Sanjivani University
School of Engineering and Technology

Applied Science (24UETBS102)
Unit -3
Water Technology

SANJIVANI UNIVERSITY

By,
Dr. Kalpana Joshi
Dr. Tanay Ghosh
Dr. Nachiketa Sahu
Prof. Priyanshi Vishnoi

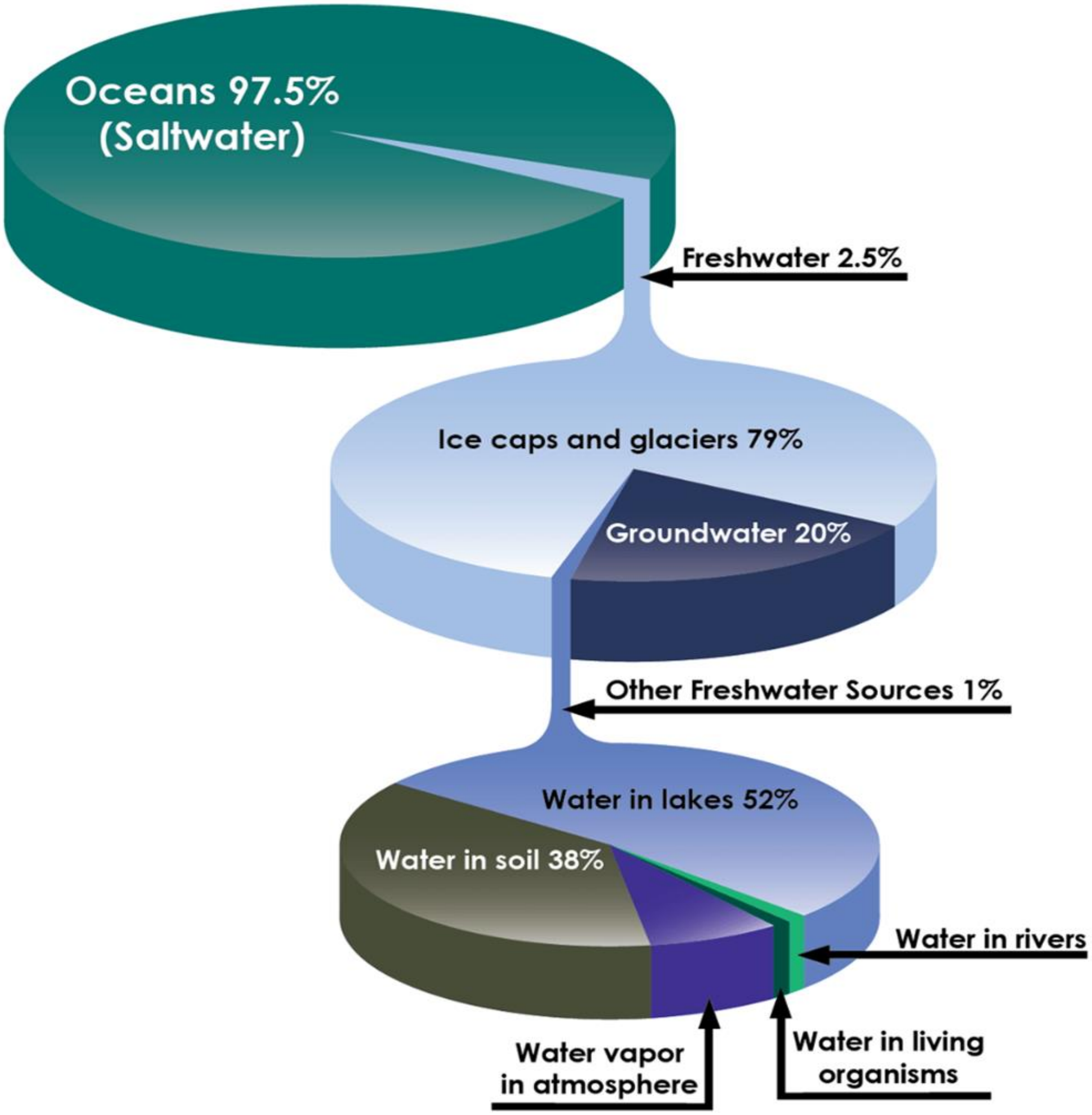
Contents

WATER

WATER

- **Water is the most precious, wonderful and useful gift of nature.**
- **It is the most abundant and essential natural resource.**
- **It covers nearly 70% of the earth's surface. It is estimated that the hydrosphere contains about 1360 million cubic kilometer (1.3 x 10^8 m^3) of water.**

Water Distribution on Earth



Introduction

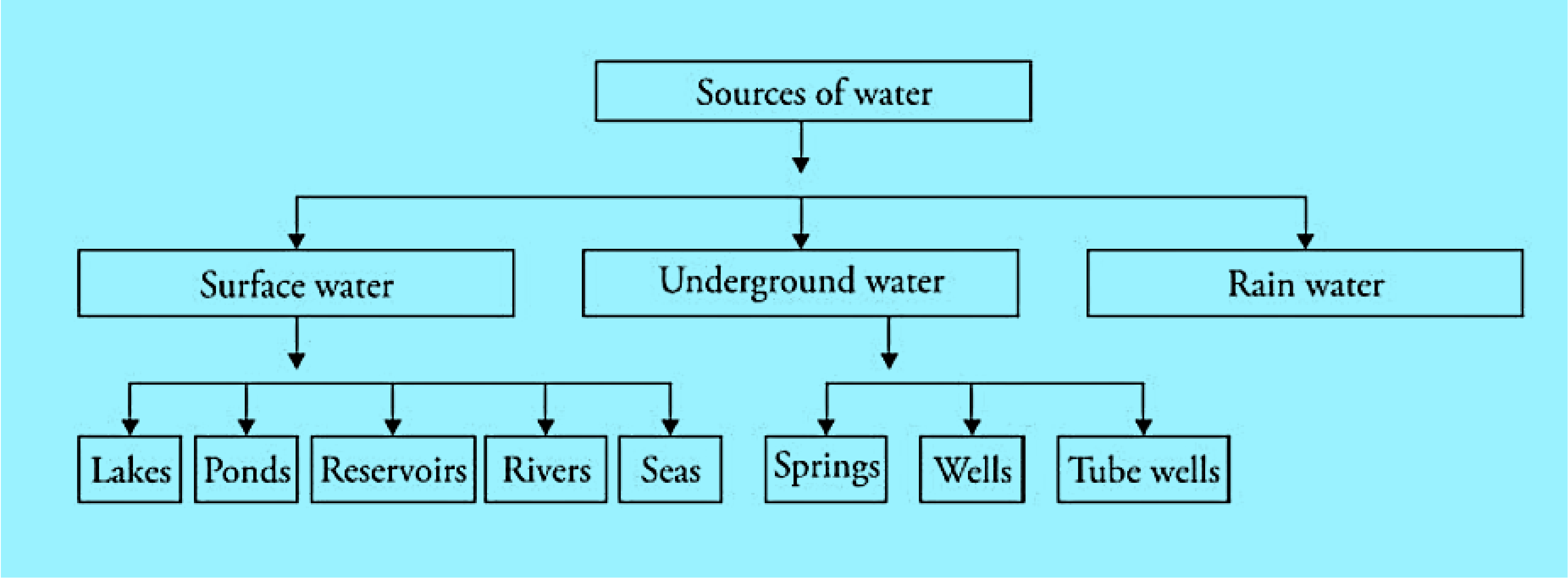
The importance of water

- **70% of earth is covered with water.**
- **97.5% of water is salt water.**
- **Only 2.5% of earth's water is fresh water.**
- **Water keeps us alive, moderates climate, sculpts lands, removes and dilutes wastes as well pollutants.**

Earth Total Water Supply	Percentage
Salt Water: 97.5%	Oceans: 97.5%
Fresh Water:2.5%	Frozen
	Ground Water
	Surface Water
	Air and Soil

Introduction

Sources of Water



Hardness of Water

It is defined as the characteristic of water that prevents lathering of soap. Originally, it was defined as the soap-consuming capacity of water.

