Engineering Chemistry

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Water and its industrial applications

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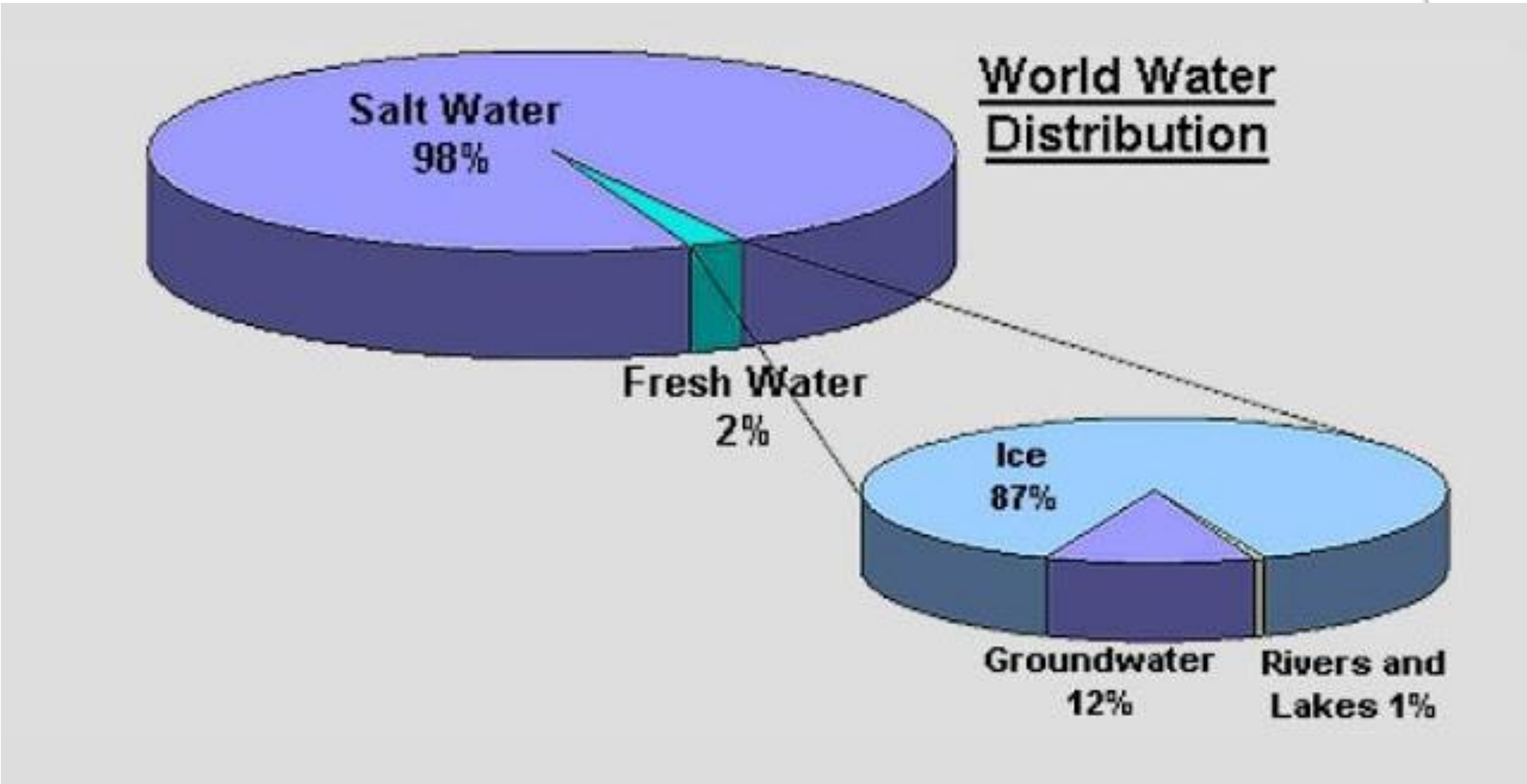
Sources of water

- Water is a precious gift of nature. It is important for sustaining life and affects every aspect of life.
- Ancient civilisations flourished along the perennial surface of water & wiped out due to improper utilisation of water resources.
- Sources include surface water, lakes and reservoirs, still water, rain water, sea water , ground water etc.
- Surface water contains dissolved CO2 & contact with basic materials dissolves them as bicarbonates.
- $CaCO_3 + CO_2 + H_2O \rightarrow$ **$Ca(HCO_3)_2$**
- $Ca(HCO_3)_2$ is soluble in water.

