Water Treatment

Water is essential for life.

Sources of water

Sources
- Surface water
  - Flowing water
    - Streams
    - Rivers
    - Seas
  - Still water
    - Ponds
    - Lakes
    - Reservoirs
- Rain water
- Underground water
  - Springs
  - Wells
  - Tubewells

Impurities in water

Dissolved impurities : salts - carbonates, bicarbonates, sulphates, chlorides of Iron, Ca, Mg & Na, K etc.
Gases - CO_2, O_2, N_2, H_2S, NH_3 etc.

Suspended impurities : Inorganic - sand, clay
Organic - Vegetable and animal matter

Colloidal impurities : Finely divided silica & clay organic waste, colour etc.

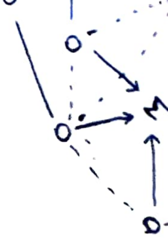
Microorganisms : Bacteria, Algae, Fungi etc.

Effect of impurities: can add colour, odour, turbidity, taste ~~etc~~ to water.

Hence water from any source must be treated before its use. The treatment depends upon the purpose for which water is to be used.

Specifications of water

Boiler feed water
Sugar Industries
Paper Mills
Laundaries, Textiles, Pharmaceutical industries, confectionaries



In all industries water is used.

Analysis of water

Hardness of water:

The water which does not form foam with soap is said to be hard water.

Hardness is the soap consuming capacity of wa.

Reasons for hardness: presence of calcium & Mg salts.

$$2C_{17}H_{35}COONa + CaSO_4 \rightarrow \underset{\text{insoluble}}{(C_{17}H_{35}COO)_2Ca} + Na_2SO_4$$

(sodium stearate)

$$2C_{17}H_{35}COONa + MgCl_2 \rightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$$

Types of Hardness:

Temporary

- due to presence of bicarbonates of Ca^{+2} & Mg^{+2}
- Removed by boiling

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$
$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2$$
$$MgCO_3 + H_2O \rightarrow Mg(OH)_2\downarrow + CO_2$$

- can be removed by adding lime

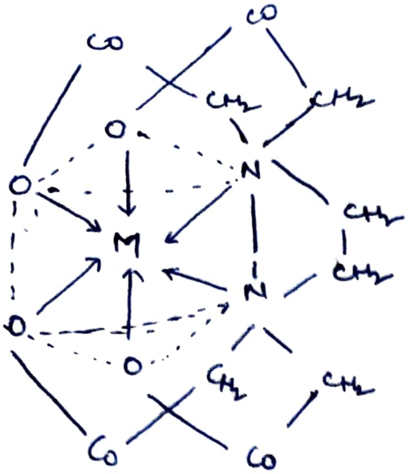
Permanent

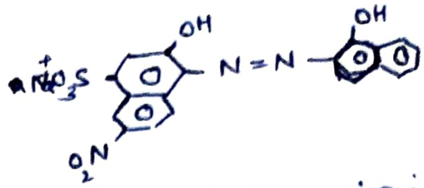
- sulphates & chlorides of Ca^{+2} & Mg^{+2}
- Cannot be removed by boiling
- Lime & soda both are required.

Hardness in terms of $CaCO_3$ equivalents

- Molecular wt of $CaCO_3$ is 100
- most insoluble substance

$$\text{Equivalents of } CaCO_3 = \frac{\text{Mass of the subs.}}{\text{Eq. wt. of the subs.}} \times \text{Eq. wt. of } CaCO_3$$





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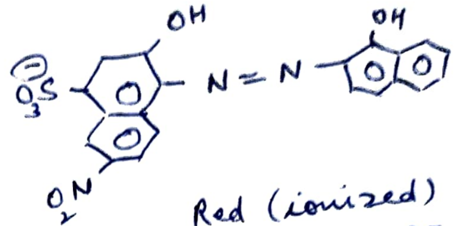


Red (ionized)

