colloids like tannin, agar-agar gel and kerosene are added to the boiler.

→ They form a coating around scale forming particles and thus prevent them from aggregating together to form scale. This method is effective in case of low-pressure boilers.

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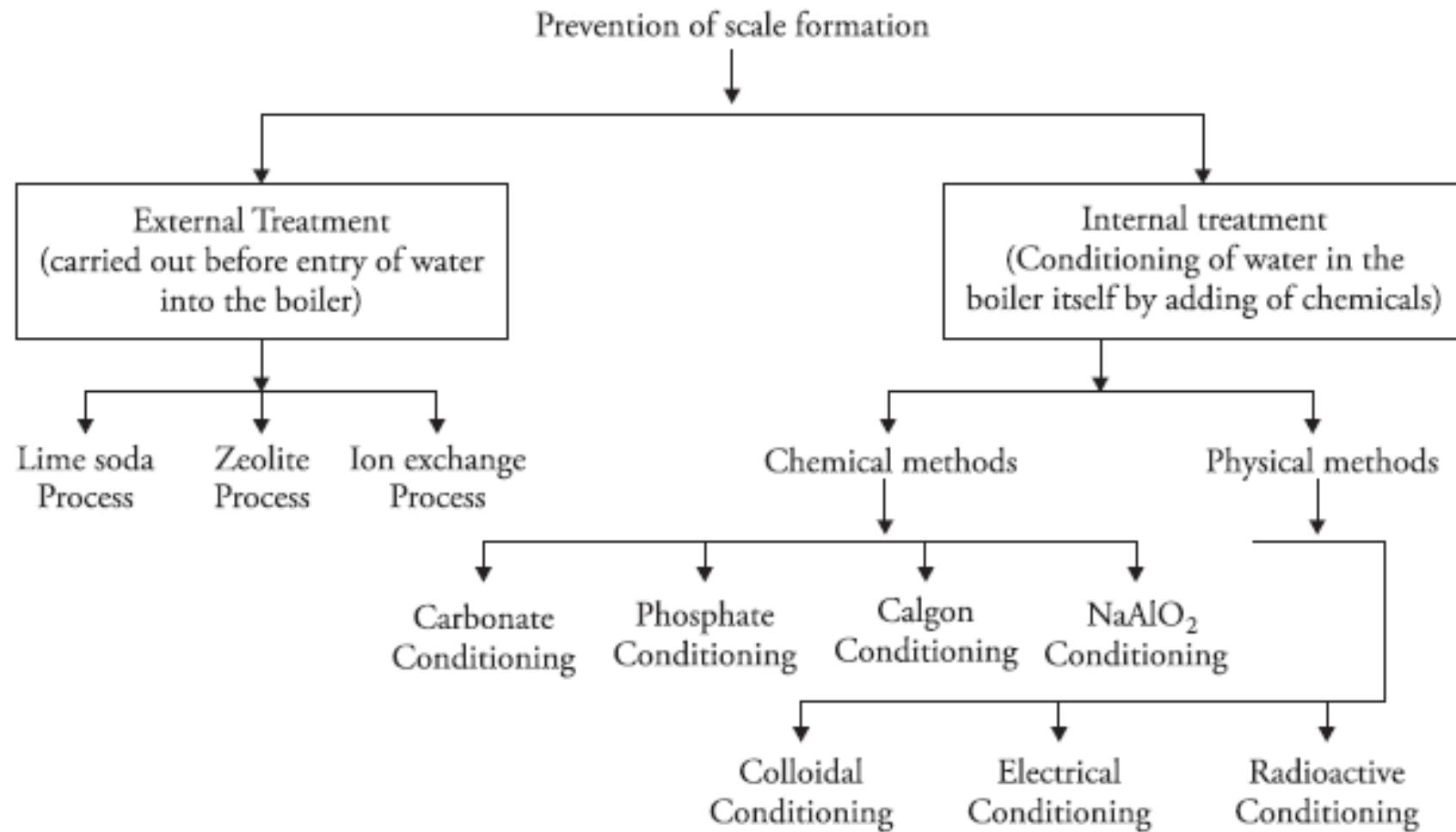
Lecture 24



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Prevention of scale formation



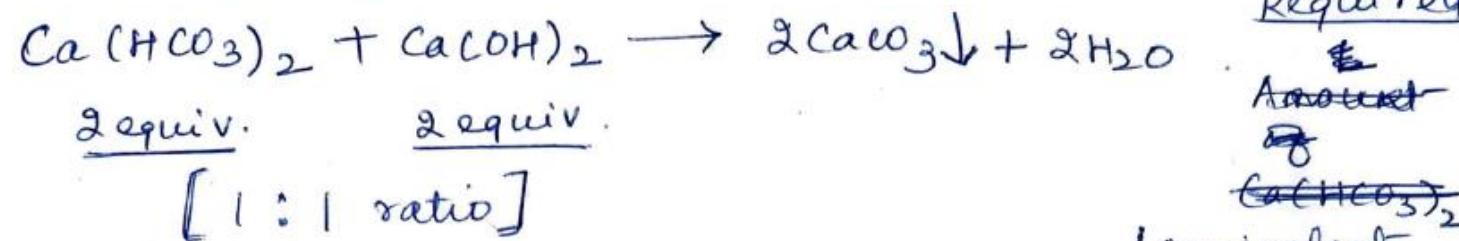
External Treatment – Lime Soda Process

- **PRINCIPLE:** To convert all the soluble hardness causing impurities into insoluble precipitates which can be removed by sedimentation and filtration.
- It involves the addition of calculated quantities of lime $\text{Ca}(\text{OH})_2$ and soda Na_2CO_3 . The hardness causing impurities react with these chemicals forming precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$. These precipitates are then filtered off to obtain soft water.
- The precipitates formed are very fine and do not settle easily causing difficulty in filtration. Therefore small amount of coagulants like alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$), ferrous sulphate (FeSO_4) or sodium aluminate (NaAlO_2) are added. They help in the quick setting of precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$ by the process of loading.
- The coagulants hydrolyse to form $\text{Al}(\text{OH})_3$ which entraps the fine precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$. The precipitates become heavy and settle fast. This process is called loading

Calculation of lime/soda requirement

→ I Impurities which require only lime.

1) Calcium temporary hardness. (CaCO_3 , $\text{Ca}(\text{HCO}_3)_2$)

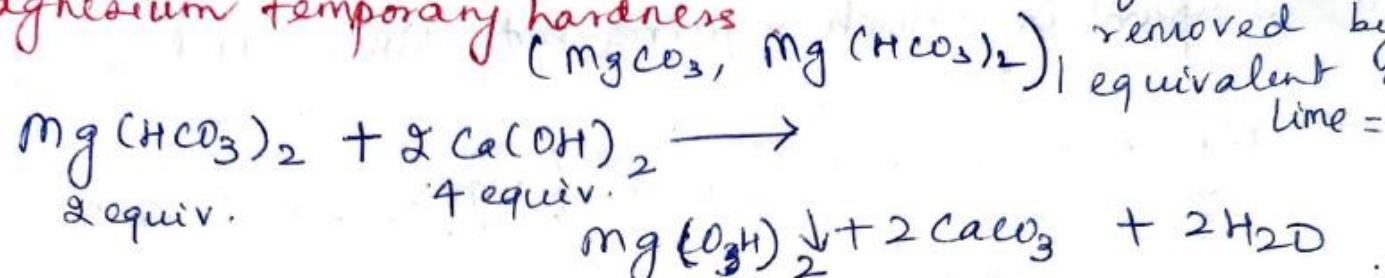


Lime Required

~~1 equiv.~~
~~2 equiv.~~
 ~~$\text{Ca}(\text{HCO}_3)_2$~~

1 equivalent
of $\text{Ca}(\text{HCO}_3)_2$ is
removed by
equivalent of
lime = L

2) Magnesium temporary hardness



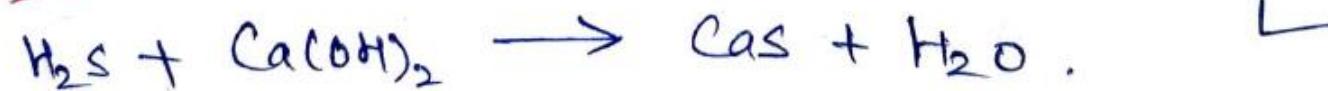
Removal of

1 equivalent of
 $\text{Mg}(\text{HCO}_3)_2$ requires 2 equiv.
∴ lime = 2L

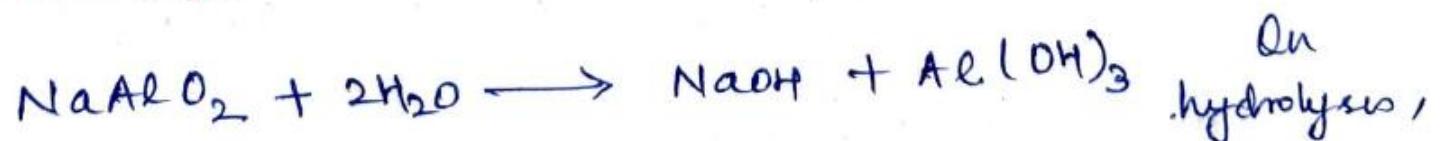
3) CO_2 .



4) H_2S



5) NaAlO_2 .