Causes of Hardness of water

Hardness of water is due to the presence of bicarbonates, sulphates, chlorides and nitrates of calcium and magnesium.

Causes of Hardness of water

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. This is because of the formation of insoluble salts of calcium and magnesium.

Causes of Hardness

Chemical reactions involved are

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

Soap(Sodium Stearate) **Calcium Stearate(Insoluble)**

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

Soap(Sodium Stearate) **Magnesium Stearate(Insoluble)**

Causes of Hardness

Other salts of calcium and magnesium like $CaSO_4$, $Ca(NO_3)_2$ and $MgCl_2$, also react in a similar way forming insoluble precipitates of calcium and magnesium salts of higher fatty acids.

Hard and Soft Water

Hard Water vs Soft Water

High mineral content like Ca^{2+}, Mg^{2+} e.g. mineral water, high pH water

Low mineral content like Na^{+}

Hard and Soft Water

S. No.	Hard Water	Soft Water
1.	It does not form lather with soap but form white precipitate.	It easily form lather with soap.
2.	It contains soluble salt of calcium magnesium and other heavy metals like aluminium, iron and manganese etc.	It does not contain any dissolved salt of calcium and magnesium.
3.	In hard water the cleansing action 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	Due to hardness, boiling point of water is elevated, therefore more fuel and time is required for cooking.	Less fuel and time is required for cooking.

Hard and Soft Water

	Hard Water	Soft Water
Appliances	• Leaves deposit of limescale • Stains water fixtures • Can leave clothes discoloured	• Cleans dishes with less water
Drinking	• Has potential of health benefits from calcium and magnesium • Generally tastes better	• Can deprive drinkers of vital minerals • Has higher levels of sodium
Skin	• May harm your hair • Can trigger eczema • Strip skins of surface oils	• Lathers soap well • Rinses shampoo from hair easier and quicker

Temporary Hardness

(a) It is also called carbonate hardness or 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.

(b) 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.

Temporary Hardness

Upon Heating:

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

Calcium Bicarbonate → **Calcium Carbonate (insoluble)**

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + H_2O + 2CO_2$$

Magnesium Bicarbonate → **Magnesium Hydroxide**

Permanent Hardness

(a) It is also called non-carbonate or non-alkaline hardness.

(b) 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 $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, $Ca(NO_3)_2$, etc.

Permanent Hardness

It cannot be removed by simple boiling. However, it can be removed by special chemical methods like lime soda process, zeolite method, etc.

Types of Water Hardness

	Temporary hardness of water	Permanent hardness of water
Definition	Temporary hardness occurs due to the presence of calcium hydrocarbonate and magnesium hydrocarbonate	Permanent hardness is due to sulfates and chlorides of magnesium and calcium
Causative Agent	Carbonates and bicarbonates of calcium and magnesium	Sulfates and chlorides of calcium and magnesium
Removal through boiling	Hardness can be easily removed when water is boiled	Hardness can not be removed by boiling
Other removal methods	Can use softeners	Using water softeners or using ion exchange columns

Degree of Hardness

Hardness is always calculated in terms of equivalent of $CaCO_3$, although hardness is never present in the form of $CaCO_3$. There are two basic reasons for choosing $CaCO_3$ as standard:

(i) Calculations become easy as its molecular weight is exactly 100 (and equivalent weight is exactly 50).

(ii) It is the most insoluble salt that can be precipitated in water treatment.

Degree of Hardness

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 ($CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, etc.) in terms of equivalent of $CaCO_3$.

Degree of Hardness

This can be done by the formula:

$$\text{Equivalent of } CaCO_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hardness producing substance}}$$

Question

Q) A water sample contains 248 mg $CaSO_4$ per liter. Calculate the hardness in terms of $CaCO_3$, equivalent.

Q) How many grams of $FeSO_4$, dissolved per liter gives 300 ppm of hardness?

(Fe = 56, S = 32, O = 16, Ca = 40, C =12)

Units of Hardness of Water

Hardness is expressed by

1. PPM: The number of grains of calcium carbonates which is present in one million grains of water is called PPM.
1 grains of calcium carbonate present in 1 million grains of water is 1 ppm.
1ppm = 1 mg/L
2. In Degrees Clarke (^{o}Cl): The number of grains of calcium carbonates which is present in 70,000 grains of water.
3. In Degrees French (^{o}Fr): It is defined as the number of parts of $CaCO_3$, equivalent hardness per 10^5 parts of water. Thus,

1° Fr = 1 part of $CaCO_3$, equivalent hardness per 10^5 parts of water.

Units of Hardness of Water

Relationship between different units of hardness As,

1 ppm = 1 part of $CaCO_3$, equivalent hardness in 10^6 parts of water.

1mg/L = 1 part of $CaCO_3$, equivalent hardness in 10^6 parts of water.

1 ^oCl = 1 part of $CaCO_3$, equivalent hardness in 70000 parts of water.

1 ^oFr = 1 part of $CaCO_3$, equivalent hardness in 10^5 parts of water.

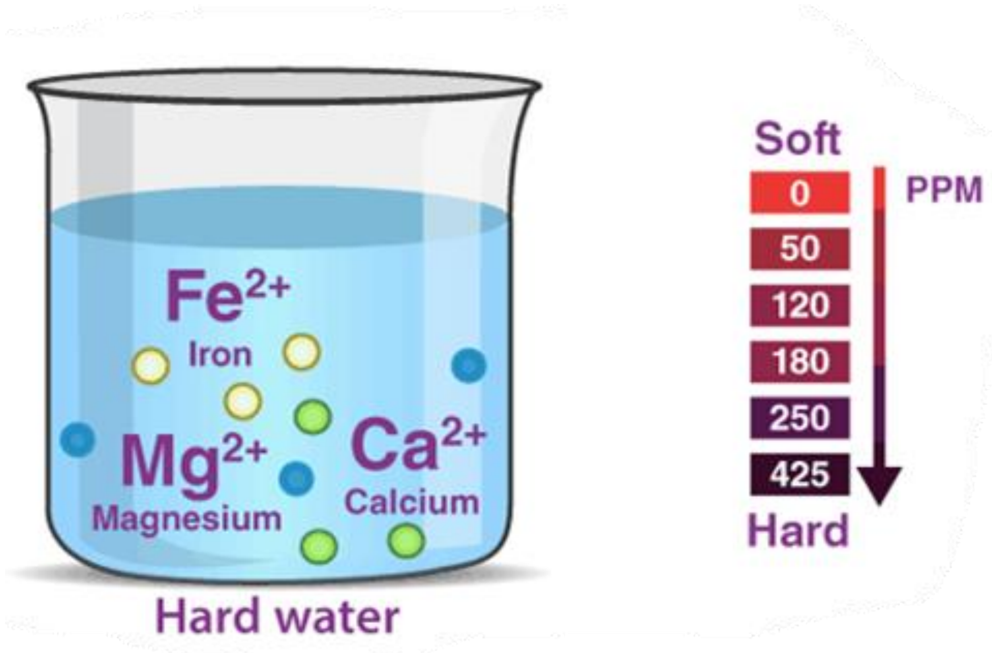
Question

Three samples P, Q and R were analyzed for their salt contents. (i) Sample P was found to contain 155 mg of magnesium carbonate per liter. (ii) Sample Q was found to contain 800 mg of calcium nitrate and 2.5 mg of silica and 5.1 mg of sodium chloride per liter. (iii) Sample R was found to contain 15 g of potassium nitrate and 3 g of calcium carbonate per liter. Find the hardness of all the above three samples in ppm and in degree Clarke.

Question

Q) A sample of water on analysis was found to contain $Ca(HCO_3)_2$ = 4 mg/L; $Mg(HCO_3)_2$ = 6 mg/L; $CaSO_4$ = 8 mg/L; $MgSO_4$ = 10 mg/L. Calculate the temporary, permanent and total hardness of water in ppm, °Fr and °Cl [Mol weight of $Ca(HCO_3)_2$=162, $Mg(HCO_3)_2$= 146; $CaSO_4$=136; $MgSO_4$ = 120].