World water distribution



Impurities in water sources

- Water has ability to dissolve to some extent virtually every chemical compound & support every form of life. It is essential ingredient inspite of impurities present.
- Raw water supplies contains many contaminants , Major categories are:

1. **Suspended particles** includes silt, pipework debris & colloids. Colloidal particles give haze or turbidity to water & degree of contamination is given by fouling index test or Turbidimetry.
2. **Dissolved inorganic salts** include hardness causing salts derived from rock strata like bicarbonates of Ca & Mg ,silicates, ferrous & ferric ions, chlorides, aluminium , phosphates etc.
3. **Dissolved organic compounds** originates from decay of vegetable matter i.e. humic & fulvic acids and from farming, paper industry.

- **Microorganisms & pathogens** including amoeba, bacteria,paramecia & disease causing bacteria.
- **Dissolved gases** like CO2 . It dissolves in water to form carbonic acid & behaves as a weak anion & is removed by strongly basic anion exchange resins.

Effects of impurities

1. Odour: Decaying matter.
2. Taste: Dissolved minerals.
3. Bitter: Fe, Al, Mn , sulphates etc
4. Soapy: $NaHCO_3$
5. Brackish: Salts in high amount.
6. Palatable: CO_2 & NO_2
7. Colour: Metallic substance Fe , Mn, Humus, tannins, peat etc.
8. pH : It is polluted by DDT, explosives & battery industries.
9. Temperature: Discharge of effluents from industries increases the temperature of water and also increases the growth of algae and reduces the dissolved oxygen (DO).

Hardness & its units

- Water is of two types : Soft and Hard.
- Soft water produces lather readily with soap solution & hardness is below 100mg/lit. It contains little amount of Ca, Mg, Fe & Al ions.
- Advantages of soft water

1. Absence of any colour
2. Non-corrosive
3. Conservation of soap in laundry works.
4. No scale formation in boilers.
5. Proper cooking and saving of fuel.

- Hard water does not produce lather (foam) with soap readily & hardness is 100mg/lit.
- Hardness is defined as the capacity of water to produce lather with soap.It is caused by soap consuming properties of calcium & magnesium ions which are derived from bicarbonates and sulphates of calcium,magnesium and other heavy metals. No lather is formed untill these ions are completely removed & thus large amount of soap is wasted.
- $2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$
- $2C_{17}H_{35}COONa + MgCl_2 \rightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$
- Here Ca and Mg stearate formed are insoluble in water.

Types of Hardness

1. **Temporary, Alkaline or Carbonate hardness**

- It is caused by bicarbonates of Ca & Mg in water.
- It can be removed by boiling
- Bicarbonates decompose on boiling & yield insoluble carbonates or hydroxides which deposit as a crust at the bottom of the vessel.

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

- $Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H_2O$
- Insoluble Ca & Mg carbonates are formed.

2. **Permanent, Non-alkaline or Non- carbonate hardness**

- It is caused by presence of sulphates & chlorides of calcium, magnesium, iron & other heavy metals.
- Hence salts responsible are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$,$Al_2(SO_4)_3$ etc.
- It is not destroyed on boiling.
- There are various chemical & physical methods to remove permanent hardness.

Degree of Hardness

- The hardness of water is usually expressed in terms of equivalent amount of $CaCO_3$ but it is never present in the form of calcium carbonate because it is insoluble in water. Reason of choosing $CaCO_3$ as standard for reporting hardness are :

1. It is the most insoluble salt that can be precipitated in water treatment.
2. Its molecular weight being 100 renders calculations easily.