(sodium 1-(1- hydroxy-2- naphthylazo) 6-nitro-2- naphthol -4- sulphonate

Principle of EDTA method:

Mg^{+2} / Ca^{+2} + EBT $\rightarrow$ [EBT- Ca/Mg]
wine red (unstable)

Mg/Ca + EDTA $\rightarrow$ [EDTA - Ca/Mg]
colourless (stable)

[EBT- Ca/Mg] + EDTA $\rightarrow$ [EDTA- Ca/Mg] + EBT
colourless Blue

Procedure

- pH maintained - 8-10
- Indicator used - EBT
- End point - wine red to Blue

Preparation of solutions

standard solution of $CaCO_3$ - 1g/L

EDTA soln - 3.7g/L

EBT soln. - 0.5g/100 ml (alcohol)

Buffer soln. - 70g NH_4Cl + 570 ml conc. NH_3
↓
soln. is made one litre

Calculations

1. Determine the strength of SHW
2. strength of EDTA
3. Total hardness
4. Permanent hardness
5. Temporary hardness.

SHW (100 ml) + Buffer + EBT

↓ wine red

↓ Bl

of EDTA

$MgSO_4$ 95g — $Ca(HCO_3)_2$ 162g

$CaCl_2$ 111g ═ $CaCO_3$ 100g ═ $Mg(HCO_3)_2$ 146g

$MgSO_4$ 120g — $CaSO_4$ 136g

Multiplication factor $= \frac{\text{Eq. wt. of } CaCO_3}{\text{Eq. wt. of substance}}$

~~100 / 2 × molar mass of substance~~

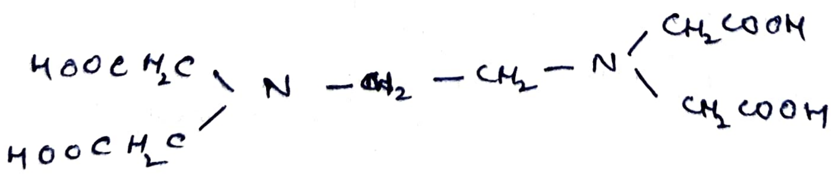
Units of Hardness

1. Parts per million (ppm) – parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.
2. Milligrams per litre (mg/L) – mg of $CaCO_3$ equivalent hardness per litre of water
3. Clarke's degree (°Cl) – $CaCO_3$ equivalent hardness per 70000 parts of water
4. Degree French (°Fr) – $CaCO_3$ equivalent hardness per 10^5 parts of water.

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1 °Fr = 0.07 °Cl$$

Determination of Hardness

EDTA method (Complexometric Titration)



Ethylene diamine tetra acetic acid

- hexadentate ligand
- Tetraprotic acid
- pH sensitive
- used as disodium salt
- forms 1:1 complex with Ca^{+2}/ Mg^{+2}

	(100 ml) + Buffer + EBT ↓ wine red ↓ ← EDTA Blue	SHW (100 ml) + Buffer + EBT ↓ wine red ↓ ← EDTA Blue	bhw + Buffer + EBT ↓ wine red ↓ ← EDTA Blue
Vol. of EDTA –	V_1 ml	V_2 ml	V_3 ml

100 ml SHW ≡ 100 mg $CaCO_3$

V_1 ml EDTA consumed for = 100 mg $CaCO_3$

1 ml $= \boxed{\frac{100}{V_1}}$

Strength of EDTA

$\frac{100}{V_1}$ mg $CaCO_3$ ≡ 1 ml EDTA

1 ml EDTA $= \frac{100}{V_1}$

V_2 — $= \frac{100}{V_1} \times V_2$

100 ml shw contains – $\frac{100}{V_1} \times V_2$

1000 ml --- – $\frac{100}{V_1} \times \frac{V_2}{100} \times 1000$

$$\boxed{\frac{V_2}{V_1} \times 1000}$$

Total hardness

1 ml EDTA = $\frac{100}{V_1}$

V_3 --- $= \frac{100}{V_1} \times V_3$

100 ml bhw $= \frac{100}{V_1} \times V_3$

1000 — $= \frac{100}{V_1} \times \frac{V_3}{100} \times 1000$

$$\boxed{\frac{V_3}{V_1} \times 1000}$$

permanent hardness

Temporary hardness = Total – permanent

Alkalinity of water

Ability of water to neutralize water.