Disadvantages of Using Hard Water for Domestic Use



Disadvantages of Using Hard Water for Domestic Use

How can water affect you and your home

Buildup of hard water mineral can lead to:

- **Extra time and money spent scrubbing skins, showers, dishes and more.**
- **Water-using appliances that break down faster and run less efficiently.**
- **Limp, dry hair and itchy, irritated skin.**
- **Stuff, dull laundry.**

What are industrial water boilers

Industrial boilers are water-containing vessels that generate heat with the help of a fuel source. It is then transferred to various tubes connecting to the various industrial equipment. The steam energy is used for running the machinery, giving industries a cost-effective way of powering their production.

Sludge and Scale Formation in Boilers

Due to heating, the salt containing water will get concentrated and changes into loose and slimy precipitates called sludge. When these precipitates becomes hard and adherent called scale.

Disadvantages of Using Hard Water for Industrial Use

Scale Formation:

Cause: **When hard water is heated in a boiler, the dissolved minerals such as calcium and magnesium ions precipitate out of the water and form solid deposits on the surfaces inside the boiler and its heating elements.**

Composition: **The scale primarily consists of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$), along with other mineral salts depending on the water chemistry.**

Effects: **Scale acts as an insulator, reducing the efficiency of heat transfer. This means more energy is required to heat the water, leading to increased energy costs. It can also lead to overheating of the boiler, potentially damaging internal components over time.**

Disadvantages of Using Hard Water for Industrial Use

Sludge Formation:

Cause: **Sludge forms when these minerals, along with other impurities like dirt and rust particles, settle at the bottom of the boiler tank or within pipes.**

Composition: **Sludge is typically a mixture of precipitated minerals, organic matter, and corrosion by-products.**

Effects: **Sludge accumulation reduces the boiler's efficiency by impeding water flow and heat transfer. It can also promote corrosion of metal surfaces due to localized concentration of dissolved oxygen and other corrosive agents trapped within the sludge.**

Disadvantages of Using Hard Water for Industrial Use

Impact of Hard Water:

Efficiency Loss: **Both scale and sludge reduce the efficiency of water boilers, leading to higher energy consumption and operational costs.**

Maintenance Issues: **Regular descaling and cleaning are necessary to prevent damage to the boiler and ensure optimal performance.**

Longevity: **Failure to address scale and sludge buildup can shorten the lifespan of the boiler and its components, requiring more frequent repairs or replacements.**

Disadvantages of Using Hard Water for Industrial Use

Preventive Measures:

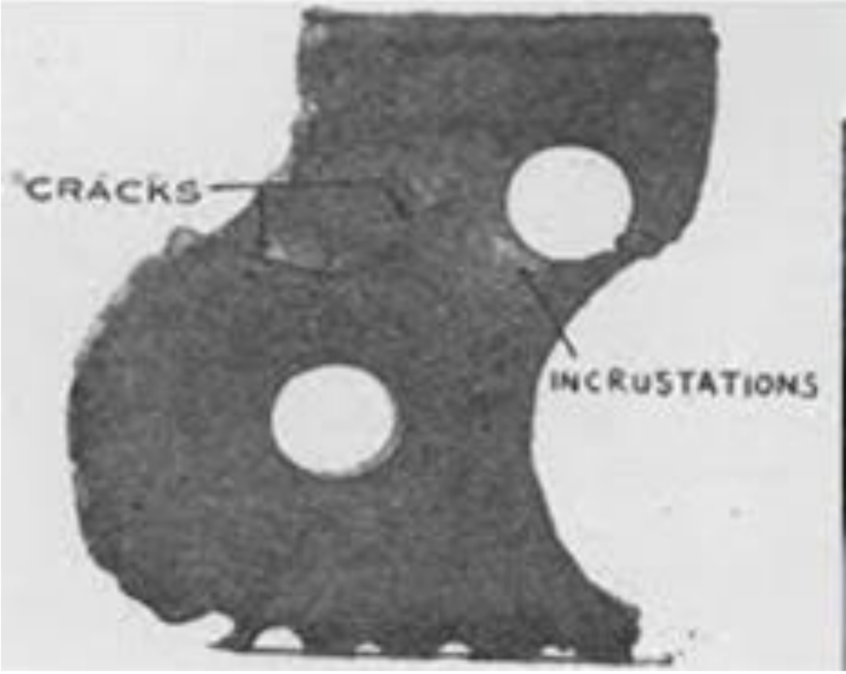
Water Softening: **Installing a water softener can reduce the hardness of water by removing calcium and magnesium ions.**

Chemical Treatments: **Using chemical additives or descaling agents periodically to dissolve scale and prevent its formation.**

Regular Maintenance: **Implementing a maintenance schedule for cleaning and inspecting the boiler to remove accumulated sludge and scale.**

Caustic Embrittlement

Caustic embrittlement in boilers caused by hard water is a specific type of damage that occurs due to the combination of high alkalinity and the presence of dissolved minerals, typically calcium and magnesium ions, found in hard water.



Disadvantages of Using Hard Water for Industrial Use

When hard water is heated in a boiler, especially in high-pressure systems, the dissolved calcium and magnesium ions undergo chemical reactions:

Calcium Bicarbonate Reaction: $Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$

Magnesium Bicarbonate Reaction: $Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H_2O$

These reactions lead to the precipitation of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$), forming solid deposits known as scale. Scale deposits accumulate on the inner surfaces of the boiler, including tubes, pipes, and heating elements.

Increase in alkalinity: As scale builds up, it depletes bicarbonate ions (HCO_3^-) in the water. This depletion, along with the dissolution of carbonate ions (CO_3^{2-}), increases the pH of the water. The pH can rise significantly, often exceeding 10 in boilers affected by hard water.

Disadvantages of Using Hard Water for Industrial Use

High pH Environment: The elevated pH of the water (typically above 10) due to the presence of dissolved alkaline salts (e.g., NaOH, KOH) from hard water minerals.

Caustic embrittlement occurs under conditions of high pH (typically above 10)

Oxide Layer Disruption: The high pH environment attacks and disrupts the protective oxide layer naturally present on the metal surfaces.

Metal Hydroxide Formation: Direct reaction between the metal surface and hydroxide ions (OH^-) forms metal hydroxides (e.g., $Fe(OH)_2$ for iron).

Prevention and Mitigation:

To prevent caustic embrittlement caused by hard water in boilers, several preventive measures are crucial:

Water Treatment: Implement water softening techniques to reduce calcium and magnesium ion concentrations in the feedwater.

Chemical Treatment: Use additives or treatments to control and maintain pH and alkalinity levels within safe limits.

Regular Maintenance: Establish a routine cleaning and descaling schedule to remove existing scale and prevent its buildup.

Material Selection: Choose boiler materials resistant to embrittlement and corrosion under high-pH conditions.

https://www.slideshare.net

Boiler Corrosion

Boiler corrosion caused by hard water is a significant issue in many industrial and residential settings. Hard water contains high concentrations of dissolved minerals, primarily calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions. When hard water is used in boilers, several types of corrosion can occur due to the presence of these minerals:

Disadvantages of Using Hard Water for Industrial Use

Corrosion of boiler metal is a serious problem and takes place if unsuitable water is used.

