(1) WATER TREATMENT

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→ Rainwater is purest form of natural water.
→ Sea water is most impure form of natural water.

Types of Impurities →

1. Dissolved Impurities
   (a) Inorganic salts → Cations
                       → Anions.
   (b) Gases (CO_2, O_2, etc.
   (c) Organic Matter.
2. Suspended impurities → Inorganic e.g clay & sand
                        → Organic, e.g oil globules, veg. etc.
3. Colloidal impurities ($10^{-4} - 10^{-6}$ mm) e.g clay & finely divided silica colloidal particles.
4. Micro-organisms eg Bacteria, fungi, algae etc.

Effect of Impurities →

→ Colour
→ Taste & odour.
→ Micro-organisms.
→ Turbidity & sediments
→ Dissolved minerals matter
   (a) hardness
   (b) Alkalinity
   (c) total solids
   (d) corrosion
→ Dissolved gas
→ Silica contents

Hardness of Water: defined as soap consuming capacity of water sample. (soap consuming capacity is mainly due to Ca, Mg & other heavy metals dissolved in it.

Soap → consist Na salts of fatty acids (Oleic, Palmitic & stearic)

→ Ca & Mg reacts with Na salts of long chain to form insoluble scums of Ca & Mg soaps.

Hard Water

→ does not produce lather or foam with soap.

→ consume more soap

contains HCO_3^-, Cl^- & other chlorides & SO_4^{2-} of Ca & Mg.

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

(Insoluble)

Soft Water

→ Soft water when treated with soap produce more lather & consume less soap as there is absence of dissolved salts of Ca & Mg.

$$C_{17}H_{35}COONa + H_2O \longrightarrow NaOH + C_{17}H_{35}COOH$$

Temporary Hardness	Permanent Hardness
→ caused due to presence of dissolved Mg & Ca HCO_3^-	→ due to presence of Cl^- & SO_4^{2-} of Ca & Mg
→ can be destroyed by boiling of water.	

→ Temporary Hardness.

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

(Insoluble)

(deposited at bottom of vessel)

$Mg(HCO_3)_2 \xrightarrow{90^\circ C} x MgCO_3 \cdot y Mg(OH)_2 \cdot z H_2O + a MgO + b H_2O + c CO_2$

Hardness :-

Equivalent of $CaCO_3$ = Mass of hardness producing substances / Chemical equivalent of hardness producing substances $\times 50$

units → ppm , mg/l , °Cl , °Fr

1ppm = 1mg/l = 0.1 °Fr = 0.07 °Cl

Estimation of Hardness :

(1) EDTA Method :

→ Eriochrome Black-T (EBT) → indicator.

pH at 9 – 10 maintain.

→ at end point colour change wine red – blue.

$(Ca^{2+}$ or $Mg^{2+}) + EBT \rightarrow [Ca\text{-}EBT](OH)[Mg\text{-}EBT]$

[Ca-EBT] (or) [Mg-EBT] + EDTA → [Ca-EDTA] or [Mg-EDTA] + E.B.T
Unstable complex (wine red) blue

$\Rightarrow M_2 = \frac{M_1 V_1}{V_2}$

M_1 = Molarity of Standard Hard water
V_1 = Volume of standard Hard water
M_2 = Molarity of EDTA
V_2 = Volume of EDTA

$M_2 \times 10^5 \Rightarrow$ permanent hardness when boiled.

Determination of Total Hardness:

M_3 (Molarity of Hard Water) $= \frac{(M_2 \cdot V_4)}{V_3}$

M_3 = Molarity of Hard Water
M_4 = Molarity of EDTA $= M_2$
V_3 = Volume of Sample Hard water
V_4 = Volume of EDTA

permanent hardness.

Total hardness $= M_3 \times 100 \times 1000$ (ml)
$= M_3 \times 10^5$ ppm

$\Rightarrow$ Temporary hardness = Total hardness − Permanent hardness.

Water Softening :-

→ Hardness in 300 - 500 mg/L as $CaCO_3$ range is considered excessive & leads to :
- → High soap consumption
- → Scaling in heating vessels & pipes.

→ even > 150 mg/L may result in consumer objection.

→ 60 - 120 mg/L as $CaCO_3$ is considered a moderate amount.

External Treatment	Internal Treatment
→ lime - soda	→ phosphate
→ Zeolite	→ Calcogen
→ Ion exchange	

LIME - SODA process :-

all soluble hardness-causing impurities are converted to insoluble which may be removed by filtration.

(Calculated amount of $Ca(OH)_2$ & Na_2CO_3 is added).

(i) Lime removes the temporary hardness.

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

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

(ii) Lime removes permanent Mg hardness

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaSO_4$$

(iii) Lime removes the dissolved iron & Al salts

$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2 \downarrow + CaSO_4$$

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 \downarrow + 3CaSO_4$$

(iv) Lime removes free mineral acids

$HCl + Ca(OH)_2 \longrightarrow CaCl_2 + H_2O$

$H_2SO_4 + 3Ca(OH)_2 \longrightarrow CaSO_4 + H_2O$

(v) Lime removes dissolved CO_2 & H_2S:

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

$H_2S + 3Ca(OH)_2 \longrightarrow CaS \downarrow + 2H_2O$

(vi) Soda removes all Ca permanent hardness.

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + NaCl$

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

Lime required for softening.