Causes presence of CO_3^{-2}, HCO_3^- & OH^- ions.

All the three ions cannot present together.

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$$

* Caustic alkalinity OH^- & CO_3^{-2}
* Bicarbonate alkalinity HCO_3^-

Determination

Neutralization Titration

Indicators used Phenolphthalein and Methyl Orange
selective use of (indicators)

① $OH^- + H^+ \rightarrow H_2O$] P

② $CO_3^{-2} + H^+ \rightarrow HCO_3^-$] P, M

③ $HCO_3^- + H \rightarrow H_2O + CO_2$] M

Reaction no. 1 & 2 are indicated by " Methyl Orange

1, 2 & 3 "

Let volume of sample taken = 100 ml

Volume of acid used upto ph. end pt = V_1 ml.

Extra " " " M.O. end pt = V_2 ml

Normality of acid = N/50

Ph. Alkalinity in terms of $CaCO_3$ equivalents (P)

acid water

$N_1 V_1 = N_2 V_2$

$N_2 = \frac{N}{50} \times \frac{V_1}{V_2}$

$= \frac{1}{50} \times \frac{V_1}{100} \times 50$ — eq. wt of $CaCO_3$

$= \frac{1}{50} \times \frac{V_1}{100} \times 50 \times 1000$ mg/L

M O Alkalinity in terms of $CaCO_3$ equivalents (M)

$M = \frac{1}{50} \times \frac{(V_1 + V_2)}{100} \times 50 \times 1000$ mg/L

	OH^-	CO_3^{-2}	HCO_3^-
P = 0	×	×	✓ M
P = ½ M	×	✓ 2P	×
P < ½ M	×	✓ 2P	M − 2P
P > ½ M	(2P − M)	2(M − P)	×
P = M	M	×	×

LIME SODA PROCESS

Principle convert all the soluble hardness into insoluble ppts which are then removed by settling & filtration.

- Calculated amount of Lime and soda are added to water.
- Coagulants like $FeSO_4$, $Al_2(SO_4)_3$, $NaAlO_2$ may be added.

ange.

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

$$Mg(HCO_3)_2 + Mg(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$$

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$$

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3$$

$$Al_2SO_4 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4$$

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

$$H_2S + Ca(OH)_2 \rightarrow CaS + 2H_2O$$

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$

$$2NaHCO_3 + Ca(OH)_2 \rightarrow Na_2CO_3 + CaCO_3 + 2H_2O$$

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

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

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$$

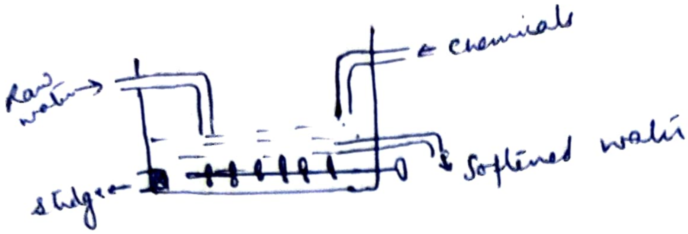
$L = \frac{74}{100}[$ $2 \times Mg(HCO_3)_2 + Ca(HCO_3)_2$ + perm. Mg + salts of Fe & Al + $CO_2 + H_2S$ + HCl + H_2SO_4 + HCO_3^- − $NaAlO_2$ in terms of $CaCO_3$ equivalents]

