3/9/22

Date: __/__/____
Page: _____

Water Chemistry

- **Hardness of water**: The property by which it prevents lather formation, is called hardness of water. Also known as soap consuming capacity of water.

Water + Soap (higher fatty acids salts of Na & K) ⟶ No lather / foam

$C_{17}H_{35}COONa/K$

Sodium/Potassium Stearate

- **Cause of Hardness of water**: due to presence of salts of (mainly) heavy metal (such as, but not limited to Mg, Ca and Fe & other heavy metals). Salts can be Carbonate, Bicarbonate (temporary hardness) and Chlorides, Sulphates (cause of permanent hardness).

- **Types of Hardness of Water**:

1.) **Temporary Hardness**: caused due to Bicarbonates ~~and Carbonates~~ of Ca & Mg (mainly) and can be removed by boiling.
and Carbonate of Mg

Removal of Temporary Hardness:

A.) By adding slaked lime ($Ca(OH)_2$)

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

Date: __/__/____
Page: _____

B. By Boiling:

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

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

2.) Permanent Hardness of Water: caused due to Chlorides and Sulphates of Ca & Mg (mainly) and can't be removed by boiling.

Removal of Permanent Hardness:

A.) Lime - soda method
B.) Zeolite method
C.) Reverse Osmosis (RO)
D.) Ion-exchange method

Disadvantages of Hardness of Water:

i.) Wastage of water in washing.
ii.) Boiler troubles → sludge & scale formation.
↳ boiler corrosion.
iii.) Harmful for body when taken in excess quantity.

Date: __/__/____
Page: _____

•	Hard Water	Soft Water
i)	Water which does not produce lather with soap	Water which produces lather/foam with soap.
ii)	It contains dissolved salts of Ca/Mg/heavy metals (Fe, Mn, Al)	It does not contains salts of Ca/Mg
iii)	Cleaning property of soap is suppressed due to dissolved salts. It is bad for washing & cleaning	Cleaning property of soap is not suppressed, hence it is ideal for washing & cleaning.
iv)	Due to presence of salts, B.P. of water is increased/elevated hence more fuel and time is required for cooking.	Less fuel & time is required for cooking ↑ if compared with hard water

- **Degree of Hardness:** also known as hardness of water in terms of $CaCO_3$ equivalents:
  Hardness of water is always calculated in terms of $CaCO_3$ for 2 main reasons:
  i) for easy calculations (mol. wt of $CaCO_3 = 100$ & equivalent wt $= \frac{100}{2} = 50$)
  ii) $CaCO_3$ is the most insoluble ppt.

Date: __/__/____
Page: _____

- **Calculation of equivalent $CaCO_3$:**

$CaCO_3$ equivalent = $\frac{\text{given mass of hardness producing salts} \times \text{equivalent wt of } CaCO_3}{\text{equivalent of given hardness producing salt}}$

- Equivalent wt of any Salt = $\frac{\text{Molecular wt of Salt}}{\text{Valency of cation}}$

- Equivalent wt of any Acid = $\frac{\text{Molecular wt. of Acid}}{\text{Basicity of acid}}$

* Basicity = replaceable H^+ ions

- Equivalent wt. of any Base = $\frac{\text{Molecular wt. of Base}}{\text{Acidity of Base}}$

* Acidity = replaceable OH^- ions

Units of Hardness of Water:

i.) **Parts per million (ppm):** 1 ppm ⇒ 1 part $CaCO_3$ equivalent hardness present in 10^6 parts of water.

ii.) **Milligrams per litre (mg/l):** 1 mg/l ⇒ 1 part $CaCO_3$ equivalent hardness present in 10^6 parts of water

iii.) **Degree french (°Fr):** 1° Fr ⇒ 1 part of $CaCO_3$ equivalent hardness present in 10^5 parts of water.

Date: / /
Page:

iv.) **Degree Clark (°Cl):** 1°Cl ⇒ 1 part $CaCO_3$ equivalent hardness present in 70,000 parts of water.