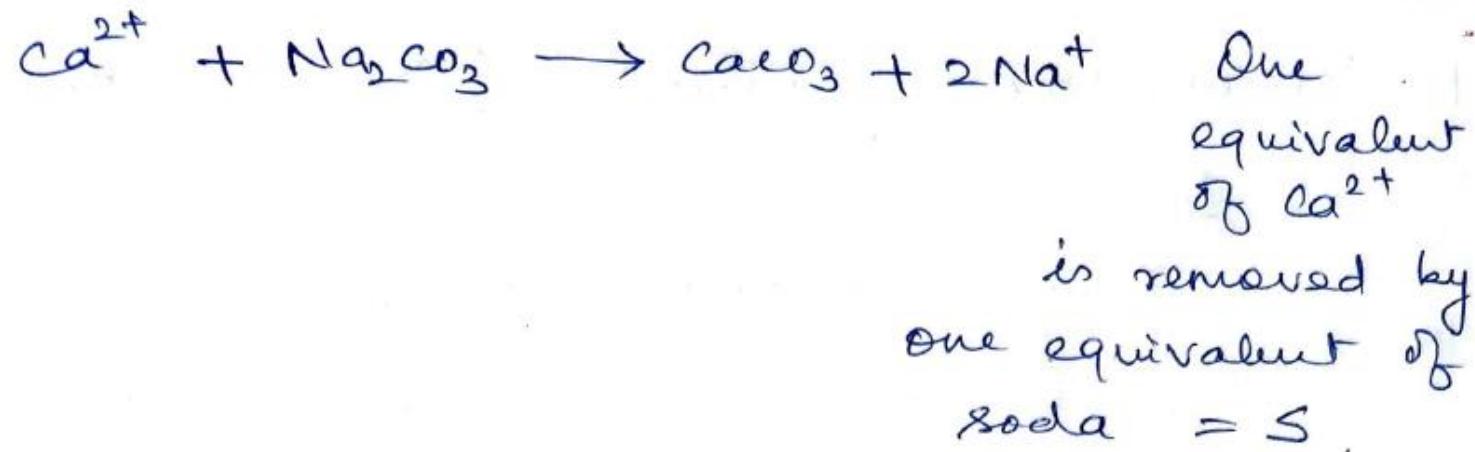
NaOH is

produced, which

considered ~~as~~ as 1
equivalent of $\text{Ca}(\text{OH})_2 \Rightarrow -L$

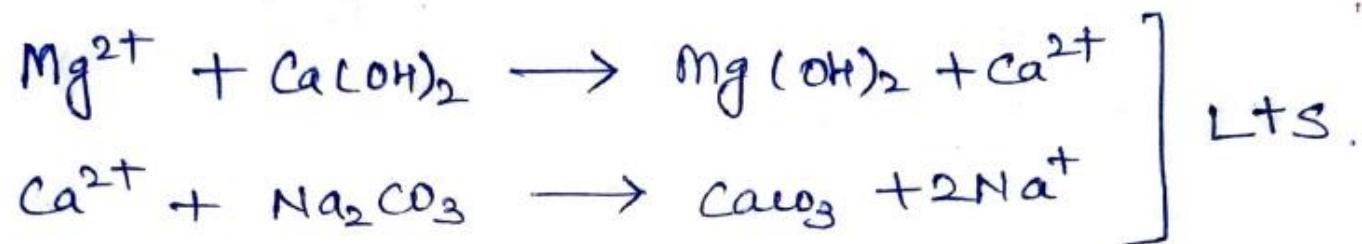
II Impurities which require only soda.

1. Ca permanent hardness ($\text{CaCl}_2, \text{CaSO}_4, \text{Ca}(\text{NO}_3)_2$)

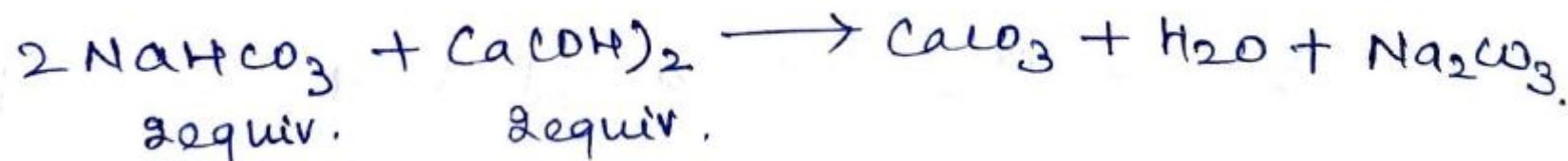


III Impurities which require both lime and soda.

1. Mg permanent hardness ($\text{MgCl}_2, \text{MgSO}_4, \text{Mg}(\text{NO}_3)_2$)

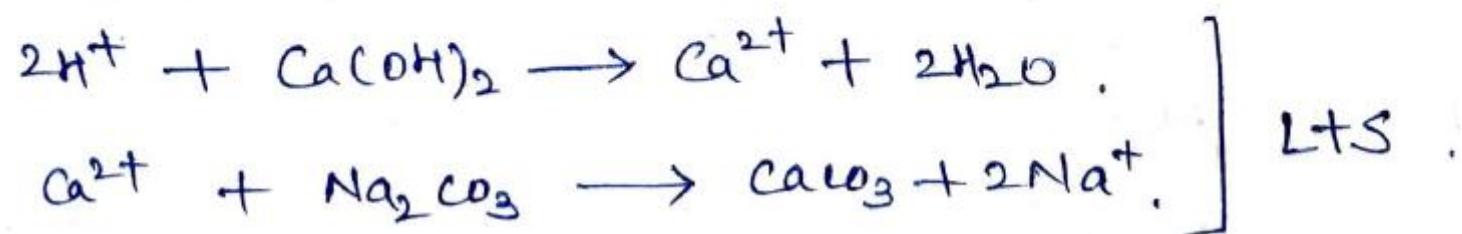


2. HCO_3^- (e.g. NaHCO_3) .

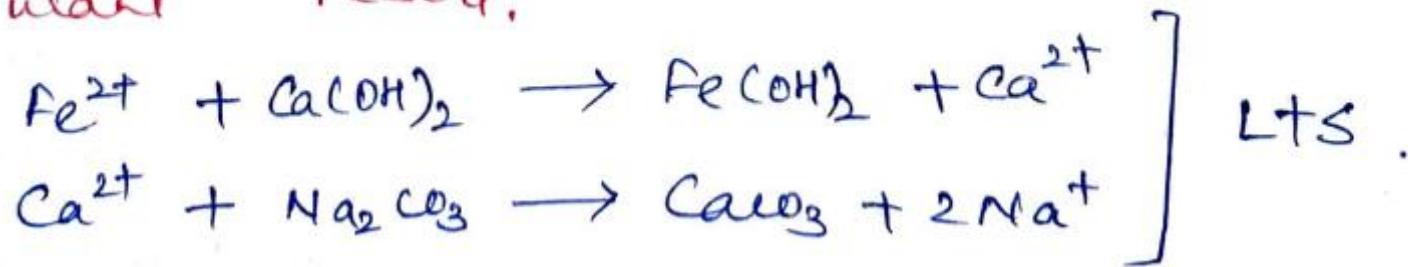


L-S

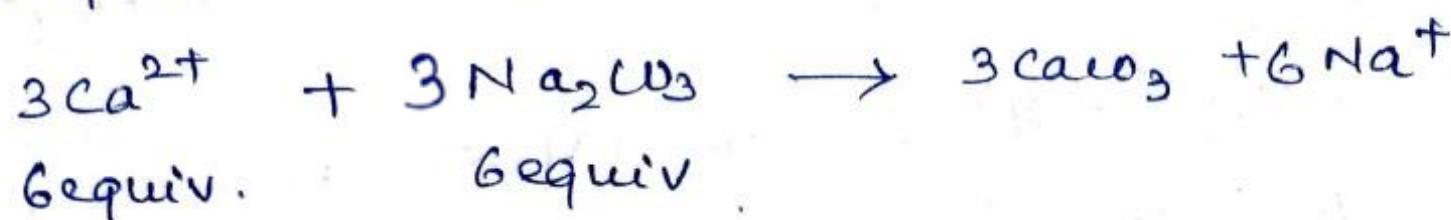
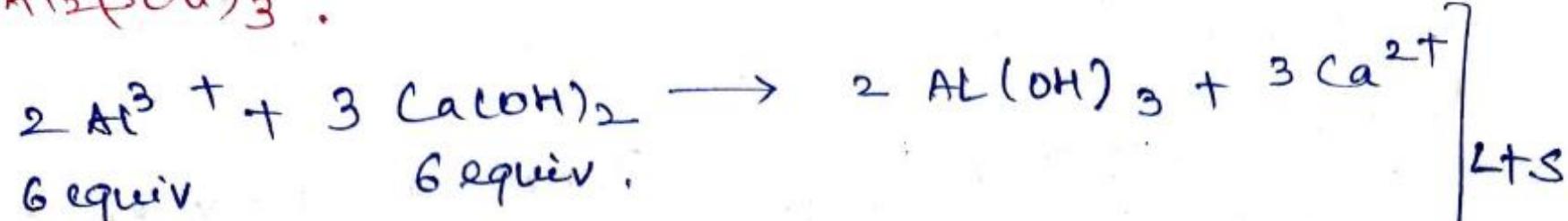
3. Free acids :



4. Coagulant - FeSO_4 .



5. $\text{Al}_2(\text{SO}_4)_3$.



LTS



Lime Requirement

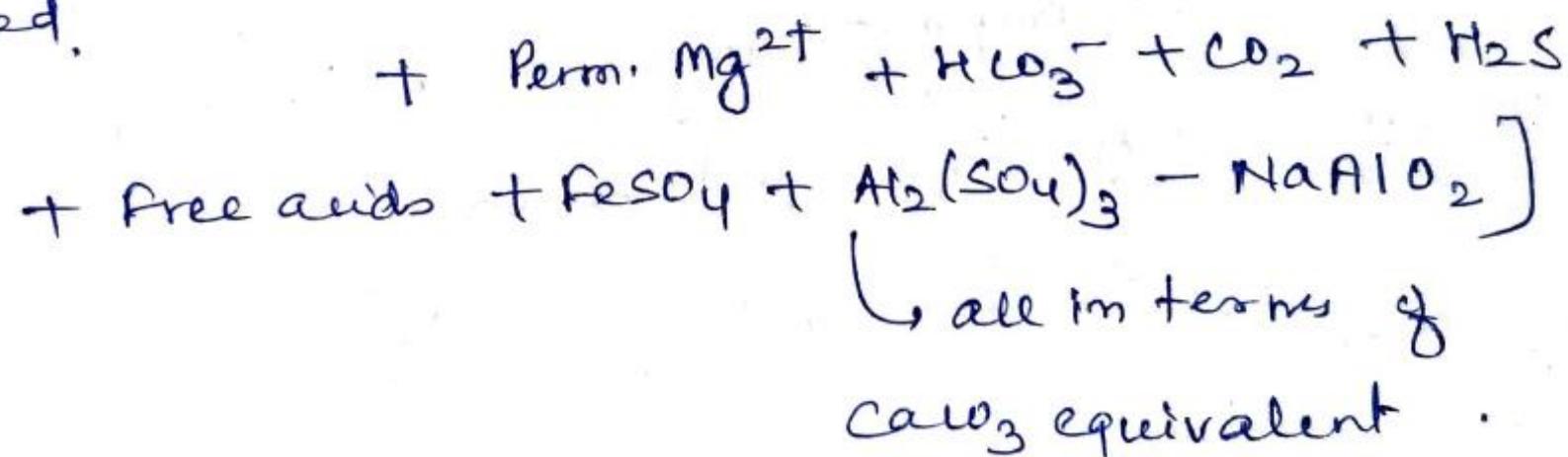
100 parts by mass of CaCO_3 equivalence \rightarrow 74 parts by mass of Ca(OH)_2 .

$$1 \text{ part by mass} = \frac{74}{100} \text{ by mass of } \text{Ca(OH)}_2$$

e.g. $x \text{ g/L Ca(HCO}_3)_2$ in terms of CaCO_3 equivalent lime = $\frac{74}{100} \times x$

$$\text{Total lime} = \frac{74}{100} [\text{Temp. } \text{Ca}^{2+} + 2 \times \text{Temp. } \text{Mg}^{2+}]$$

required.