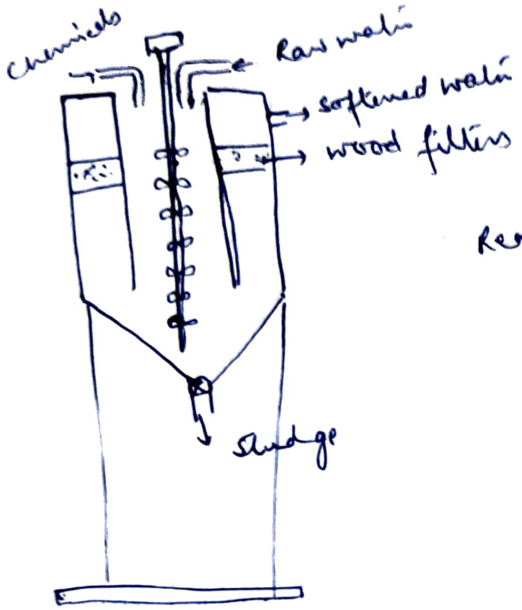
$S = \frac{106}{100}[$ Perm. Ca + perm. Mg + salts of Fe & Al + HCl + H_2SO_4 − HCO_3^- in terms of $CaCO_3$ equivalents]

* In Treated water
  - OH^- (added in lime as well as soda)
  - CO_3^{-2} (added in soda requirement)

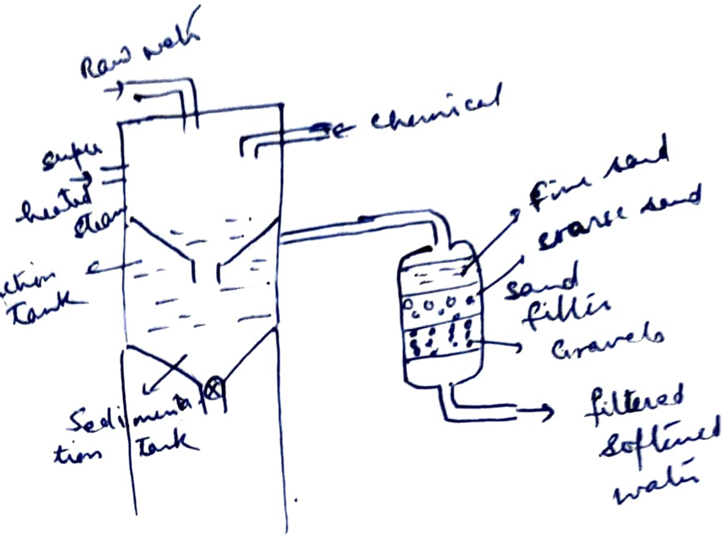
Lime Soda process

- Cold
  - Intermittent
  - continuous
- Hot
  - Batch
  - continuous





Cold continuous



Hot continuous

Zeolite Process

Or

Base Exchange process

Zeolites = Aluminosilicates minerals

$Na_2O \cdot Al_2O_3 \cdot x SiO_2 \cdot y H_2O$ $x = 2-10$, $y = 2-6$

Natural zeolite = green in colour, Thomsonite ($Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$)

Synthetic zeolite = porous, gel structure eg. permutit

can be represented as Na_2Z

Principle of water softening:

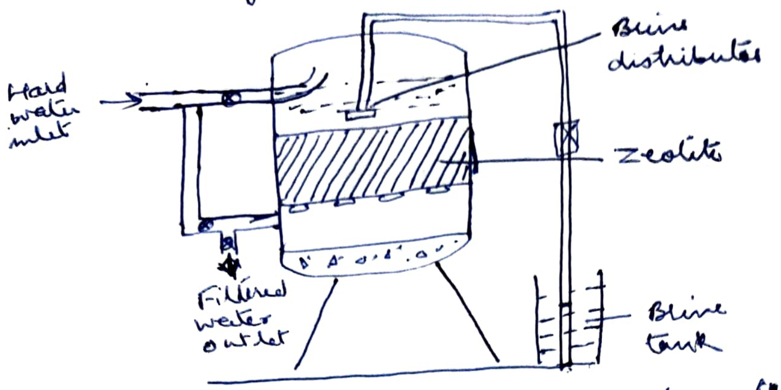
A reversible exchange of ions between a liquid phase (H_2O) and a solid phase (Na_2Z)