1 ppm = 1 mg/L = 0.1 °Fr = 0.07 °Cl

- **Zeolite / Permutit Method:** (External Method)

$Na_2O \cdot Al_2O_3 \cdot x\,SiO_2 \cdot y\,H_2O$ — Sodium Zeolite

$x = 2-10$ $\quad y = 2-6$

(Na_2Ze) or (Hydrated Sodium Alumino Silicate)

- **Types of Zeolite:**

	Natural Zeolite	Synthetic Zeolite
i.)	Non-porus.	Porus
ii.)	Amorphous	gel-like structure
iii.)	Durable	mix ($Na_2CO_3 + Al_2O_3 + SiO_2$) in proper ratio with water

Date: __/__/____
Page: _____

Working Principle:

A.) Softening of Water:

Hard Water → Zeolite Layer → Soft Water

(Ca / Mg salt containing water) || (Na₂ Ze) ⇓ gets exhausted → (Ca Ze / Mg Ze)

Na⁺ salt containing water (not responsible for hardness of water)

B.) Regeneration of Exhausted Bed:

Exhausted Zeolite Layer (Ca Ze / Mg Ze) → Brine Solution (10% NaCl) → Zeolite Layer (Na₂Ze) ⟹ will get out washings containing Ca^{++} and Mg^{++} ions

- Chemical Rxns:

A) Softening of Water

(Hard Water)		(Zeolite Bed)		(Exhausted Zeolite Bed)	(Soft water)
$Ca(HCO_3)_2$	+	Na_2Ze	→	$CaZe$	+ $2NaHCO_3$
$Mg(HCO_3)_2$	+	Na_2Ze	→	$MgZe$	+ $2NaHCO_3$
$CaCl_2$	+	Na_2Ze	→	$CaZe$	+ $2NaCl$
$MgCl_2$	+	Na_2Ze	→	$MgZe$	+ $2NaCl$
$CaSO_4$	+	Na_2Ze	→	$CaZe$	+ Na_2SO_4
$MgSO_4$	+	Na_2Ze	→	$MgZe$	+ Na_2SO_4