Soda requirement

100 parts of $\text{CaCO}_3 \rightarrow$ 106 parts of Na_2CO_3 .

$$\text{Total soda required} = \frac{106}{100} [\text{Perm. } \text{Ca}^{2+} + \text{Perm. } \text{Mg}^{2+} - \text{HCO}_3^- \\ + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3] \\ \hookrightarrow \text{all in } \text{CaCO}_3 \text{ equivalent}$$

If V litres of water is present and lime & soda are impure.

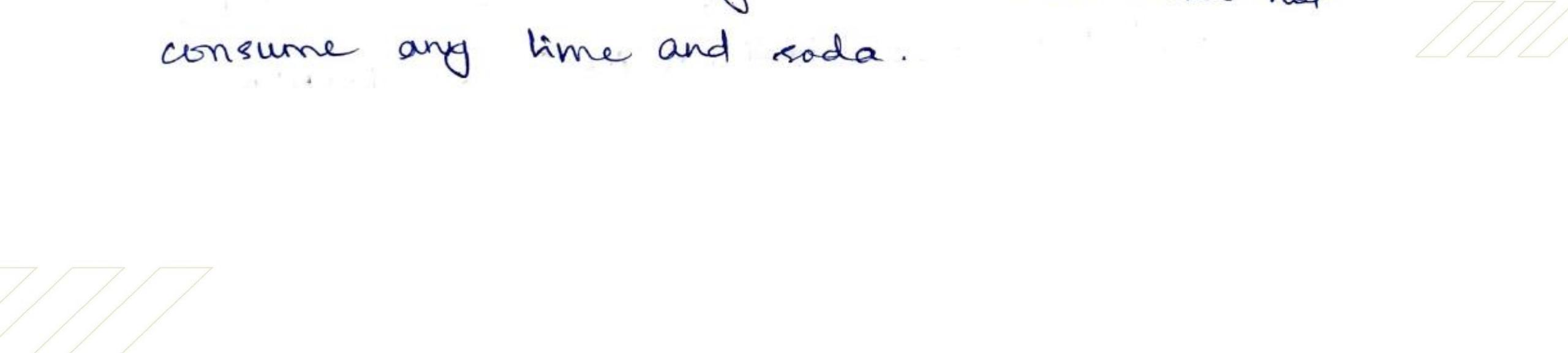
$$\Rightarrow \text{lime required} = \frac{74}{100} [\text{Temp. } \text{Ca}^{2+} + 2 \times \text{Temp. } \text{Mg}^{2+}$$

$$+ \text{Perm. } \text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}_2\text{S} + \text{Free acids} + \\ \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \text{NaAlO}_2] \times V \times \frac{100}{\% \text{ Purity}}$$

$$\Rightarrow \text{soda required} = \frac{106}{100} [\text{Perm. } \text{Ca}^{2+} + \text{Perm. } \text{Mg}^{2+} \\ - \text{HCO}_3^- + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3] \times V \times \frac{100}{\% \text{ Purity}}$$

1116

Note: KCl , SiO_2 , Fe_2O_3 , Na_2SO_4
do not impart any hardness and does not
consume any lime and soda.



THANK YOU



APPLIED CHEMISTRY

Paper Code: BS103/ BS104
Lecture 25



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Numericals on soda-lime process

1. Calculate the amount of lime required for softening 50,000 liters of hard water containing;

$\text{CaCO}_3 = 25 \text{ ppm}$; $\text{MgCO}_3 = 144 \text{ ppm}$; $\text{CaCl}_2 = 111 \text{ ppm}$; $\text{MgCl}_2 = 95 \text{ ppm}$; $\text{Na}_2\text{SO}_4 = 15 \text{ ppm}$; $\text{Fe}_2\text{O}_3 = 25 \text{ ppm}$.

2. A water sample contains the following impurities

$\text{Ca}^{2+} = 20 \text{ ppm}$; $\text{Mg}^{2+} = 18 \text{ ppm}$; $\text{HCO}_3^- = 183 \text{ ppm}$; $\text{SO}_4^{2-} = 24 \text{ ppm}$. Calculate the amount of lime and soda needed for softening.

3. A sample of water on analysis was found to contain the following in mg/L

$\text{CaSO}_4 = 0.45$; $\text{MgCO}_3 = 0.50$; $\text{CaCO}_3 = 2.50$; $\text{MgSO}_4 = 0.85$; $\text{MgCl}_2 = 0.80$; $\text{SiO}_2 = 2.90$; $\text{NaCl} = 2.80$.

Calculate the amount of lime and soda required to soften 25,000 liters of water per day for a year if the purity of lime and soda is 90%.

4. Calculate the amount of lime and soda required for softening 30,000 liters of hard water,

which is analysed as follows:

Analysis of raw water

$\text{Ca}^{2+} = 400 \text{ ppm}$; $\text{Mg}^{2+} = 288 \text{ ppm}$; $\text{HCO}_3^- = 1586 \text{ ppm}$; dissolved $\text{CO}_2 = 88 \text{ ppm}$; Ferrous sulphate = 139 ppm (commercial grade)

Analysis of treated water

$\text{CO}_3^{2-} = 30 \text{ ppm}$; $\text{OH}^- = 34 \text{ ppm}$

Purity of lime is 94% and that of soda is 86%.

SOLUTION 1

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
CaCO_3	25 ppm	$\frac{25 \times 100 / 2}{100 / 2} = 25$ ppm	L
MgCO_3	144 ppm	$\frac{144 \times 100 / 2}{84 / 2} = 171.43$ ppm	2L
CaCl_2	111 ppm	$\frac{111 \times 100 / 2}{111 / 2} = 100$ ppm	S
MgCl_2	95 ppm	$\frac{95 \times 100 / 2}{95 / 2} = 100$ ppm	L + S
Na_2SO_4	15 ppm	Does not impart hardness	
Fe_2O_3	25 ppm	Does not impart hardness	

Lime required for softening 50,000 liters of hard water

$$= \frac{74}{100} [\text{CaCO}_3 + 2 \times \text{MgCO}_3 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water.}$$

$$= \frac{74}{100} [25 + 2 \times 171.43 + 100] \text{ mg/L} \times 50,000 \text{ L}$$

$$= \frac{74}{100} [467.86] \text{ mg/L} \times 50,000 \text{ L} = 1,73,10,820 \text{ mg} = 17.311 \text{ kg} \quad (1 \text{ kg} = 10^6 \text{ mg})$$

Lime Required = 17.311 kg

SOLUTION 2

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
Ca^{2+}	20 ppm	$\frac{20 \times 100 / 2}{40 / 2} = 50 \text{ mg/L}$	S
Mg^{2+}	18 ppm	$\frac{18 \times 100 / 2}{24 / 2} = 75 \text{ mg/L}$	L+S
HCO_3^-	183 ppm	$\frac{183 \times 100 / 2}{61 / 1} = 150 \text{ mg/L}$	L-S
SO_4^{2-}	24 ppm	-	-

As the volume of water is not given in the question hence calculations may be done for one liter water.

Lime required

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{74}{100} [75 + 150] \times 1$$

$$= \frac{74}{100} [225] \times 1 = 166.5 \text{ mg}$$

$$\text{Lime} = 166.5 \text{ mg}$$

Soda requirement

$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{106}{100} [50 + 75 - 150] \times 1$$

$$= \frac{106}{100} [-25] = -26.50 \text{ mg}$$

The answer is negative, which shows that soda formed from bicarbonate is more than the amount of soda required for the removal of various impurities. Hence, the amount of soda to be added will be zero. **Soda = Nil**

SOLUTION 3

Conversion into equivalents of CaCO_3

Constituent	Amount(mg/L)	Equivalents of CaCO_3	Requirement L/S
CaSO_4	0.45	$\frac{0.45 \times 100 / 2}{136 / 2} = 0.3309$	S
MgCO_3	0.50	$\frac{0.50 \times 100 / 2}{84 / 2} = 0.595$	2L
CaCO_3	2.50	$\frac{2.50 \times 100 / 2}{100 / 2} = 2.5$	L
MgSO_4	0.85	$\frac{0.85 \times 100 / 2}{120 / 2} = 0.708$	L + S
MgCl_2	0.80	$\frac{0.80 \times 100 / 2}{95 / 2} = 0.842$	L + S
SiO_2	2.90	Does not impart hardness and does not consume lime and soda	
NaCl	2.80	Does not impart hardness and does not consume lime and soda	

Volume of water = 25,000 liters a day for a year.