The disadvantage of corrosion are

- **Reducing life of the boiler.**
- **Leakage of joints and rivets.**
- **Increased cost of repairs and maintenance.**

It may be due to three major reasons:

i) Dissolved Oxygen

ii) Dissolved CO_2

iii) Dissolved salts like $MgCl_2$

Disadvantages of Using Hard Water for Industrial Use

Corrosion Due to dissolved oxygen:

Dissolved oxygen in presence of water, causes corrosion.

$$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3 \text{ (Rust)}$$

Corrosion due to CO_2:

Salts like calcium bicarbonate on heating produces CO_2. CO_2 dissolves in water to form carbonic acid which corrodes the boiler metal.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$
$$H_2O + CO_2 \rightarrow H_2CO_3$$

Corrosion due to Dissolved salts like $MgCl_2$:

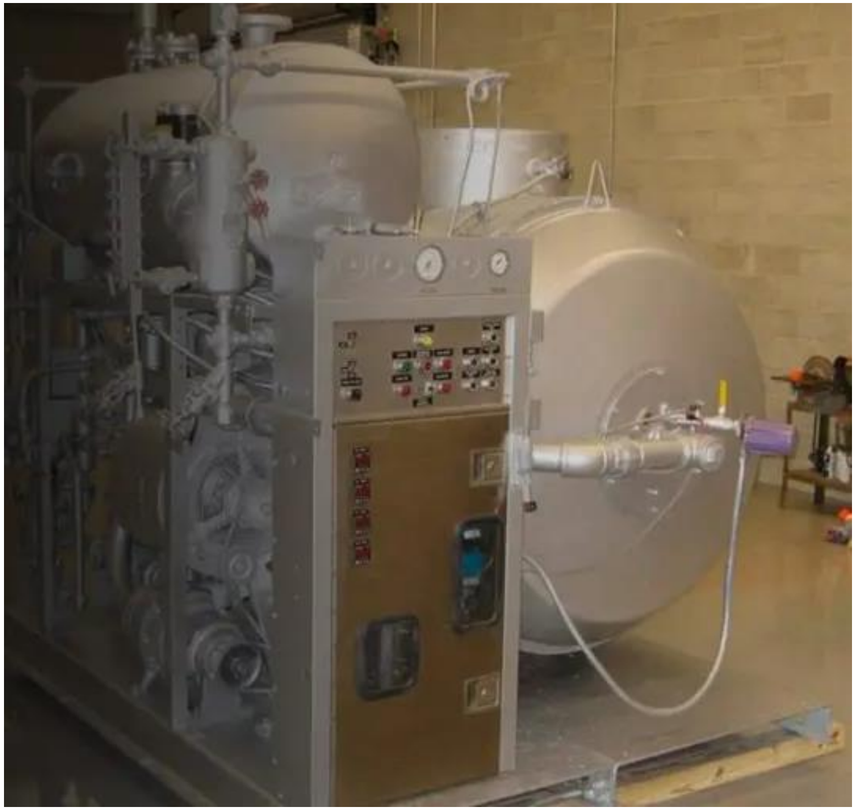
Dissolved salts like $MgCl_2$ cause acid formation. This will be prevented by alkali neutralization.

$$MgCl_2 + 2\,H_2O \rightarrow Mg(OH)_2 + 2\,HCl \text{ (Corrosive acid)}$$

Disadvantages of Using Hard Water for Industrial Use

Prevention

The most effective way to slow down the corrosion process is by treating the feedwater that enters your boiler. You can also prevent corrosion by checking the vessel periodically for signs of physical damage.



Necessity of Softening Hard Water

Hard Water Softening Processes

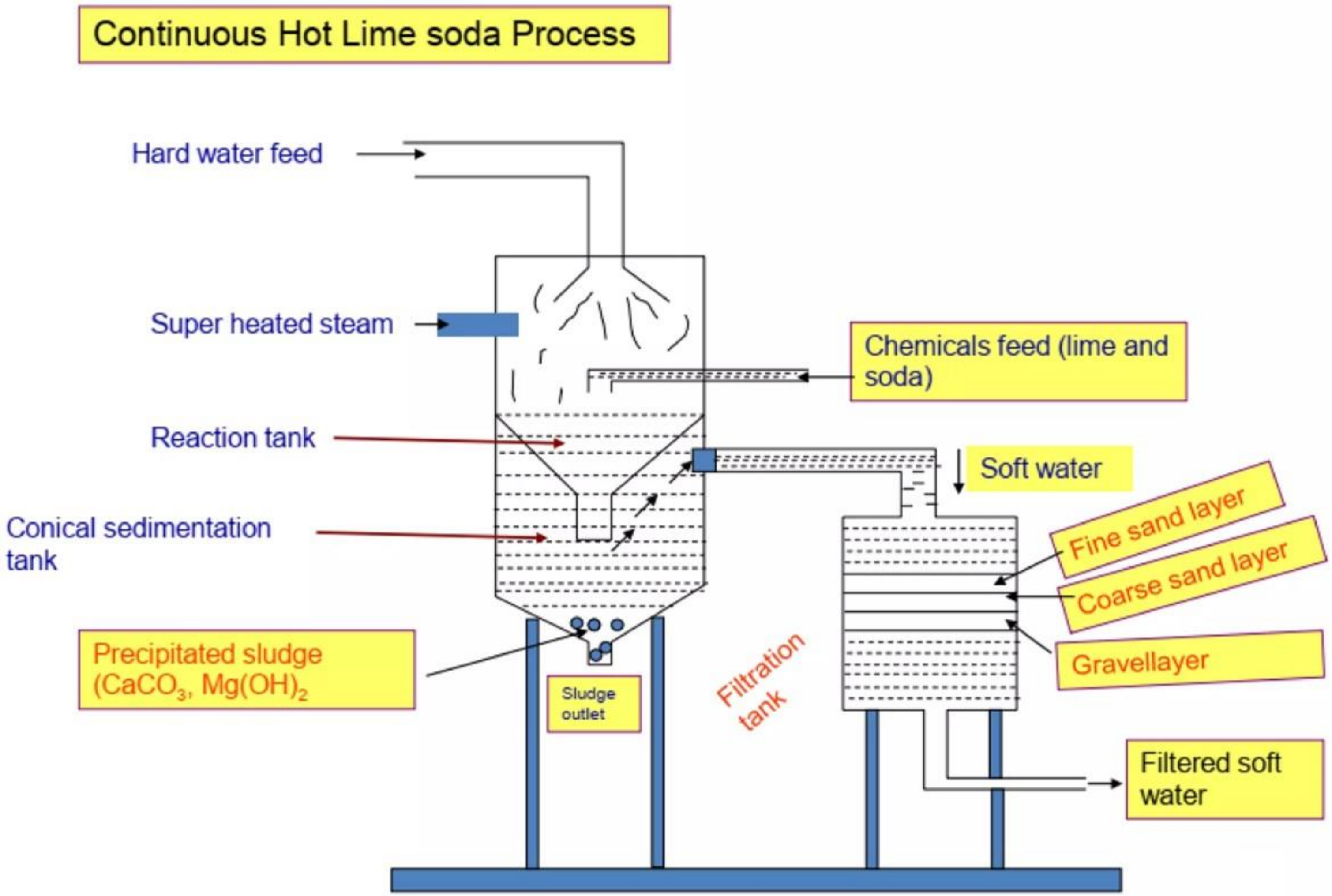
Softening of water: The process of removing or reducing concentrations of salts from water is called as softening of water.

Methods used for softening of water

- **Lime soda process**
- **Zeolite process or permutit**
- **Ion-exchange or deionization or Demineralization process**

Hard Water Softening Processes

Lime Soda Process



Lime Soda Process

Lime Soda process is a method of softening hard water.

- **This process is very useful for the treatment of large volumes of hard water.**

- **In this process Calcium and Magnesium ions are precipitated by the addition of lime ($Ca(OH)_2$) and soda (Na_2CO_3).**

Hard Water Softening Processes

Lime Soda Process

This process is a standard water-softening process.