Equivalents of $CaCO_3$

$$= \frac{[\text{Mass of hardness producing substance in Mg/Lit}] * [\text{Chemical equivalent of } CaCO_3] * 2}{[\text{Chemical equivalent of hardness producing substance}] * 2}$$

= [Mass of hardness producing substance in Mg/Lit]*[100/2*Chemical equivalent of hardness producing substance]

= [Mass of hardness producing substance in Mg/Lit]* (Multiplication factor)
in mg/lit **Or** ppm

Multiplication factors for different salts

Constituent salt/ion	Molar mass	n- factor	Chemical equivalent molar mass n-factor	Multiplication factor for converting equivalent of $CaCO_3$
$Ca(HCO_3)_2$	162	2	162/2=81	100/(2*81)=100/162
$Mg(HCO_3)_2$	146	2	146/2=73	100/(2*73)=100/146

Advantages and disadvantages of hardwater

- Advantages

1. Some people like its taste which is due to Ca & Mg.
2. Ca produces strong teeth and bones.

- Disadvantages

1. More minerals in water uses more soap in laundry works.
2. Bathing with it produces sticky curd like substance which causes skin irritation & hair becomes dull & unmanagable.
3. Produces scales which clogs pipes & decreases the life of flushing units.
4. Laundering in hardwater, decreases the life of clothes.

- Soap curd deposits on dishes, bathtub, showers etc.
- Boiling point of water increases due to salts therefore more fuel and time is wasted in cooking.
- Bad for digestive system.

Units of hardness

- Ppm (Parts per million)

  It is parts of $CaCO_3$ equivalent hardness per million parts of water.

  1ppm = 1 part of $CaCO_3$ in 10^6 part of water.

  i.e. unit weight of solute per million unit of solution.

- Milligram per litre (mg/lit)

  Number of milligram of $CaCO_3$ equivalent hardness present per litre of water.

  1 part of $CaCO_3$ equivalent per 106 parts of water.

- Clark degrees [° Clark] / English degree [°E]

One degree clark corresponds to one grain of calcium carbonate in one gallons of water which is equivalent to 12.48 parts of $CaCO_3$ in 1,000,000 parts of water.

1 part of $CaCO_3$ equivalent = 70000 parts of water.

- French degrees [°Fr]

One degree french corresponds to one part of calcium carbonate in 100000 parts of water.

1 part of $CaCO_3$ equivalent = 10^5 parts of water.

- Mili equivalent per million (e.p.m)

It is the number of equivalents of substance present per million , hence known as equivalent per million.

- Degree of general hardness (dGH)

One degree of general hardness corresponds to 10 mg of calcium oxide or magnesium oxide per litre of water. The precise mixture of minerals dissolved in the water together with the acidity or alkalinity (pH) and temperature will determine the behaviour of the hardness, so single number on a scale does not give a full description.

Softening of water by various methods

- The removal of ions causing hardness like Ca^{2+} and Mg^{2+} is termed as softening of water.
- Softening is important because hardwater is unsuitable for domestic or industrial process.

1. External treatment

- In external treatment water is treated externally before it is fed into the boiler by following methods:

a. Lime soda process
b. Zeolite or permutit process
c. Ion exchange or demineralisation process

Lime-soda process

- Here soluble hardness causing impurities are converted into insoluble precipitate which can be removed by settling and filteration.
- Soluble bicarbonate is converted into insoluble carbonate by raising pH near10.3 by using quick lime (CaO) or hydrated limeCa(OH)2.
- $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + H_2O$
- For non-carbonate hardness , soda ash Na2CO3 with Ca(OH)2 is added.
- $MgSO_4 + Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 + Mg(OH)_2$

- Small quantity of coagulant like alum $K_2(SO_4)\cdot Al_2(SO_4)_3\cdot 24H_2O$ is added to entrap fine ppt. Of $CaCO_3$ and $Mg(OH)_2$.