∴ Total volume of water to be softened = 25000×365 days

Purity of lime and soda = 90%

Lime required

$$= \frac{74}{100} [2 \times \text{MgCO}_3 + \text{CaCO}_3 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{74}{100} [2 \times 0.595 + 2.5 + 0.708 + 0.842] \times 25000 \times 365$$

$$= 35383100 \text{ mg}$$

Hence lime actually added = $35383100 \times \frac{100}{90} \text{ mg} = 39314555.56 \text{ mg} = 39.31 \text{ kg}$

Lime added = 39.31 kg

Similarly soda can also be calculated using the same analogy

Soda Requirement

$$= \frac{106}{100} [\text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [0.3309 + 0.708 + 0.842] \times 25000 \times 365 \times \frac{100}{90}$$

$$= \frac{106}{100} [1.8809] \times 25000 \times 365 \times \frac{100}{90} = 20214450.28 \text{ mg} = 20.214 \text{ kg.}$$

Conversion into equivalents of CaCO_3

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
Analysis of raw water			
Ca^{2+}	400 ppm	$\frac{400 \times 100 / 2}{40 / 2} = 1000$ ppm	S
Mg^{2+}	288 ppm	$\frac{288 \times 100 / 2}{24 / 2} = 1200$ ppm	L + S
CO_3^{2-}	88 ppm	$\frac{88 \times 100 / 2}{44 / 2} = 200$ ppm	L
HCO_3^-	1586 ppm	$\frac{1586 \times 100 / 2}{61 / 1} = 1300$ ppm	L - S
Ferrous sulphate (commercial grade)	139 ppm	$\frac{139 \times 100 / 2}{278 / 2} = 50$ ppm	L + S
Analysis of treated water			
OH^-	34 ppm	$\frac{34 \times 100 / 2}{17 / 1} = 100$ ppm	L + S
CO_3^{2-}	30 ppm	$\frac{30 \times 100 / 2}{60 / 2} = 50$ ppm	S

Volume of water = 30,000 liters

Purity of lime = 94%; purity of soda = 86%

Lime required

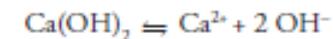
$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{74}{100} [1200 + 1300 + 200 + 50] \times 30,000 \times \frac{100}{94}$$

$$= \frac{74}{100} [2750] \times 30,000 \times \frac{100}{94} = 64946809 \text{ mg} = 64.95 \text{ kg}$$

$$\text{Lime} = 64.95 \text{ kg}$$

The excess lime added for treatment of water gives OH^- ions in treated water



∴ Excess lime added

$$= \frac{74}{100} [\text{OH}^- \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{74}{100} [100] \times 30,000 \times \frac{100}{94} = 2361702.1 \text{ mg} = 2.362 \text{ kg}$$

$$\text{Total lime} = 64.95 + 2.362 = 67.312 \text{ kg}$$



Soda Requirement

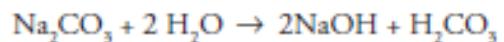
$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- + \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [1000 + 1200 - 1300 + 50] \times 30,000 \times \frac{100}{86}$$

$$= \frac{106}{100} [950] \times 30,000 \times \frac{100}{86} = 35127907 \text{ mg} = 35.128 \text{ kg}$$

Soda = 35.128 kg

The excess soda added during softening process contributes to both CO_3^{2-} and OH^- in treated water.



Excess soda added

$$= \frac{106}{100} [\text{OH}^- + \text{CO}_3^{2-} \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [100 + 50] \times 30,000 \times \frac{100}{86} = \frac{106}{100} [150] \times 30,000 \times \frac{100}{86}$$

$$5546511.6 \text{ mg} = 5.546 \text{ kg}$$

$$\text{Total soda} = 35.128 + 5.546 = 40.674 \text{ kg}$$

Homework questions

1. A water works has to supply 1 m³/s of water. Raw water contains:

$Mg(HCO_3)_2 = 219$ ppm; $Mg^{2+} = 36$ ppm; $HCO_3^- = 18.3$ ppm; $H^+ = 1.5$ ppm. Calculate the cost of treating water per day, if lime (90% pure) and soda (95% pure) cost Rs. 500 per ton and Rs. 7000 per ton, respectively.

(Total cost = 1, 60, 860)

2. Calculate the amount of lime (90% pure) and soda (98% pure) required for the treatment of one million liters of water containing

$Ca(HCO_3)_2 = 8.1$ ppm; $CaCl_2 = 33.3$ ppm; $HCO_3^- = 91.5$ ppm; $MgCl_2 = 38$ ppm; $Mg(HCO_3)_2 = 14.6$ ppm. The coagulant $Al_2(SO_4)_3$ was added at a rate of 17.1 mg/L of water. (Lime = 127.44 kg; Soda = 10.82 kg)

3. Calculate the amount of lime and soda needed for softening 75,000 liters of hard water. The results of analysis of raw water and treated water are as follows:

Analysis of raw water

$HCO_3^- = 212$ mg/L; $H^+ = 3$ mg/L; $Ca^{2+} = 55.5$ mg/L; $Mg^{2+} = 42$ mg/L; $CO_2 = 66$ mg/L;

Analysis of treated water

$CO_3^{2-} = 90$ mg/L; $OH^- = 45$ mg/L.

(Total Lime = 42.67 kg; Total Soda = 45.5 kg)

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APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 7



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Zeolite or Permutit Process

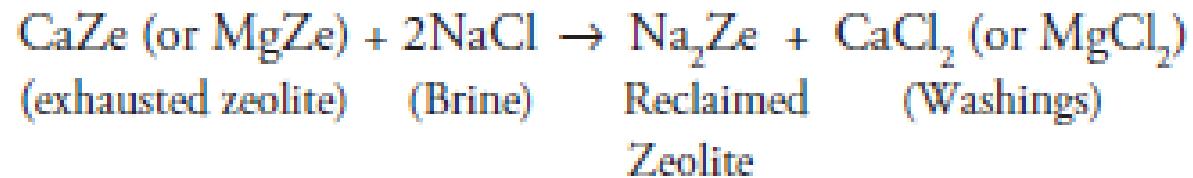
- They occur naturally as hydrated alumino silicate minerals like $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x = 2-10$ and y is $2-6$. They are capable of exchanging reversibly sodium ions for hardness producing ions in water.
- Zeolites are of two types**
 - Natural Zeolites:** Non porous, amorphous and durable, for example, 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 Zeolites:** Porous with gel-like structure. They are prepared by heating sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2).
- Process for hardwater treatment:**
 - Hard water is percolated at a specified rate through a bed of zeolite stacked in a cylindrical unit
 - The hardness causing elements (Ca^{2+} , Mg^{2+}) are retained by zeolite as CaZe and MgZe , while the outgoing water contains sodium salts.



- After some time, all the sodium ions in zeolite are replaced by Ca and Mg ions giving CaZe/ MgZe. Such a zeolite bed is unable to soften water further and is said to be exhausted.
 - It has to be regenerated to enable it to soften water again.

- Regeneration

- When the zeolite bed is exhausted the supply of hard water is stopped and it is regenerated by treating with a concentrated brine (10% NaCl) solution.



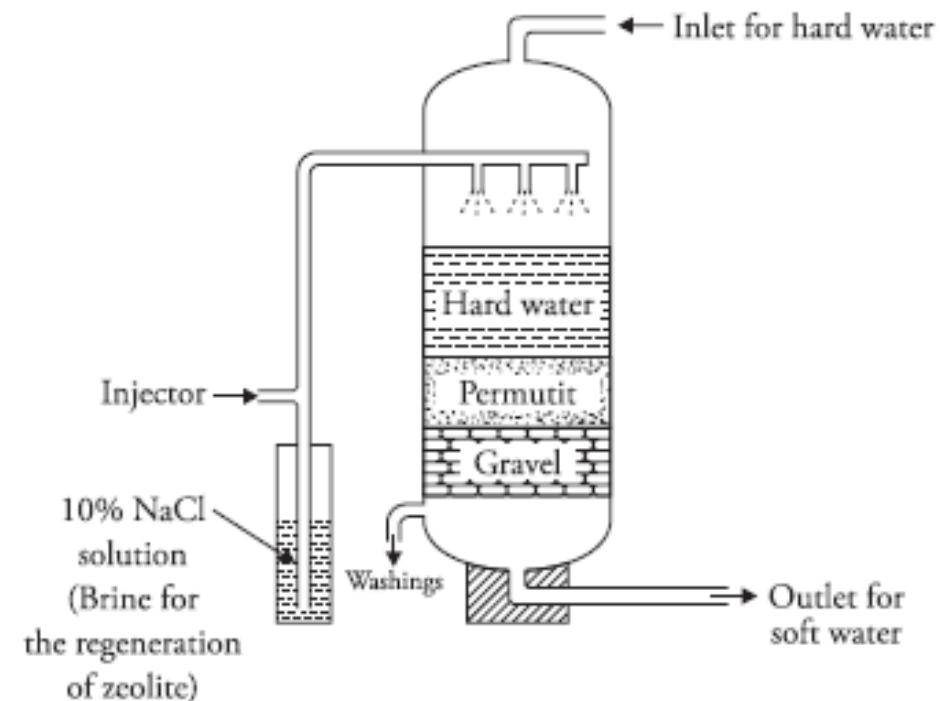
- The washings (containing CaCl_2 , MgCl_2) are led to drain and the regenerated zeolite bed is used again for softening.
 - NaNO_3 , KCl , KNO_3 , etc. can also be used for regeneration instead of NaCl , but NaCl is mostly used because of its low cost and the products of regeneration process (CaCl_2 or MgCl_2) are highly soluble and can be easily rinsed out of the zeolite bed

• Limitations and Disadvantages of Zeolite Process

1. If the water supplied is turbid, the turbidity/suspended matter is to be removed (by coagulation, filtration, etc.) before the water is admitted to the zeolite bed otherwise turbidity will clog the pores of zeolite bed making it inactive.
2. If the water contains ions like Mn^{2+} and Fe^{2+} , they must be removed first because these ions react with zeolite bed to give manganese and iron zeolites which cannot be easily regenerated.
3. Minerals acids, if present in water, destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding water into the zeolite bed.
4. This method does not remove anions. The bicarbonates present in hard water get converted into $NaHCO_3$ which goes into soft water effluent. If this water is used in boiler, $NaHCO_3$ dissociates as $NaHCO_3 \rightarrow NaOH + CO_2$. $NaOH$ leads to caustic embrittlement and CO_2 makes the water acidic and corrosive.
5. The treated water contains more sodium salts than in lime-soda process.
6. Moreover high cost of the plant and material also acts as limiting factor.

- **Advantages of Zeolite Process**

1. Hardness is removed almost completely and the residual hardness is about 10 ppm.
2. The equipment is compact and occupies less space.
3. It is a clean and rapid process. Sludge is not formed as the impurities are not precipitated.
4. It requires less skill for maintenance as well as operation



<i>S.No.</i>	<i>Property</i>	<i>Lime-Soda Process</i>	<i>Zeolite Process</i>
1.	Size of plant	Bulky and Large	Compact and small.
2.	Supervision	Requires careful and skilled supervision because lime and soda have to be added in calculated quantities.	Automatic and easy to operate.
3.	Pretreatment	Turbid waters can be treated.	Highly turbid waters are difficult to treat because the suspended impurities clog the pores of zeolite.
4.	Sludge trouble	Large quantity of sludge is formed which poses problems of disposal.	No sludge is formed and therefore no problem of sludge disposal.
5.	Post treatment if needed.	Coagulation, settling filtration and, removal of precipitates involved.	No such post treatment is required.
6.	Dissolved solids	Treated water contains more amount of dissolved sodium salts.	Treated water contain lesser amount of sodium salts.
7.	Results obtained	This can produce waters of hardness not less than about 50 ppm. Therefore, useful for public supplies only.	Water of zero hardness can be obtained. Therefore, useful for industrial supplies also.