- ❖ **Carried out either through hot or cold condition.**
- ❖ **Uses lime ($Ca(OH)_2$) and soda (Na_2CO_3) to reduce the hardness of the treated water by precipitating the dissolved calcium and magnesium salts as insoluble calcium carbonate and magnesium hydroxide respectively.**

Hard Water Softening Processes

Lime Soda Process

The lime will react with bicarbonate hardness as follows:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

Calcium Hydroxide — Calcium bicarbonate — Calcium carbonate

$$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + 2H_2O$$

Calcium Hydroxide — Magnesium bicarbonate — Magnesium Hydroxide — Calcium carbonate

The soda will react with hardness producing salts as follows:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

Calcium Sulfate — soda — Calcium carbonate — Sodium Sulfate

Hard Water Softening Processes

Lime Soda Process

The soda will react with hardness producing salts as follows:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$$

Calcium Chloride, Soda, Calcium carbonate, Sodium Chloride

Simultaneously both soda and lime will react with hardness as follows:

$$MgSO_4 + Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4 + Mg(OH)_2\downarrow$$

Magnesium sulfate, calcium hydroxide, Sodium carbonate, Calcium Carbonate, Sodium Sulfate, Magnesium hydroxide

Hard Water Softening Processes

Hot and Cold Lime Soda Process

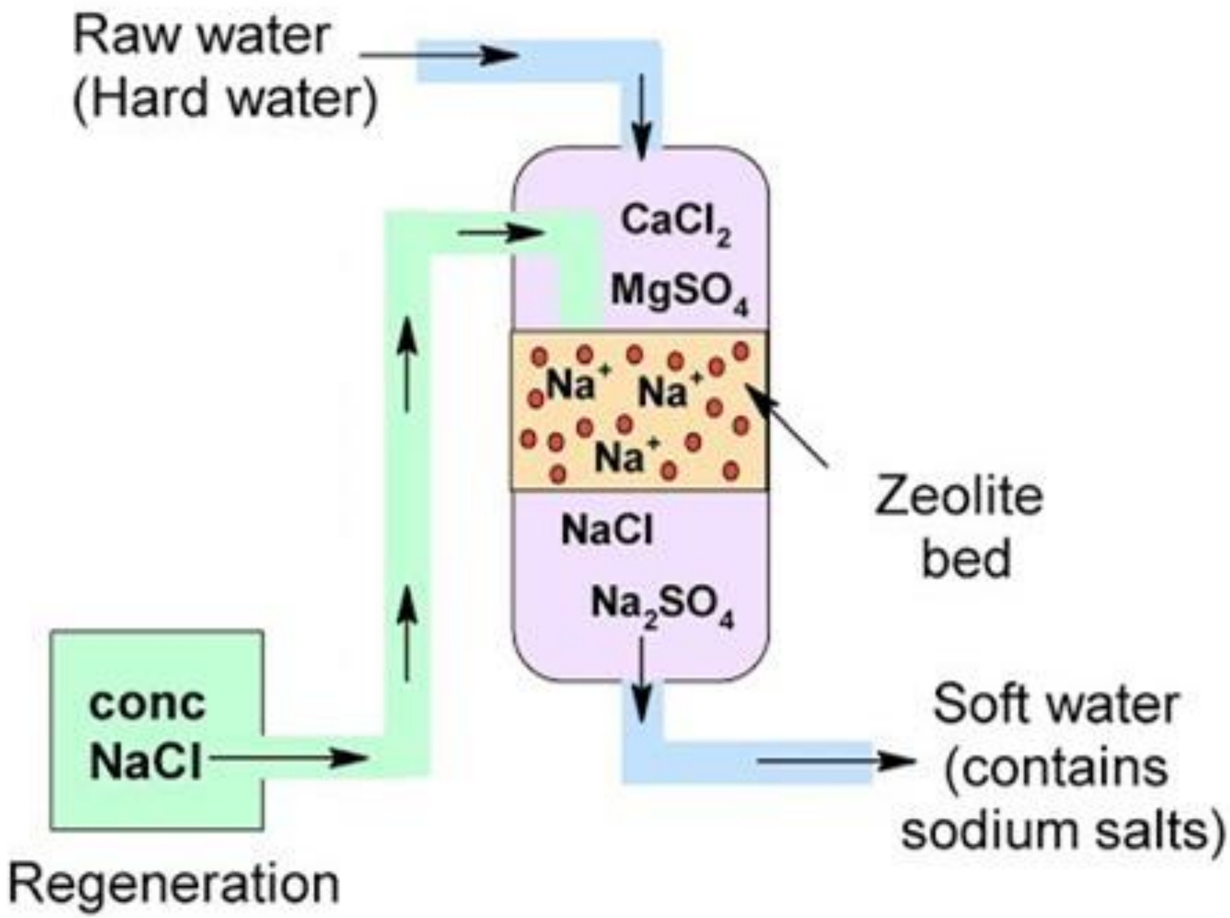
The lime soda process can be carried out under both hot and cold conditions.

- ❖ Cold lime soda process – carried out at 25 ^{o}C. (Reactions are slow)
- ❖ Hot lime soda process – carried out at 90 ^{o}C. (Reactions are fast)

- ❖ Cold lime soda process – Residual Hardness is 50 to 60 ppm.
- ❖ Hot lime soda process – Residual Hardness is 15 to 30 ppm.

Hard Water Softening Processes

Permutit (Zeolite) Process



Hard Water Softening Processes

Permutit (Zeolite) Process

Zeolite is hydrated sodium aluminosilicate capable of exchanging reversibly their sodium ions for hardness producing ions in water. They are also known as permutits.

Hydrated sodium aluminosilicate - $Na_2O.Al_2O_3.xSiO_2.yH_2O$; ($Na_2Ze$)
$x = 2\text{-}10$, $y = 2\text{-}6$

Zeolites are both natural and artificial.

Sodium zeolite – Na_2Ze which exchange Na^+ ions with the hardness producing ions like Ca^{2+}, Mg^{2+} in water.

Hard Water Softening Processes

Permutit (Zeolite) Process

1. Hard water is passed through bed of zeolite.

2. The hardness causing ions (Ca^{2+}, Mg^{2+}) are captured by zeolite.

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow Ca\,Ze + 2\,Na(HCO_3)$$

$$Na_2Ze + CaCl_2 \rightarrow Ca\,Ze + 2\,NaCl$$

$$Na_2Ze + MgSO_4 \rightarrow Mg\,Ze + 2\,Na_2SO_4$$

Hard Water Softening Processes

Permutit (Zeolite) Process

The zeolite mineral gets exhausted when all the Na+ are replaced by Ca $^{2+}$ and Mg $^{2+}$.

Zeolite can be regenerated by passing through NaCl solution.

$$\text{Ca Ze} + 2\text{NaCl} \rightarrow \text{CaCl}_2 + \text{Na}_2\text{Ze}$$

$$\text{Mg Ze} + 2\text{NaCl} \rightarrow \text{MgCl}_2 + \text{Na}_2\text{Ze}$$

Hard Water Softening Processes

Advantages of Permutit (Zeolite) Process

- In this process water about less than 10-15 ppm is obtained.
- It requires less time for softening.
- Process automatically adjust depending upon hardness of water.
- Water obtained is quite clear.
- Equipment requires less space.
- Less maintenance as well as operation skills.

Hard Water Softening Processes

Ion-Exchange Process

Ion-exchange resins are complex organic molecules having giant hydrocarbon framework.

Ion Exchange Resins

Cation Exchange Resins

Anion Exchange Resins

Hard Water Softening Processes

Ion-Exchange Process

Cation Exchange Resins

The ion exchange resins containing acidic groups are called cation exchange resin.

Example- R-COOH, $R\text{-}SO_3H$

$$2R\text{-}COOH + Ca^{2+} \longrightarrow (R\text{-}COO)_2Ca + 2H^+$$

$$2R\text{-}COOH + Mg^{2+} \longrightarrow (R\text{-}COO)_2Mg + 2H^+$$

Hard Water Softening Processes

Ion-Exchange Process

Anion Exchange Resins

The ion exchange resins containing basic groups are called anion exchange resin.

Example- R-NH_3OH

$$R\text{-}NH_3OH + Cl^- \longrightarrow R\text{-}NH_3Cl + OH^-$$

$$2R\text{-}NH_3OH + SO_4^{2-} \longrightarrow (R\text{-}NH_3)_2SO_4 + 2OH^-$$

Hard Water Softening Processes

Ion-Exchange Process

Recharge of Ion Exchange Resins

The exhausted cation exchange resins can be regenerated by reaction with dilute HCl or dilute H_2SO_4.