Date: __/__/____
Page: _____

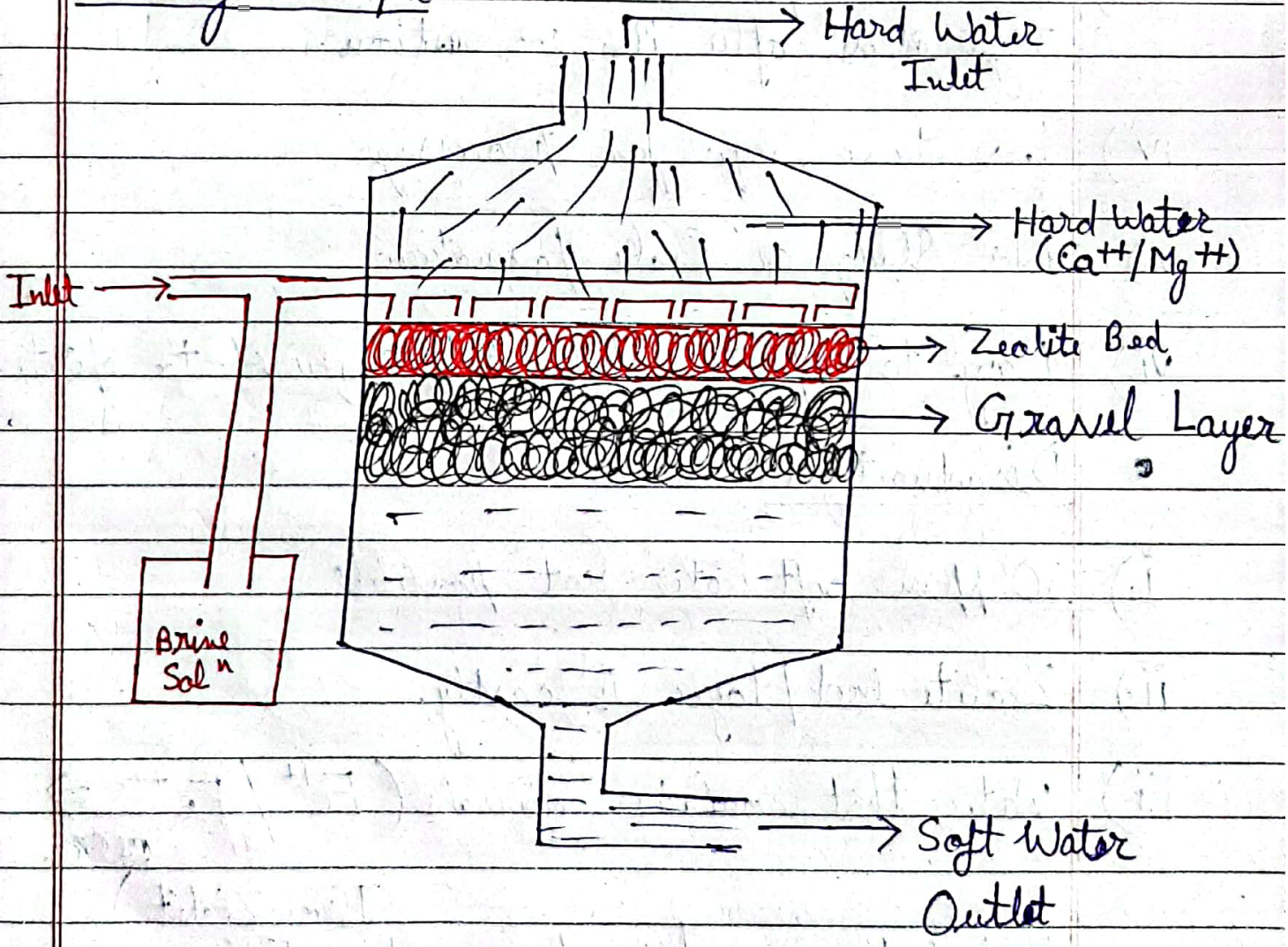
b) Regeneration

Brine Soln. (10% NaCl)

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$
$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

(Exhausted Zeolite Layer) (Brine Solution) (Regenerated Zeolite Layer) (Washing out)

- **Working Principle:**



Date: __/__/____
Page: _____

- **Advantages of Zeolite / Permutite Method:**

i.) Hardness of water, after passing thru zeolite/permutit method, is around ≈ 10 ppm which is the acceptable range of soft water.

ii.) Apparatus is compact.

iii.) Economic process as Zeolite bed can be regenerated after its exhaustion.

iv.) Less time req. for processing.

v.) No Sludge or Scale formation

vi.) Easy to operate, less skill required to operate.

- **Disadvantages:**

i.) 0 ppm soft water not possible.

ii.) Zeolite bed / layer is costly.

iii.) Water that contains minerals (Fe^{++} / Fe^{+++} ⇒ Iron Zeolite) that destroys zeolite layer and can't be regenerated.

iv.) Excess of Na^+ ions in soft water produced; that is responsible for boiler corrosion.

Date: / /
Page:

V.) There are acidic ions (HCO_3^-, CO_3^{--}) are present in water which needs further purification.

- **Steps to Calculate Hardness of Water by Zeolite Method:**

Amount of NaCl required for regeneration of Zeolite Bed (replacing Ca & Mg from $CaZe$ & $MgZe$) $\Longrightarrow$ amt of Ca & Mg salts present in water causing hardness of water.

Step 1: Calculation of amt of NaCl required for regeneration of exhausted Zeolite bed

Amt of NaCl required = Conc of NaCl soln (Mg in mg/l) × Volume of Brine soln (NaCl soln)

Step 2: Total Hardness ($CaCO_3$ equivalent of NaCl used)

$$\text{Total hardness} = \frac{\text{amt of NaCl} \times 100/2}{58.5}$$

Step 3:

$$\text{Hardness of water} = \frac{\text{Total Hardness}}{\text{Total volume of hard water supplied to Zeolite apparatus}}$$

Date: __/__/____
Page: _____

Final formula:

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

V_1 = Total volume of Water to be softened

V_2 = Volume of NaCl soln

m = mass of NaCl in V_2 volume (in gram)

- **Ion Exchange Process – Deionization and Demineralization of Water:**

Ion exchange Resin (Resin ⇒ a type of polymer, that show network-like structure)

In Ion-Exchange:

$CaCl_2 \longrightarrow Ca^{++}, Cl^-$

$MgSO_4 \longrightarrow Mg^{++}, SO_4^{--}$

Ca^{++}, Mg^{++} replaced by H^+ ions

Cl^-, SO_4^{--} replaced by OH^- ions