8.	Removal of colour due to iron and manganese.	Can remove the colour due to iron and manganese, but only to a very small extent.	Can remove the colour due to iron and manganese, although very costly for treating such waters, because the exhausted Mn and Fe zeolites cannot be regenerated.
9.	The pH of the treated water.	Increases the pH value of water, which reduces the corrosion of distribution pipes.	The pH value of the water is not affected.
10.	Acidic Water	Acidic water can also be treated.	Acidic water cannot be treated since acidic water attack zeolite.
11.	Care needed in handling materials.	Careful handling is required because the materials i.e. (lime and soda) are corrosive.	Brine solution is required to be handled, which does not require much care.
12.	Economy	Process is economical and can be easily combined with usual water treatment methods at slight extra cost.	Process is costlier.

- Calculation of water hardness

$$\text{Hardness (H)} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

V_1 = Total volume of water softened

V_2 = Total volume of NaCl solution used for regeneration

m = Amount of NaCl in g/L present in V_2

Numericals

1. A zeolite softener was used to remove the hardness of 95,000 liters of hard water completely. The softener required 475 liters of NaCl solution containing 18 g/liter of NaCl for regeneration. Calculate the hardness of hard water in ppm.
2. An exhausted zeolite softener was regenerated by 325 liters of NaCl solution containing 60 g/liter of NaCl. How many liters of hard water of hardness 250 mg/L can be softened by the zeolite softener.

Solution 1

$$\text{Hardness (H)} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

V_1 = Total volume of water softened = 95,000 liters

V_2 = Total volume of NaCl solution used for regeneration = 475 liters

m = Amount of NaCl present in V_2 = 18 g

$$\text{Hardness (H)} = \frac{50 \times 18 \times 475 \times 10^3}{58.5 \times 95,000} = 76.92 \text{ ppm}$$

Hardness (H) = 76.92 ppm

Solution 2

V_1 = Total volume of water softened = ?

$$V_1 = \frac{50 \times 60 \times 325 \times 10^3}{58.5 \times 250} = 66666.67 \text{ liters}$$

V_2 = Total volume of NaCl solution used for regeneration = 325 liters

Total volume of hard water softened = 66666.67 liters.

m = Amount of NaCl present in V_2 = 60 g/liter

Hardness (H) = 250 mg/liter = 250 ppm

Formula

$$\text{Hardness (H)} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

$$250 = \frac{50 \times 60 \times 325 \times 10^3}{58.5 \times V_1}$$

Homework questions

1. A zeolite softener was completely exhausted after softening 145,000 liters of hard water. To regenerate the zeolite softener 540 liters of NaCl solution containing 110 g/liter of NaCl is required. Calculate the hardness of one liter water sample in ppm.

(Ans = 350.13 ppm)

2. 200 liters of NaCl solution containing 85 g/liter of NaCl was required to regenerate a completely exhausted zeolite softener. How many liters of hard water of hardness 600 ppm can be softened by the softener.

(Ans = 24216.5 liters)

THANK YOU



APPLIED CHEMISTRY

Paper Code: BS103/ BS104
Lecture 27+28



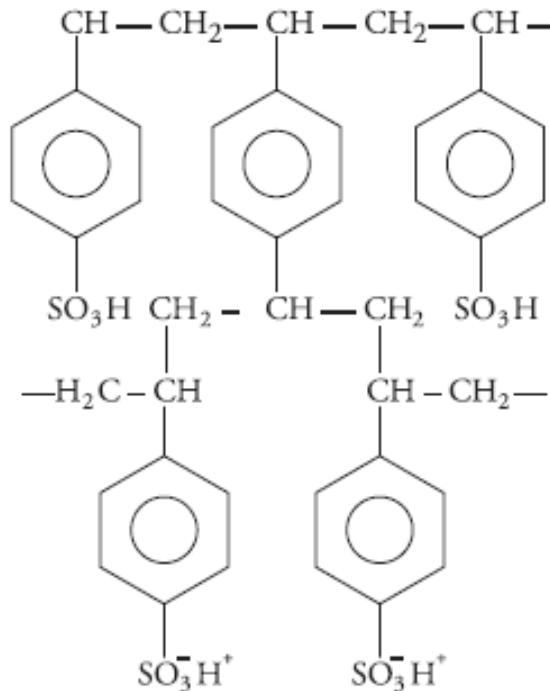
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- Ion exchange process is defined as the reversible exchange of ions in the structure of an ion exchanger to ions in solution that is brought in contact with it
- The **resins** used for the purpose are called **ion exchange resins**. They are porous, insoluble, cross linked, long chain organic polymers capable of exchanging ions.
- **Types of ion exchange resins:**

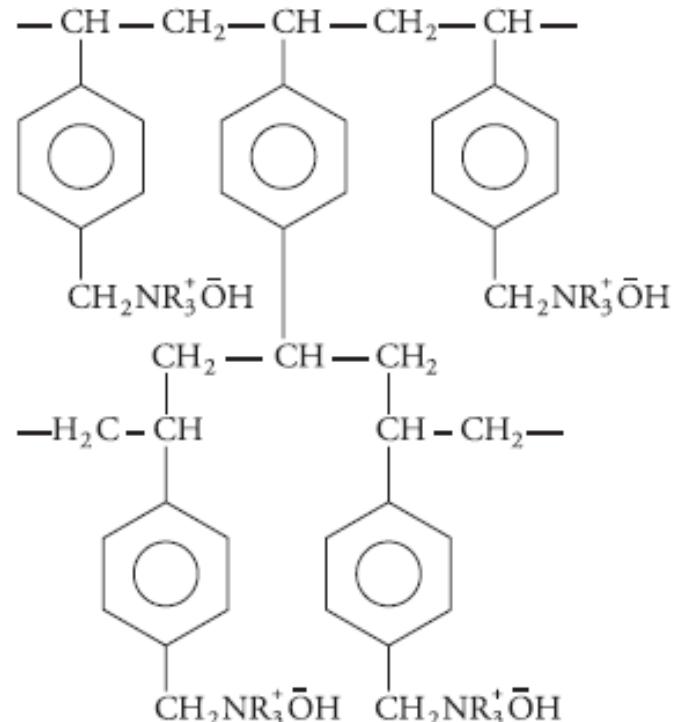
1. Cation exchange resin

- They are **materials** capable of exchanging a cation in their structure to the cation in solution.
- For softening of water, the resins used should be capable of exchanging H^+ ions in their structure to other cations in solution.
- Examples: styrene divinyl benzene copolymers, which on sulphonation or carboxylation become capable of exchanging hydrogen ions with the cations in water, Amberlite IR-120 and Dowex-50.



2. Anion exchange resin

- They are materials capable of exchanging an anion in their structure
- styrene divinyl benzene or amine formaldehyde copolymers, which contain basic functional group such as amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups. These after treatment with dilute NaOH solution become capable of exchanging OH⁻ ions with the anions in water. They are represented as R⁺OH⁻
- Examples: Amberlite 400 and Dowex-3



PROCESS

- The hard water is **first passed through a column containing cation exchange resin**
- cations are removed and equivalent amount of H⁺ ions are released from this column to water



- After this the water is passed into second column containing anion exchange resin.
- Anions are removed and an equivalent amount of OH^- ions are released.



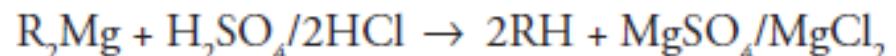
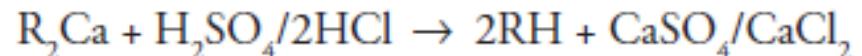
- The H^+ ions released from cation exchange column and OH^- ions released from anion exchange column combine to produce water molecule.



Regeneration

→ For cation exchange resin

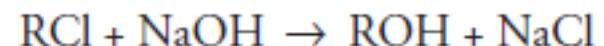
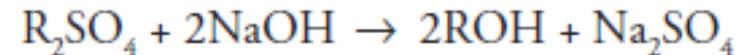
- The exhausted cation exchange resin is regenerated by passing a solution of HCl or H₂SO₄.