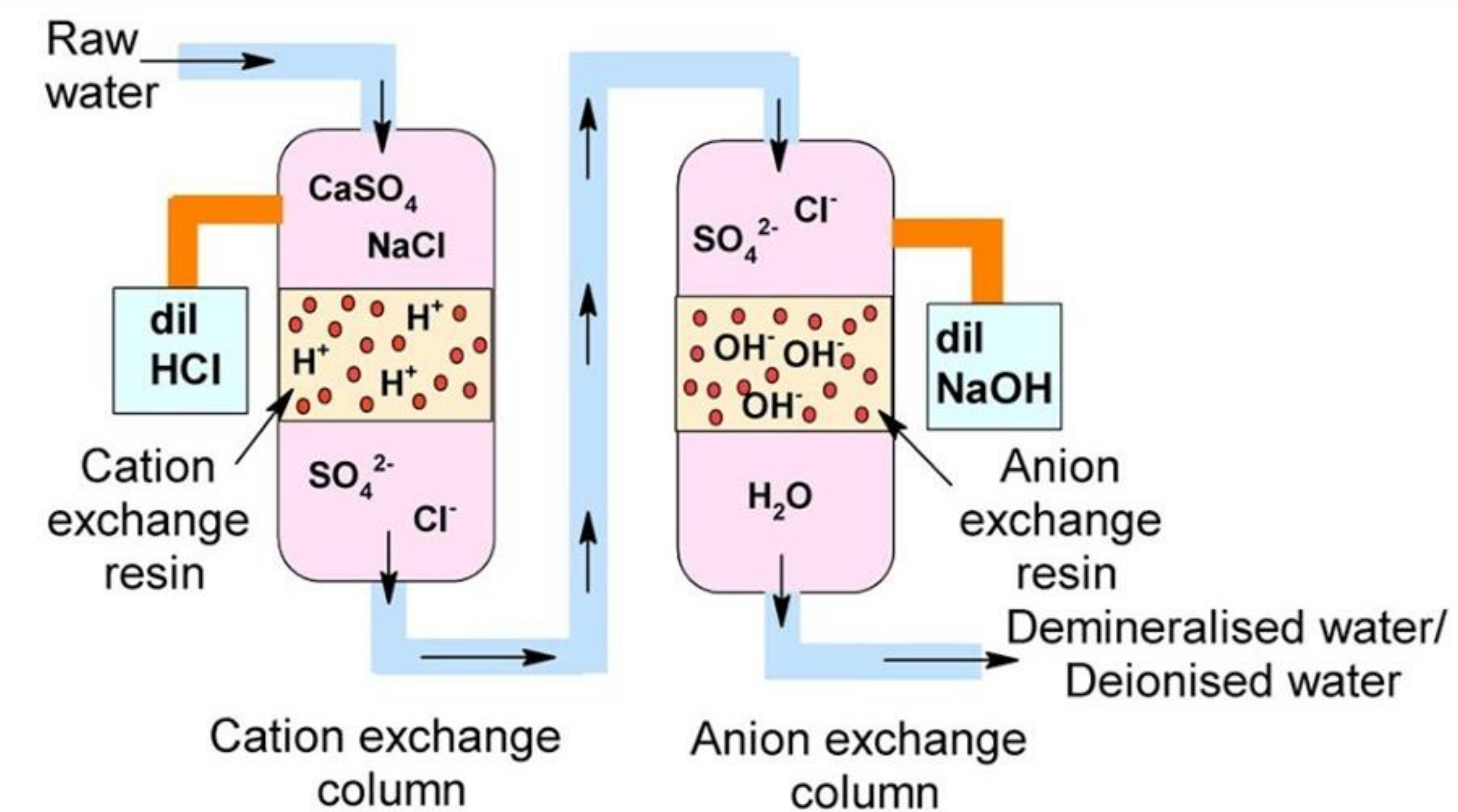
$$(R\text{-}COO)_2Ca + 2\,HCl \longrightarrow 2\,R\text{-}COOH + CaCl_2$$

The exhausted anion exchange resins can be regenerated by reaction with dilute NaOH.

$$(R\text{-}NH_3)_2SO_4 + 2\,NaOH \longrightarrow 2\,R\text{-}NH_3OH + Na_2SO_4$$

Hard Water Softening Processes

Ion-Exchange Process



Hard Water Softening Processes

Ion-Exchange Process

- ❖ **This process removes almost all the ions present in water.**
- ❖ **Soft water does not contain hardness producing Ca^{2+} and Mg^{2+} ions but it may contain other ions like Na^{+}, K^{+}.**
- ❖ **Every soft water is not demineralized water whereas every demineralized water is soft water.**
- ❖ **Ion exchangers are resins with a long chain, cross-linked, insoluble organic polymers with a microporous structure. The functional groups attached to the chains are responsible for the ion exchanging properties.**

Properties of Ion-Exchange Process

1. Non toxic.
2. Possess high ion exchange capacity.
3. Physically durable
4. Resistance to chemical attack.
5. Cheap and commonly available.
6. Capable of being regenerated and back washed easily and economically.
7. Possesses large surface area.

Hard Water Softening Processes

Difference Between Lime Soda, Permutit and Ion-Exchange Processes

Sr.no.	Lime-Soda process	Permutit (Zeolite) Process	Ion exchange (de-ionization) process
1.	Lower initial investment but running cost is high.	High initial investment but low running cost.	High initial investment but low running cost.
2.	Residual Hardness is 50 to 60 ppm.	Residual Hardness is about 10 ppm.	Treated water contains almost zero to 2 ppm hardness.

Hard Water Softening Processes

External and Internal Treatment of water

External Treatment

Carry out before its entry in to the boiler.

- **Lime-soda**
- **Zeolite**
- **Ion-exchange**

Internal Treatment

Suitable chemicals are added to the boiler water either to precipitate or to convert scale in to compounds.

- **Phosphate Conditioning**
- **Carbonate Conditioning**
- **Calgon Conditioning**
- **Sodium metaaluminate conditioning**

Hard Water Softening Processes

Phosphate Conditioning

Phosphate conditioning: It is used equally in low- and high-pressure boilers. Magnesium chloride which hydrolyses to form $Mg(OH)_2$ scale can be removed by adding appropriate sodium phosphate like NaH_2PO_4, Na_2HPO_4, or Na_3PO_4.

Hard Water Softening Processes

Phosphate Conditioning

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

$$3MgCl_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2\downarrow + 6NaCl$$

The choice of phosphate salt depends upon the alkalinity of the boiler feed water. Calcium can be precipitated properly at a pH of 9.5 or above so a phosphate is selected that adjusts pH to optimum value (9.5–10.5).

Hard Water Softening Processes

Carbonate Conditioning

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.**

$$\underset{\text{hard scale}}{CaSO_4} + Na_2\,CO_3 \rightarrow \underset{\text{loose sludge}}{CaCO_3\downarrow} + Na_2\,SO_4$$

Calgon Conditioning

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.

Hard Water Softening Processes

Calgon Conditioning

$$Na_2\,[Na_4\,(PO_3)_6] \rightarrow 2Na^+ + [Na_4\,(PO_3)_6]^{2-}$$

$$2CaSO_4 + [Na_4\,(PO_3)_6]^{2-} \rightarrow [Ca_2\,(PO_3)_6]^{2-} + 2Na_2SO_4$$

Soluble complex ion

$$2Na^+ + [Ca_2\,(PO_3)_6]^{2-} \rightarrow Na_2[Ca_2\,(PO_3)_6]$$

Soluble complex

Hard Water Softening Processes

Sodium metaaluminate ($NaAlO_2$) conditioning

Sodium metaaluminate ($NaAlO_2$) conditioning: Sodium metaaluminate gets hydrolyzed forming NaOH and a gelatinous precipitate of aluminum hydroxide.