$$Ca(HCO_3)_2 + Na_2Z \rightarrow CaZ + 2NaHCO_3$$
$$Mg(HCO_3)_2 + Na_2Z \rightarrow MgZ + 2NaHCO_3$$
$$CaSO_4 + Na_2Z \rightarrow CaZ + Na_2SO_4$$
$$MgSO_4 + Na_2Z \rightarrow MgZ + Na_2SO_4$$
$$CaCl_2 + Na_2Z \rightarrow CaZ + 2NaCl$$
$$MgCl_2 + Na_2Z \rightarrow MgZ + 2NaCl$$

Sodium zeolite is converted

generation:

$$CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$$
$$MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$$



Advantages:
- water having low hardness (10 ppm) is produced.
- Plant is compact
- No sludge formation
- Running and maintenance cost is less.

Disadvantages:
- Not suitable for treatment of turbid water.
- Fe & Mn salts can be exchanged on zeolite bed.
- Process leaves $NaHCO_3$, cause of priming & foaming.
- Acidic or alkaline water can damage the zeolite bed

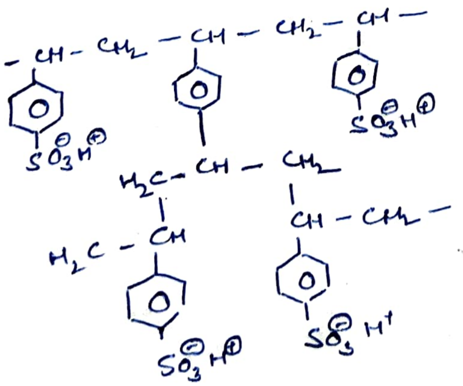
ION Exchange process

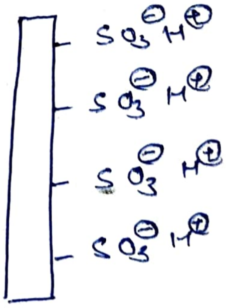
or

Deionization (Demineralization)

Ion Exchange resins
- Cross linked, long chain organic polymers
- microporous structure
- functional groups are responsible for ion exchange
- usually consist of styrene-divinylbenzene copolymer

Cation exchange resins
- contain acidic groups eg. $-COOH$, $-SO_3H$
- also called H-form cation exchanger.





- Exchangeable ion = $H^{\oplus}$
- $SO_3^{\ominus}H^{\oplus}$ strongly acidic
- $COOH$ weakly acidic
- Represented as $RH^{\oplus}$

Anion Exchange resin - contain basic functional groups amines, substituted amines, quaternary ammonium

- exchangeable ion - OH^-
- $-NH_2$, $=NH$ weakly basic
- quaternary ammonium salts = strongly basic
- represented as $R\,OH^-$