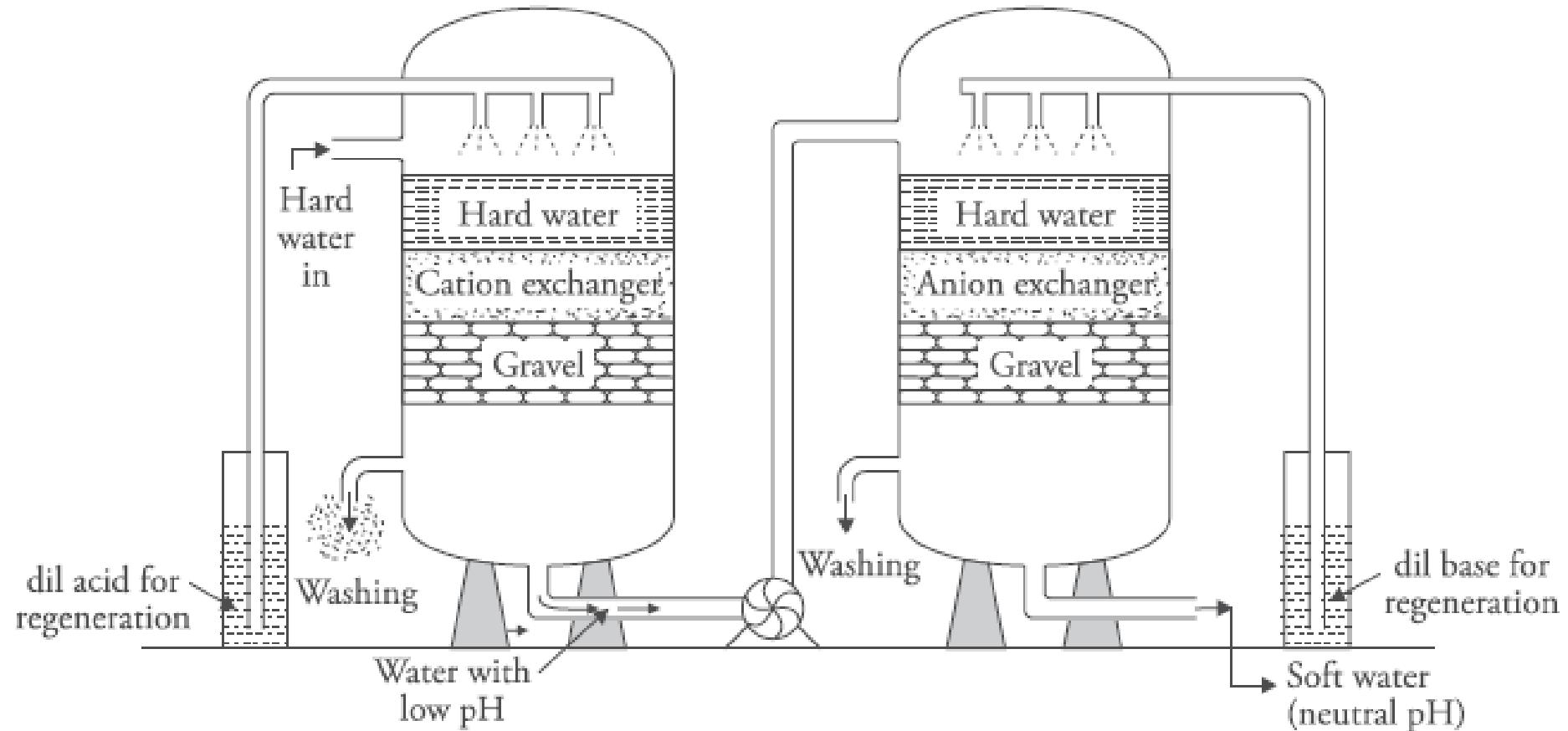
- The column is then rinsed with distilled water to remove the salts formed

→ For anion exchange resin

- The anion exchange resin is regenerated by passing a dilute solution of NaOH and then washing with distilled water



NaCl, Na₂SO₄ are removed by washing with distilled water.



- **Advantages**

1. The process can be used to soften highly acidic or alkaline water.
2. Unlike zeolite process the soft water does not contain sodium ions.
3. It removes all cations and anions other than H^+ and OH^- ions.
4. All ionisable impurities are removed.
5. It produces water of very low residual hardness (about 2 ppm).

- **Disadvantages**

1. The process is expensive, both the equipment and resin are costly.
2. Turbid water decreases the efficiency of the process.

Municipal Water Supply

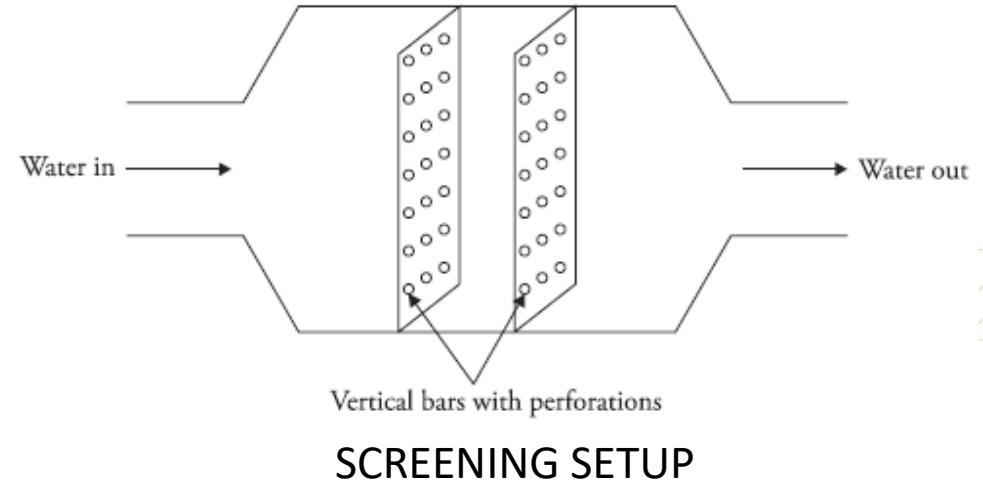
- Common requirements for potable water are:
 1. It should be clear, colorless, free from solids.
 2. It should have good taste and should be odorless.
 3. It should be soft.
 4. It should be abundant and cheap.
 5. Micro-organism and disease producing bacteria should not be present.
 6. It should not have objectionable dissolved gases but sufficient dissolved oxygen should be present.
 7. It should be free from harmful metallic salts.
 8. Radioactive substance should not be present.
 9. It should be free from fluorides, chlorides and phenolic compounds.
 10. Corrosive metals should not exist.

Water treatment for domestic use employs the following steps:

1. Screening
2. Sedimentation
3. Filtration
4. Disinfection

→Screening

- Screens are vertical bars with perforations.
- Screens are used to remove suspended impurities by passing water through screens having large number of holes when the floating materials are retained by them.
- To ensure complete removal of such impurities water is first passed through coarse screens and then through fine screens, which consist of woven wire, cloth or perforated plates mounted on a rotating disc or drum partially submerged in the flow.

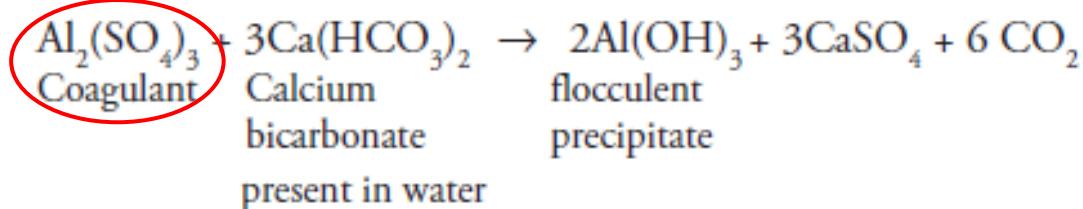
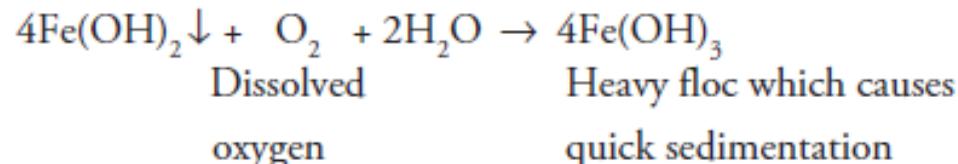
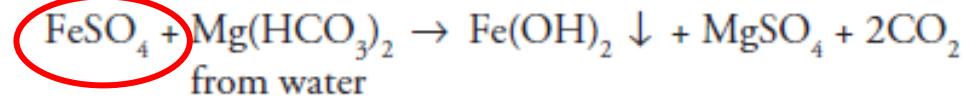


→ Sedimentation

- Process of removing fine, suspended, colloidal impurities by allowing water to stand undisturbed in big tank about 5 m deep.
- Most of the suspended particles settle down at the bottom, due to the force of gravity. The clear supernant water is then drawn from the tank with the help of pumps.
- Fine suspended particles like mud particles and colloidal matter present in the water cannot settle by plain sedimentation. They are removed by sedimentation with coagulation.

➤ Sedimentation with coagulation

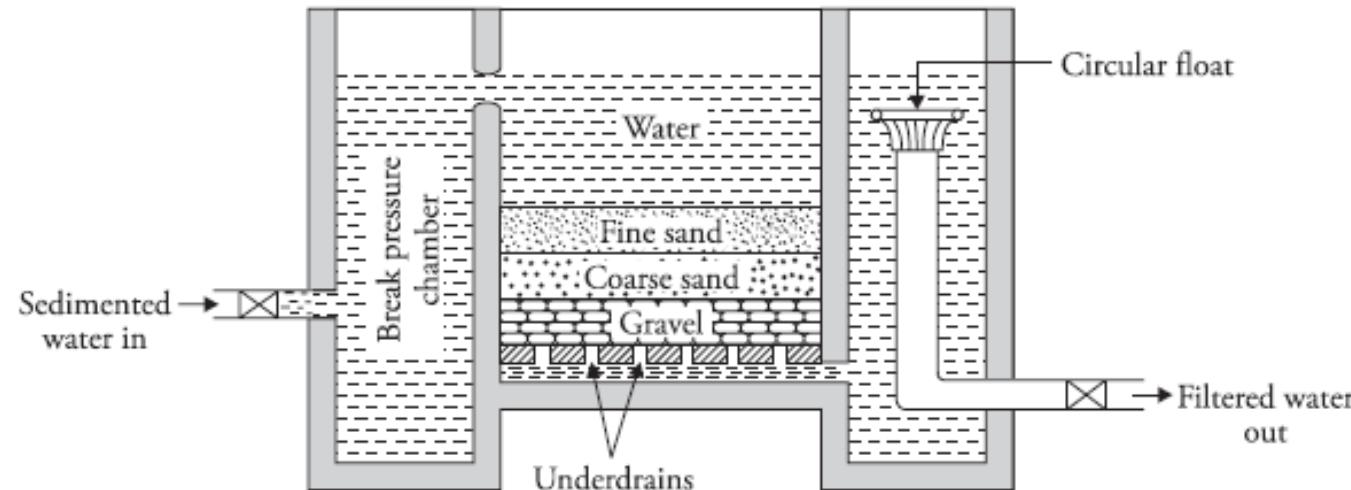
- It is the process of removing fine suspended and colloidal impurities by addition of requisite amount of chemicals (coagulants) to water before sedimentation.
- Coagulant, when added to water, forms an insoluble gelatinous, flocculent precipitate, which traps very fine suspended impurities forming bigger flocs, which settle down.
- Examples of coagulants: Alum, FeSO_4 , NaAlO_2 , $\text{Al}_2(\text{SO}_4)_3$



- The coagulants provide positive ions Fe^{3+} or Al^{3+} which neutralise the negative charge on the colloidal clay particles. After losing their charge the tiny particles come nearer to one another and combine to form bigger particles, which settle down, due to the force of gravity.