$\Rightarrow \frac{74}{100}$ (Temp. Ca^{2+} + 2 × Temp. Mg^{2+} + Perm ($Mg^{2+} + Fe^{2+} + Al^{3+}$) + ($CO_2 + H^+$ (HCl or H_2SO_4) + HCO_3^-]

Soda required for softening

$= \frac{106}{100}$ (perm ($Ca^{2+} + Mg^{2+} + Fe^{2+} + Al^{3+}$) + CO_2 + H^+ (HCl or H_2SO_4) - HCO_3^-]

Cold lime Soda process:-

Use of $NaAlO_2$ as coagulant also helps the removal of silica as well as oil if present in water.

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

$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2$

Advantages of high temp:

→ rxn proceeds faster

→ Softening capacity is increased

→ Much of dissolved gases are driven out of water.

→ Viscosity of soften water is lower, so filtration of water becomes easier.

⇒ Advantages of lime soda process:-

→ It is very economical.

→ The process increases the pH of the treated water.

→ If the process is combined with sedimentation lesser amount of coagulants shall be needed.

⇒ Disadvantages of lime soda process:-

→ Disposal of large amount of sludge poses a problem.

→ For efficient & economical softening, careful operat^n & skilled supervision is requisite.

→ This can remove hardness upto 15ppm which is not good for boiler.

WATER SOFTENING:

Ion exchange or dionizat^n or demineralizat^n process:-

→ Ion-exchange resins are insoluble, cross linked, long chain organic polymers with micro porous str. & the F.Gr attached to the chains are responsible for ion exchange properties

⇒ Resins containing acidic functional grps (-COOH, $-SO_3H$) are capable of exchanging their H^+ ions with other cations known as cation exchange resins (RH^+).

e.g Styrene-divinyl benzene copolymer on sulphonation

⇒ Resins containing basic functional groups ($-NR_3^+OH^-$) are capable of exchanging their anions with other anions which comes in their contact known as Anion exchange resins (ROH^-)

e.g Styrene-divinyl benzene on treated with aq. NaOH.

process →

$2RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$

$2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$ (remove all the cations)

$ROH^- + Cl^- \rightarrow RCl^- + OH^-$

$2ROH^- + SO_4^{2-} \rightarrow R_2SO_4^{2-} + 2OH^-$

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

Ion free water → deionized water.

Regeneration →

Cation exchange column + dil HCl or dil H_2SO_4

$R_2Ca^{2+} + H^+ \rightarrow 2RH + Ca^{2+}$

Exhausted anion exchange colum + dil NaOH

$R_2SO_4^{2-} + 2OH^- \rightarrow 2ROH + SO_4^{2-}$

Advantages.

→ Can be used to soften highly acidic or alkaline water.
→ It produces water of very low hardness

Disadvantages.

→ equipments costly
→ expensive chemicals are needed.
→ Output of process is reduced if water contains turbidity.

Zeolite (Permutit) method of softening of water :-

→ Zeolite (NaSAS), capable of exchanging reversibly its sodium ions for hardness producing ions in water.

$Na_2O \cdot Al_2O_3 \cdot x SiO_2 \cdot y H_2O$ ℰ

→ porosity or cavity size of synthetic zeolite structure can be controlled by varying the Si/Al ratio.

→ Ion-exchange process of zeolite structure is associated with Na ions.

Process of softening of by zeolite method :-

→ The hardness causing ions such as Ca^{2+}, Mg^{2+}, are retained by the zeolite bed as CaZe & MgZe.

The following rxns takes place during softening process.

To remove temporary hardness

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$
$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$

To remove permanent hardness

$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$
$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$

Regeneration of Zeolite bed :

$$\underset{\text{used zeolite}}{CaZe\ (or)\ MgZe} + \underset{\text{10\% brine}}{2NaCl} \longrightarrow Na_2Ze + \underset{\text{washings drained}}{CaCl_2\ (MgSO_4)}$$

Limitations of Zeolite process :-

→ If H_2O is turbid : then the turbidity causing particles clogs the pores of the zeolite & making it inactive.

→ The ions such as Mn^{+2} & Fe^{+2} forms stable complex zeolite which can not be regenerated ~~that easily~~ ~~by both~~

→ Any acid present in H_2O (acidic water) should be neutralized with soda before admitting the water to plant.

Advantages of Zeolite process:

→ Soft water of 10-15 ppm can be produced by this method
→ The equipment occupies less space
→ No impurities are precipitated
→ It does not require more time & more skill.

Disadvantages of Zeolite process:

(1) Soft water contains more Na salts than in lime soda process
(2) It replaces only Ca^{2+} & Mg^{2+} with Na but leaves all the other ions like HCO_3^- & CO_3^{2-} in the softened water
(3) It also causes caustic embrittlement due Na_2CO_3 hydrolysis to give NaOH.

Internal Treatment

phosphate Conditioning → Calgon → Colloidal Conditioning

phosphate conditioning

Scale formation can be avoided by

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$$

non-adherent & easily removable soft sludge of Ca & Mg phosphate.

Trisodium phosphate → alkalinity ↓
Disodium " → alkalinity suff.
Monosodium " → alkalinity of boiler water ↑

Calgon Conditioning

prevents the scale & sludge formation.

$$[Na_6(PO_3)_6] \longrightarrow 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

Calgon (Sodium hexa meta phosphate)

$$2CaSO_4 + [Na_4P_6O_{18}]^{-2} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

soluble complex ion.

Colloidal conditioning:

Scale formation can be avoided by adding organic substances like kerosene, tannin etc. which get coated on over the scale forming precipitate, yielding non-sticky & loose deposits.