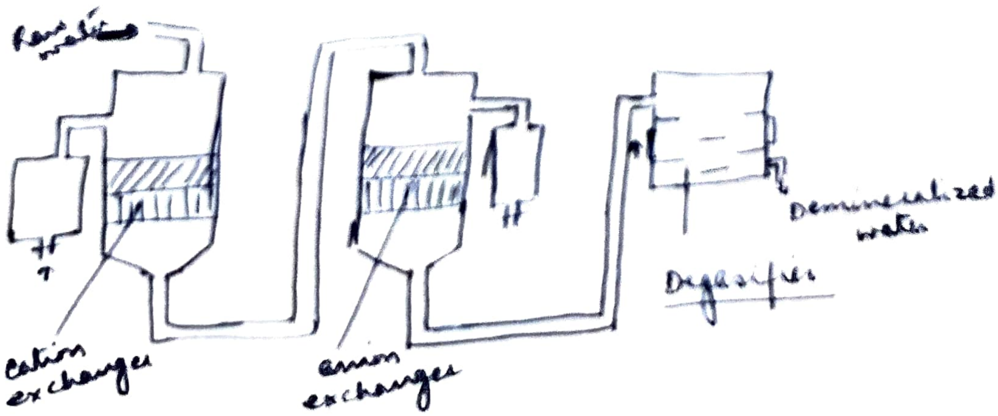
Reactions

$$2ROH^- + CaSO_4 \rightarrow R_2Ca^{+2} + H_2SO_4$$
$$2ROH^- + MgSO_4 \rightarrow R_2Mg^{+2} + H_2SO_4$$
$$2ROH^- + CaCl_2 \rightarrow R_2Ca^{+2} + 2HCl$$
$$2ROH^- + MgCl_2 \rightarrow R_2Mg^{+2} + 2HCl$$
$$R\bar{O}H + Cl \rightarrow RCl^- + \bar{O}H$$
$$2R\bar{O}H + SO_4^{2-} \rightarrow R_2SO_4^{2-} + 2OH$$
$$2ROH + CO_3^{-2} \rightarrow R_2CO_3 + 2OH$$
$$H^+ + OH^- \rightarrow H_2O$$

Regenerations

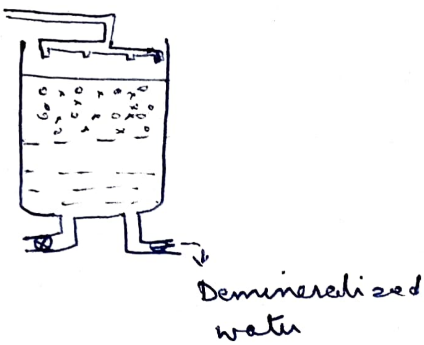
$$R_2Ca^{+2} + H_2SO_4 \rightarrow 2R\bar{H} + CaSO_4$$
$$R_2Mg^{+2} + H_2SO_4 \rightarrow 2R\bar{H} + MgSO_4$$
$$R_2Ca^{+2} + 2HCl \rightarrow 2RH^+ + CaCl_2$$
$$R_2Mg^{+2} + 2HCl \rightarrow 2RH^+ + MgCl_2$$
$$R_2SO_4^{2-} + 2NaOH \rightarrow 2R\bar{O}H + Na_2SO_4$$
$$R_2Cl^- + NaOH \rightarrow R\bar{O}H + NaCl$$

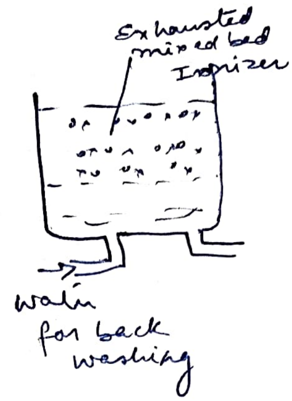
Advantages
- Highly acidic or alkaline water can be softened.
- water of very low hardness is produced (2 ppm)
- Anions as well as cations are removed therefore problems like caustic embrittlement and corrosion are reduced when treated water is used for boiler feed purpose

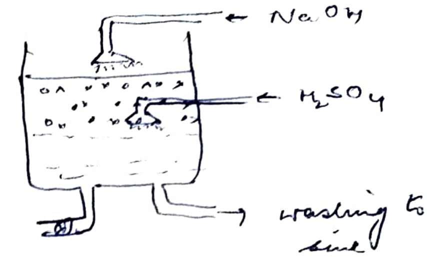


Disadvantages
- Equipment is costly
- Turbid water decreases the efficiency of process.

Mixed bed deIonizer







BOILER FEED WATER