→Filtration

- It is the process of separating colloidal and suspended impurities from water by passing it through a porous bed made of fine sand and other proper sized granular materials.
- Filtration is carried out in a sand filter. It consists of a top thick layer of fine sand, placed over coarse sand layer followed by gravel.
- Water comes from the top and the suspended particles present in water that are of bigger size than the voids in the sand layer are retained there itself and the water becomes free of them.
- Removes all suspended particles, colloidal impurities and organic matter.

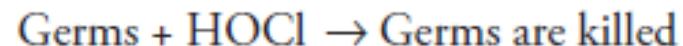
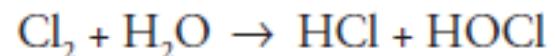
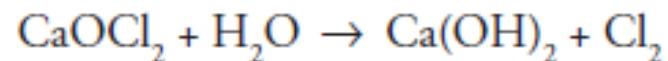


→Disinfection

- It is the process of removing pathogenic bacteria, viruses and protozoa from water.

Different methods available are:

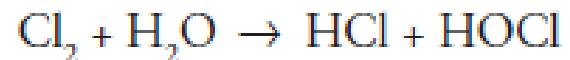
1. **Boiling:** it is useful only for small quantities of water. For proper disinfection, water should be boiled vigorously for 20–25 minutes.
2. **By adding bleaching powder:** About 1 kg of bleaching powder per 100 kiloliters of water is mixed and water is allowed to stand undisturbed for several hours. **The chemical action produces hypochlorous acid which is a powerful germicide and kills all the germs.**



- **Drawbacks**

- (1) Introduces calcium in water and hence increases its hardness.
- (2) Bleaching powder deteriorates during storage.
- (3) Excess CaOCl₂ gives bad taste and odor to treated water.

3. Direct chlorination Chlorine (either gaseous or in concentrated solution form) produces hypochlorous acid, which is a powerful germicide.



Germs + HOCl → Germs are killed

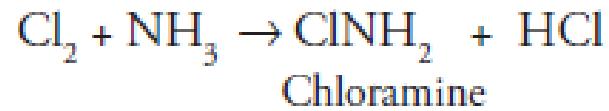
- **Advantage**

- Economical, requires little space for storage.
- Stable, does not deteriorate on storage.
- Does not introduce calcium.

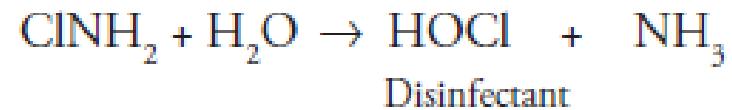
- **Disadvantages**

- Excess chlorine produces unpleasant taste and odor.
- Excess produces irritation on mucous membrane.

4. By adding chloramines (ClNH_2): Chloramine is formed by reacting chlorine and ammonia in the ratio 2:1



It is more lasting than chlorine alone, hence it is a better disinfectant

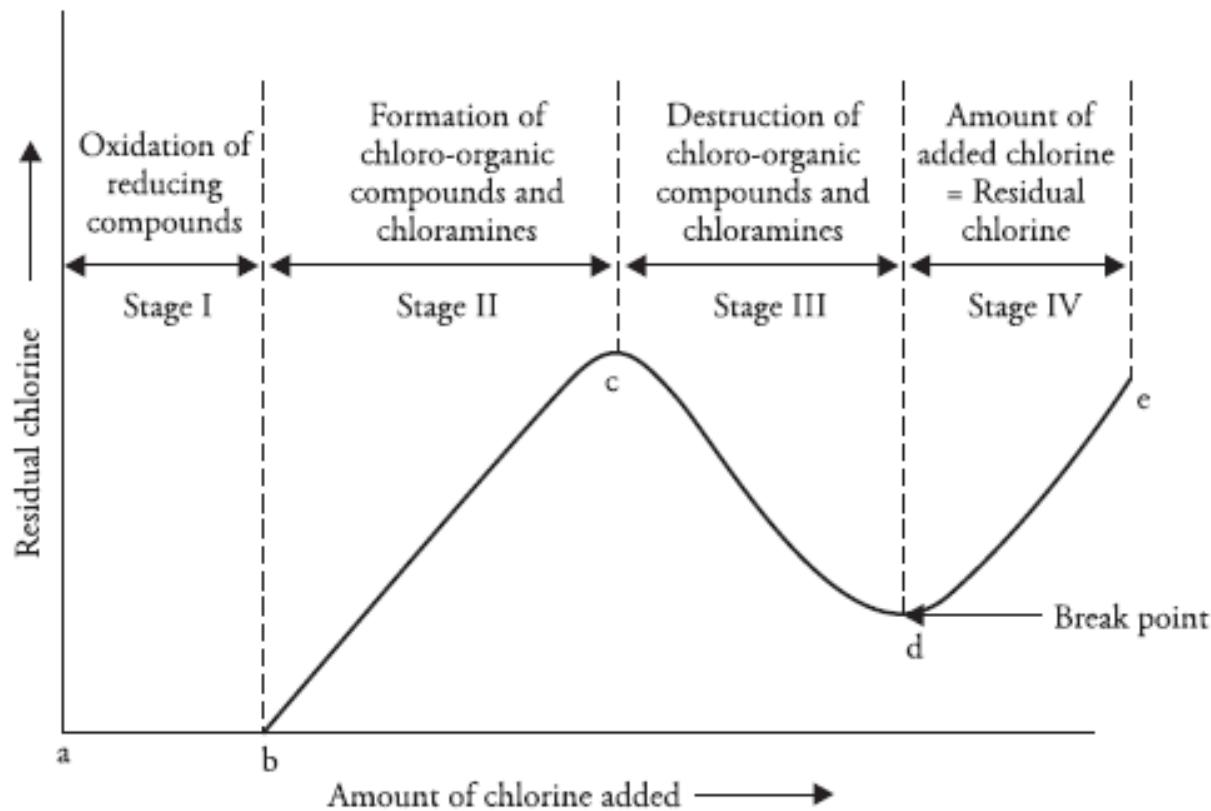


- **Advantages**

- (1) Excess does not produce irritating odor.
- (2) It imparts good taste to treated water.

• Break point chlorination or free residual chlorination

- When chlorine is added to water and the sample of water is analysed for available chlorine it is found that the available chlorine is less than added. → This is because the chlorine added in water is consumed not only for destroying the germs but also for oxidising the organic impurities, reducing substances and coloring matter in water.



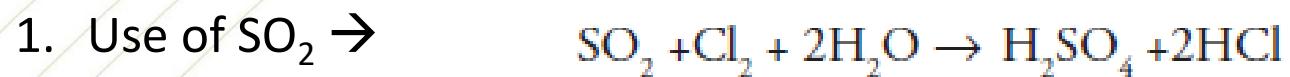
- This graph has four stages:
 - **Stage I:** For lower doses of chlorine all the added chlorine is used in oxidising the reducing compounds in water hence there is no residual chlorine in water (part *ab* of the graph).
 - **Stage II:** → On further addition of chlorine formation of chloro-organic compounds and chloramines takes place.
→ Chloramines act as chlorine reserve and contribute in the chlorine test just as free chlorine does. Hence the graph shows an increase in residual chlorine to a maximum level shown by *bc* in the curve.
 - **Stage III:** → On further addition of chlorine, the oxidation of chloramines and chloro-organic compounds takes place. The amount of residual chlorine decreases and reaches a minimum shown by point *d* in the graph.
- This point *d* is termed as the break point. At this point water is completely free of all kinds of impurities and is of potable water quality.
- Addition of chlorine until the break point is termed as break point chlorination, which may be defined as the chlorination of water to such an extent that not only the pathogenic bacteria but also the organic matter, reducing impurities, coloring matter and odours from water is oxidised.

- *Stage IV:* After the break point chlorine is not consumed further and the added chlorine is equal to the available chlorine and the graph once again shows an increase in the level of residual chlorine (part *de* in the graph.)

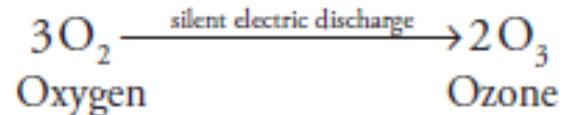
- **Advantages of break point chlorination:**

- (1) It removes all compounds that impart colour, bad odour and unpleasant taste to water.
- (2) It destroys all organic matter, dissolved ammonia and microorganisms in water and prevents the growth of weeds in water.

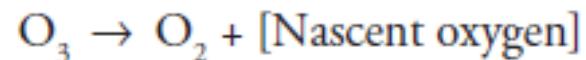
- **Dechlorination:** The excess chlorine added in water after break point imparts bad taste and colour to water and hence it has to be removed. It can be removed by passing water over activated charcoal or by the addition of SO_2 or by the use of Na_2SO_3



5. Ozonisation: Ozone is produced by passing silent electric discharge through cold and dry oxygen



→Ozone is highly unstable and breaks down liberating nascent oxygen



→ Nascent oxygen is a powerful oxidising agent and kills all the bacteria as well as oxidises the organic matter present in water.

→ For disinfection by ozone, ozone is passed through water in a sterilising tank. The contact period is about 10–15 minutes and dose is 2–3 ppm.

- **Advantages**
- Ozone sterilises, bleaches, decolorises and deodorises water.
- Excess of ozone in water is not harmful as it decomposes to give oxygen.
- There is no irritation of mucous membrane as is in the case of chlorine treatment.
- Ozone improves the taste of water. Highly potable water is thus sterilised with ozone.

- **Disadvantages** Ozonisation is a very expensive process. Moreover ozone is a corrosive agent. It corrodes stainless steel, cast iron, copper, rubber and ebonite.

6. By adding KMnO₄: → It is generally used to disinfect surface water systems containing bad taste and odor.

→ When KMnO₄ is added to water, it gives purple color to water which finally disappears when the oxidation is completed.

→ It removes H₂S, Fe and Mn.

→ The normal dosage of KMnO₄ is about 1–2 mg/L within a period of 4–6 hours. It is generally used in rural areas where supplies are from wells.