Hard Water Softening Processes

Sodium metaaluminate ($NaAlO_2$) conditioning

$$NaAlO_2 + 2H_2O \rightarrow NaOH + \underset{\text{Gelatinous precipitate}}{Al(OH)_3}$$

The sodium hydroxide so formed precipitates Mg^{2+} as $Mg(OH)_2$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$

Chemical Survey of Water

Why we need chlorination of water

Water comes from a variety of sources, such as lakes and wells, which can be contaminated with germs that may make people sick. Germs can also contaminate water as it travels through miles of piping to get to a community. To prevent contamination with germs, water companies add a disinfectant, usually either chlorine or chloramine that kills disease-causing germs such as Salmonella, Campylobacter, and norovirus.

Chemical Survey of Water

What is chlorination of water

Chlorination is the process of adding chlorine to drinking water to kill parasites, bacteria, and viruses. Different processes can be used to achieve safe levels of chlorine in drinking water. Using or drinking water with small amounts of chlorine does not cause harmful health effects and provides protection against waterborne disease outbreaks.

Chlorine levels up to 4 milligrams per liter (or 4 ppm) are considered safe in drinking water. At this level, harmful health effects are unlikely to occur.

Analysis of Free Chlorine

Chlorine Added

Initial chlorine is added to water

Total Chlorine

Remaining chlorine left after chlorine demand of water

Chlorine Demand

Amount of chlorine reacted with organic, inorganic material and other compounds present in water prior to disinfection

Free Chlorine

Residual chlorine which has not reacted with any contaminants and is available for disinfection

Combined Chlorine

Chlorine combined with nitrogen and ammonia present in water and is unavailable for disinfection

Analysis of Free Chlorine

Chlorine is widely used for the disinfection of water. Chlorination is generally done with the help of bleaching powder or chlorine gas or with chloramines.

Excess of free chlorine present in water, makes the water unfit for drinking purposes as it not only imparts unpleasant taste to water but also adversely affects human metabolism. Hence the amount of free chlorine is estimated in municipal water before supplying it for domestic use.

Analysis of Free Chlorine

The estimation of free chlorine is based on the oxidation of KI by free chlorine i.e. by iodometric titration.

Thus when water sample containing free chlorine is treated with potassium iodide solution, the free chlorine present in water oxidizes potassium iodide and liberates an equivalent amount of iodine.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

Analysis of Free Chlorine

Q) Chlorine usage in the treatment of 25000 m^3/day is 9 kg/day. The residual chlorine after 10 minutes of contact is 0.2 mg/l. Calculate the dosage in milligram per liter and the chlorine demand of the water.

Chemical Survey of Water

Analysis of Free Chlorine

Solution:

Water treated per day = 25000 m^3 = 25 × 10^6 liters/ day

Chlorine consumed per day = 9 kg =9×10^6 mg/day

∴ Chlorine used per liter of water =$9 \times 10^6 / 25 \times 10^6$

= 0.36 mg/L

Also, residual chlorine (free chlorine) = 0.2 mg/L

Chlorine demand = 0.36 - 0.2 = 0.16 mg/L

Chemical Survey of Water

Total Alkalinity of Water

It is due to the presence of those types of substances in water which have tendency to increase the concentration of OH^- ions either by hydrolysis or by dissociation of water.

The presence of CO_3^{2-}, HCO_3^- ions which undergo hydrolysis and consume H^+ ions of water. As a result concentration of OH^- ions increases in water and water becomes alkaline.

Chemical Survey of Water

Total Alkalinity of Water

Alkalinity is a measure of ability of water to neutralize the acids.

- **Alkalinity in water is mainly due to HO^-, CO_3^{2-} and HCO_3^- ions.**

Determination of alkalinity by titrimetric method:

- **A known volume of hard water sample is titrated against standard acid using methyl orange and phenolphthalein as indicators.**

Colour change at end point:

- **Methyl orange: pale yellow to red**
- **Phenolphthalein: pink to colourless**

Total Alkalinity of Water

Involved reactions:

$OH^- + H^+ \rightarrow H_2O$

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

P alkalinity

$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2$

M alkalinity

- **Alkalinity caused by OH^- is called caustic alkalinity.**
- **Alkalinity caused by CO_3^{2-} is called carbonate alkalinity.**
- **Alkalinity caused by HCO_3^- is called bicarbonate alkalinity.**

Chemical Survey of Water

Total Alkalinity of Water

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.**

Total Alkalinity of Water

Q) 50 mL of a sample of water required 5 mL of N/50 HCl using methyl orange as indicator but did not give any coloration with phenolphthalein. What type of alkalinity is present?
Express the same in ppm.

Total Alkalinity of Water

Solution:

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 HCl

∴ 50 mL × N_M = 5 mL × N/50

or Normality = 5 mL × N/50 × 1/50 mL = 1/500 N (g/L)

Strength of alkalinity in terms of $CaCO_3$ equivalents

= N_M × Equivalent Weight of $CaCO_3$

1/500 g/L× 50 g

= 1/500 × 50 × 1000 mg/L

=100 mg/L

= 100 ppm

So, Alkalinity due to HCO_3^- ions = 100 ppm.

Hardness of Water

The hardness of water is due to the presence of soluble bicarbonates, chlorides and sulfates of calcium and magnesium. Water which does not give lather with soap is hard water.

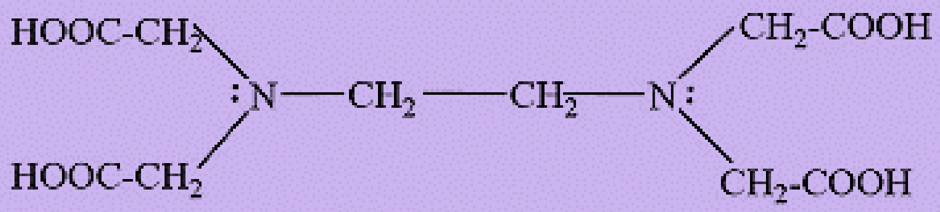
Types of hardness of water:

- **Temporary hardness – Due to hydroxides, carbonates and bicarbonates of Ca and Mg.**
- **Permanent hardness – Due to Sulfates, nitrates and chlorides of Ca and Mg.**

Determination of Hardness of Water

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 EDTA

Chemical Survey of Water

Determination of Hardness of Water

EDTA method

In order to determine hardness, hard water is buffered to a pH value of 10 using NH_4OH-NH_4Cl buffer and a few drops of Eriochrome black-T indicator (EBT) are added. EBT forms a weak unstable wine red complex with metal ions.

$$M^{2+} + EBT \longrightarrow M\text{-}EBT\ complex$$

($M^{2+} = Ca^{2+}, Mg^{2+}$) **(Unstable)**

Determination of Hardness of Water

EDTA method

During the course of titration of water sample against EDTA, EDTA combines with free Ca^{2+} or Mg^{2+} ions to give very stable metal–EDTA complex which is colorless.

$$\text{M-EBT complex} + \text{EDTA} \rightarrow \underset{\text{(stable)}}{\text{M-EDTA}} + \text{EBT}$$

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

Determination of Hardness of Water

Q) 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 ?