THANK YOU



APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 29



SCHOOL OF
ENGINEERING AND
TECHNOLOGY



Desalination of Water

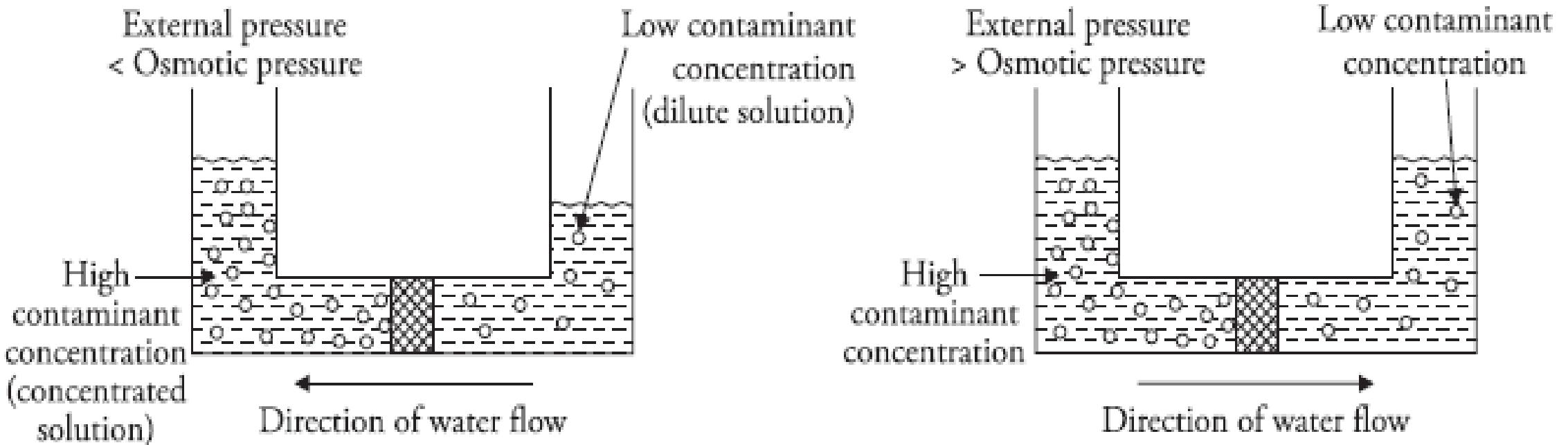
- Water is a good solvent. It contains dissolved solids in it, depending upon the amount of dissolved solid water may be grouped as follows:
 1. Fresh water (having < 1000 ppm of dissolved solids)
 2. Brackish water (having > 1000 ppm but < 35000 ppm of dissolved solids)
 3. Sea water (having > 35000 ppm of dissolved solids)
- Water containing large quantities of salts is salty in taste and is unfit for domestic and industrial purpose. This water can be put to good use by removing the salt content from it. *The process used for the removal of salts from water is called desalination.*
- Various **techniques employed for desalination** are
 1. Reverse osmosis
 2. Electro dialysis
 3. Ultra filtration
 4. Flash evaporation

- **Reverse Osmosis:**

- Osmosis is defined as the process of spontaneous flow of solvent particles through a semi permeable membrane from a dilute solution to a concentrated solution (from lower concentration to higher concentration).
- The diffusion of solvent particles takes place on account of hydrostatic pressure called osmotic pressure, which drives solvent molecules in search of equilibrium.
- If an external pressure equal to osmotic pressure is applied on the concentrated solution the process of osmosis will stop and if the external pressure exceeds osmotic pressure, solvent will be squeezed out of the concentrated solution. This process is called reverse osmosis.
- In reverse osmosis, pure water is separated from its contaminants rather than removing contaminants from water.
- semi permeable membranes are usually made up of cellulose acetate, polymethacrylate or polyamide polymers.

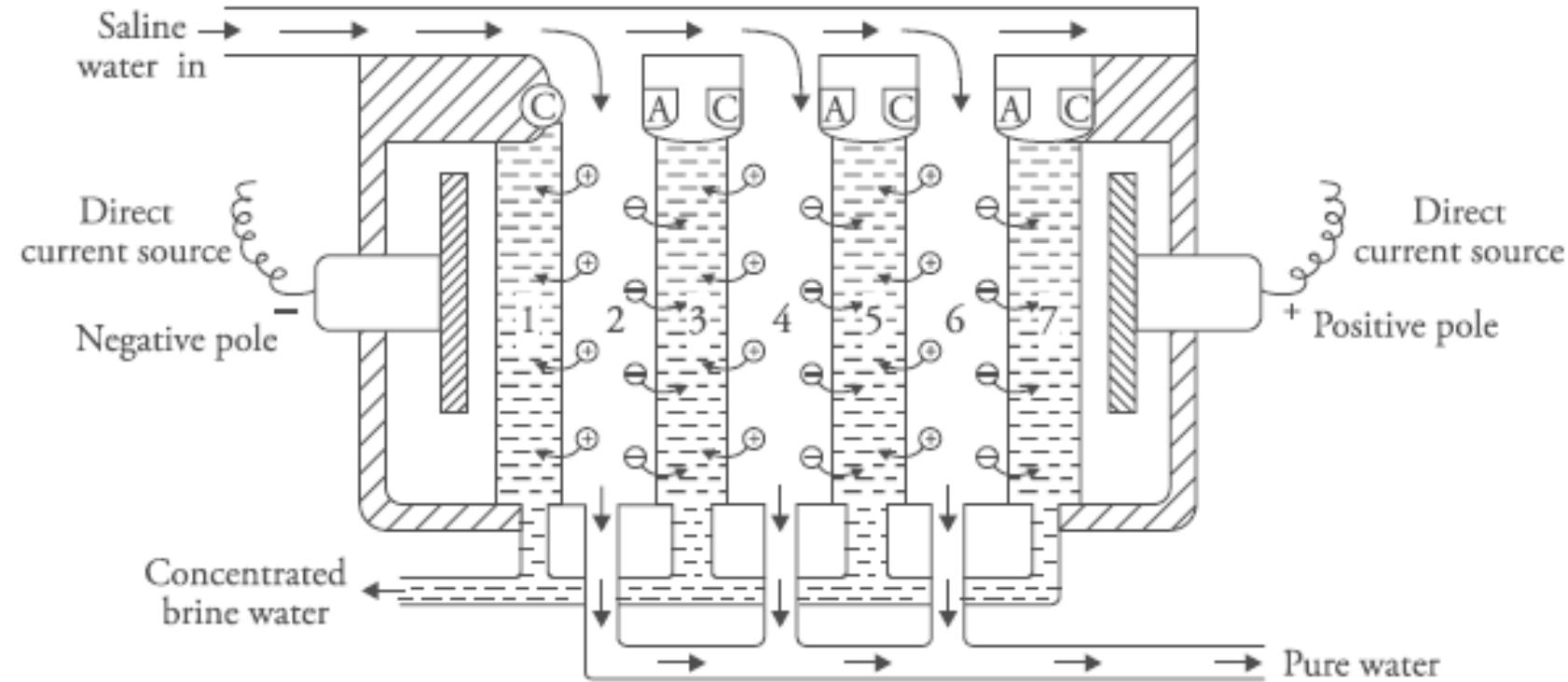
Advantages This process removes lead, calcium, magnesium, sodium, potassium, aluminium, chloride, nitrate, fluoride, sulphate, boron, most microorganisms and organic chemicals from water.

Disadvantages It requires large volume of water. *It may take as much as 90 liters water to recover 5 liters of useable water.*



• Electrodialysis

- It is a method in which the charged ions (salts) are removed from water by passing direct current, using electrodes and thin rigid ion selective semi permeable membranes.
- An electrodialysis cell consists of alternate cation and anion selective membranes. The cathode is placed near the cation selective/permeable membrane and the anode is placed near the anion selective membrane.
- Saline water is passed under a pressure of about $5\text{--}6 \text{ kg m}^{-2}$ between membrane pairs and an electric field is applied perpendicular to the direction of water flow
- Under the influence of the strong electric field the sodium ions (Na^+) start moving towards cathode through the cation exchange membrane towards cathode (negative pole) and the chloride ions (Cl^-) move towards anode (positive pole) through the anion exchange membrane.
- As a result, there is depletion of ions in the even numbered compartments and the concentrations of ions in the odd numbered compartments increases.
- The desalinated water, free of ions is collected separately, whereas concentrated water of the odd numbered compartments is replaced from time to time by fresh lot of saline water.



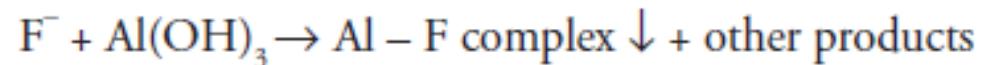
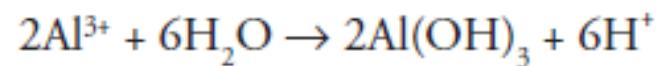
- A = Anion permeable membrane
- C = Cation permeable membrane

• Defluoridation

- Acceptable limit for fluoride in water → 1 ppm
- Within permissible limits fluoride helps to protect teeth enamel and makes it more resistant but excess fluorine in water causes fluorosis which leads to weakening and bending of bones, decay of teeth, etc.
- The commonly used defluoridation (removal of excess fluoride) techniques are as follows:
 1. **Adsorption:** Fluoride can be removed from water by adsorption on bone charcoal, activated carbon, activated alumina, tamarind gel, etc.
 2. **Ion exchange:** Anion exchange resins with quarternary ammonium functional groups are used which replace fluoride with chloride attached to these functional groups and on saturation, the resin is backwashed with supersaturated sodium chloride salt.
 3. **Reverse Osmosis**
 4. **Nalgonda Technique**

Nalgonda Technique

- This technique owes its name to the village Nalgonda in Telangana where it was pioneered. It was first developed by NEERI scientists in India and its first report was published in 1975.
- The process involves five steps namely mixing, flocculation, sedimentation, filtration and disinfection.
- **Mixing:** Calculated quantity of alum and lime are added to water and the water is thoroughly mixed so that the chemicals react with the fluoride in water and form suitable precipitates
- **Flocculation:**



- **Sedimentation:** Flocs containing fluorides, turbidity, bacteria and other impurities are allowed to stand for sometime so that they settle down.
- **Filtration:** Water standing above is decanted carefully and is filtered using sand filters (discussed earlier).
- **Disinfection:** The filtered water is collected and disinfected by further addition of bleaching powder and then distributed.

Limitations

- The method fails if the fluorine content in water is very high.
- The quantity of alum and lime has to be carefully controlled for proper results.
- Large quantities of sludge is formed which should be disposed off carefully.

- Lime soda process-
 - a) Hot lime soda process
 - b) Cold lime soda process

GIVEN IN ASSIGNMENT

THANK YOU