Chemical Survey of Water

Determination of Hardness of Water

Solution:

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

13 mL of 0.022 M EDTA =

$1 \times 13 \times 0.022 / 1 \times 0.01 = 28.6$ mg of $CaCO_3$

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

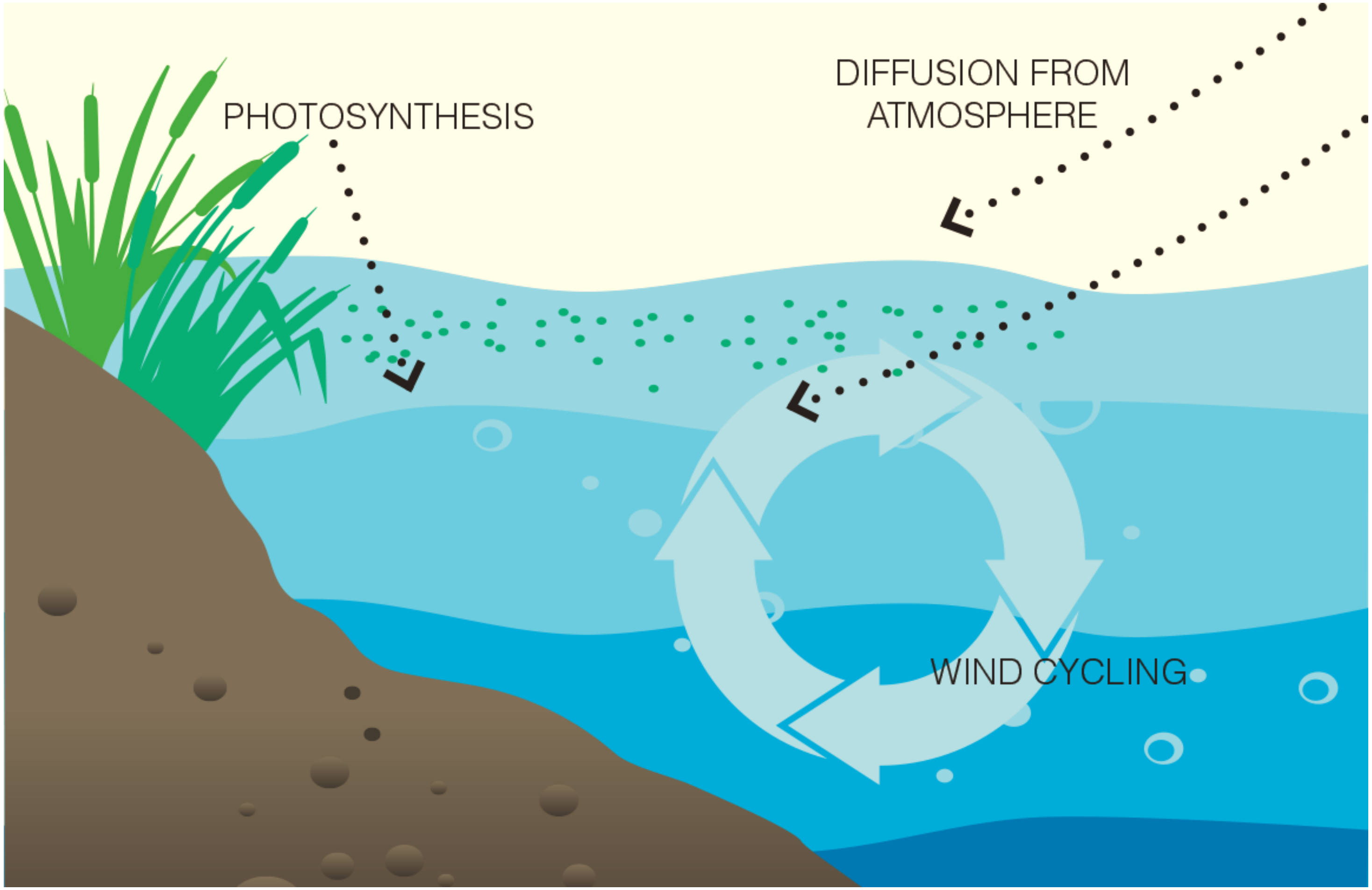
Hardness present in 1 liter = $28.6/250 \times 1000 = 114.4$ ppm

Chemical Survey of Water

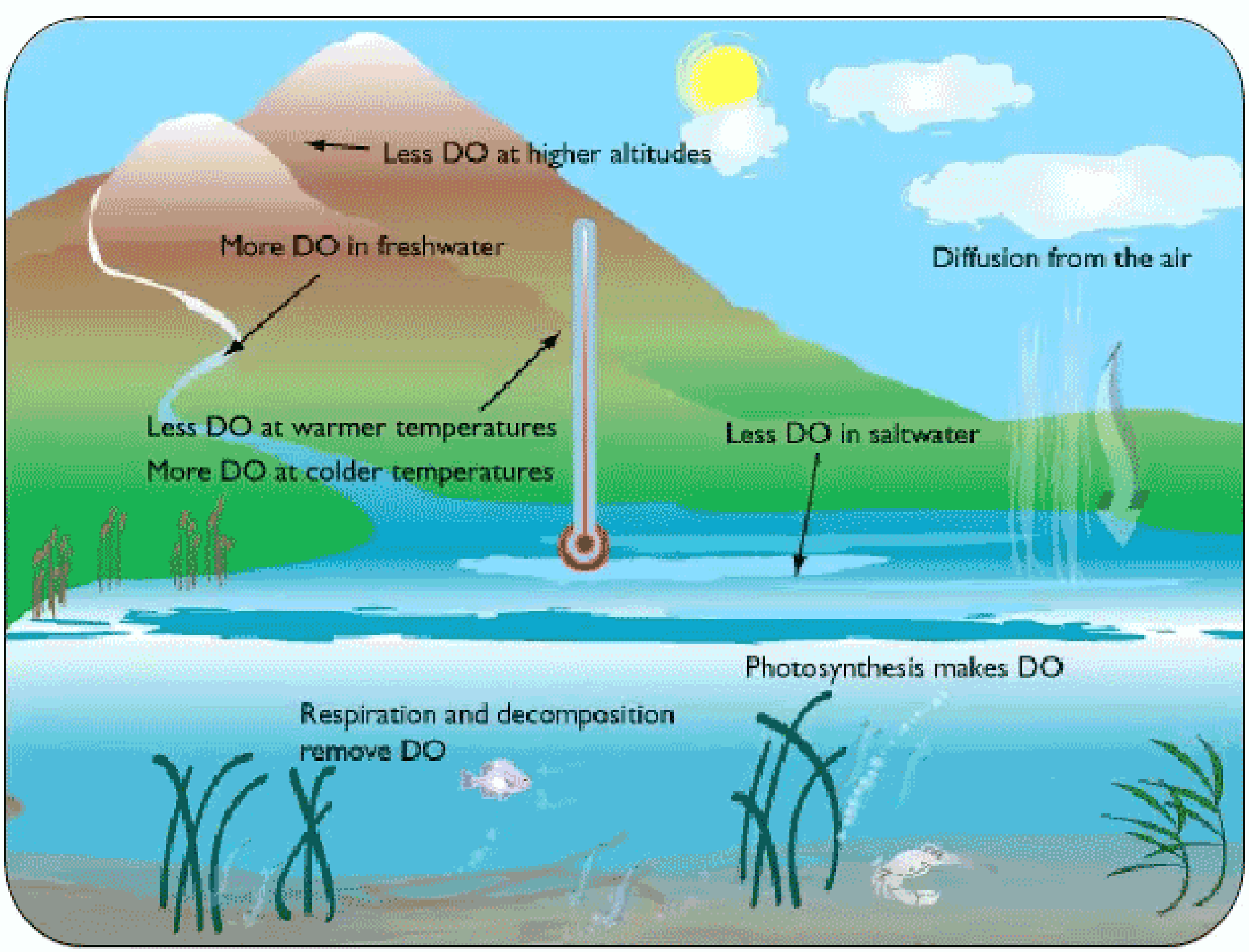
Dissolved oxygen of Water

- ❖ **Dissolved oxygen is the amount of gaseous oxygen present in water in its dissolved state.**
- ❖ **Dissolved oxygen is one of the most important indicator of health of a water body and its capacity to support a balanced aquatic ecosystem of plants and animals.**
- ❖ **A higher dissolved oxygen level indicates a better water quality.**
- ❖ **If dissolved oxygen level is too low some fish and other organisms may not be able to survive.**

Dissolved oxygen of Water



Dissolved oxygen of Water



Determination of Dissolved oxygen of Water

Dissolved oxygen levels can be measured by a basic chemical analysis method (titration method), an electrochemical analysis method (diaphragm electrode method), and a photochemical analysis method (fluorescence method). The diaphragm electrode method is the most widely used method.