- Types of lime soda process-
- 1. Cold lime soda process
- 2. Hot lime soda process

Cold lime soda process

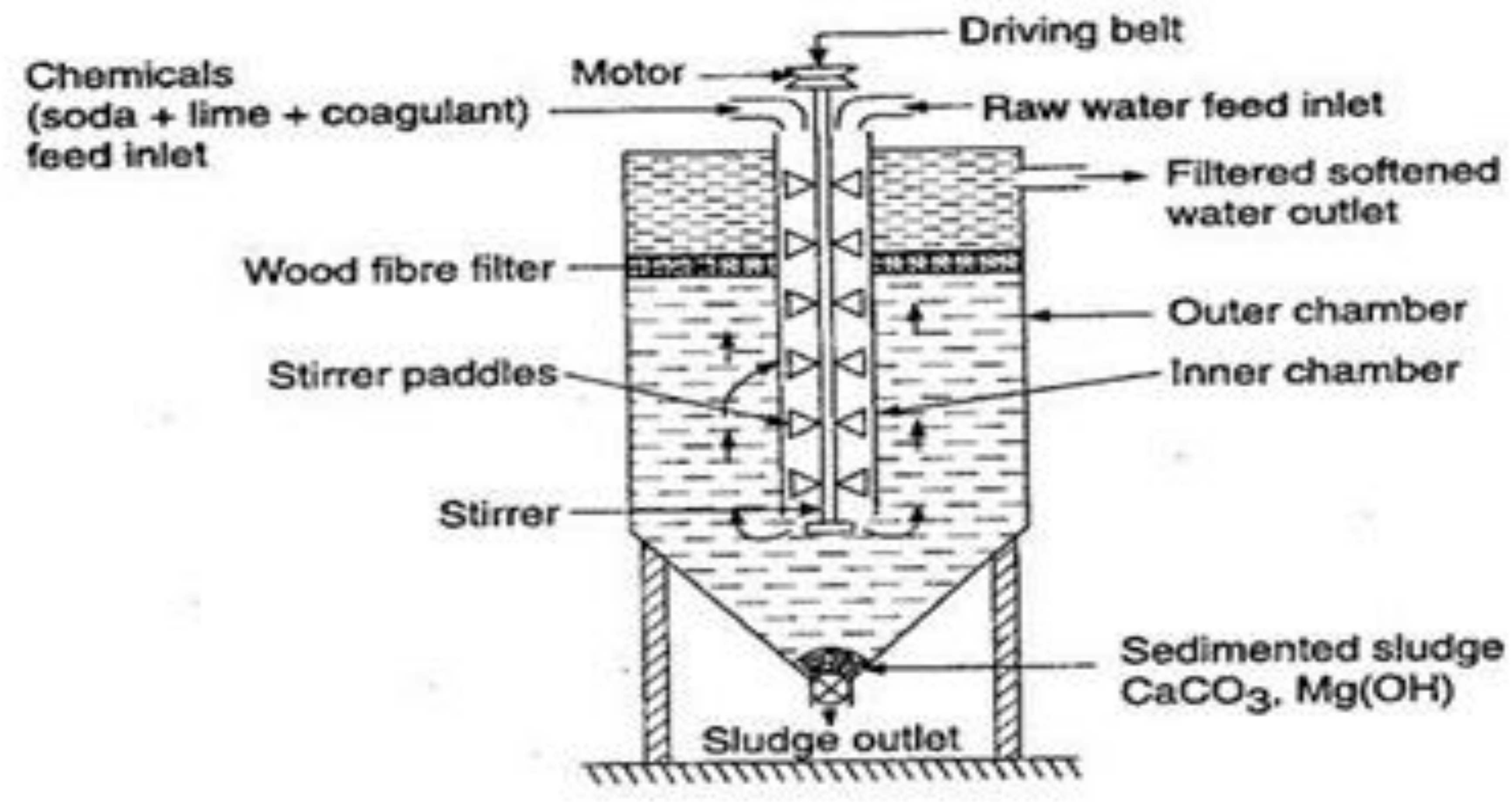
- Hard water is analysed and fed into vertical circular chamber fitted with stirrer .
- Now calculated quantity of lime & soda ash is added.
- Coagulant like alum is added to entrap precipitate of CaCO3 , Mg(OH)2 , silica and oil.
- Constant stirring and mixing causes softness.
- Sludge settles down in outer chember & softened water comes up.

- $\mathbf{3}Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow \mathbf{3}CaSO_4 + \mathbf{2}Al(OH)_3$

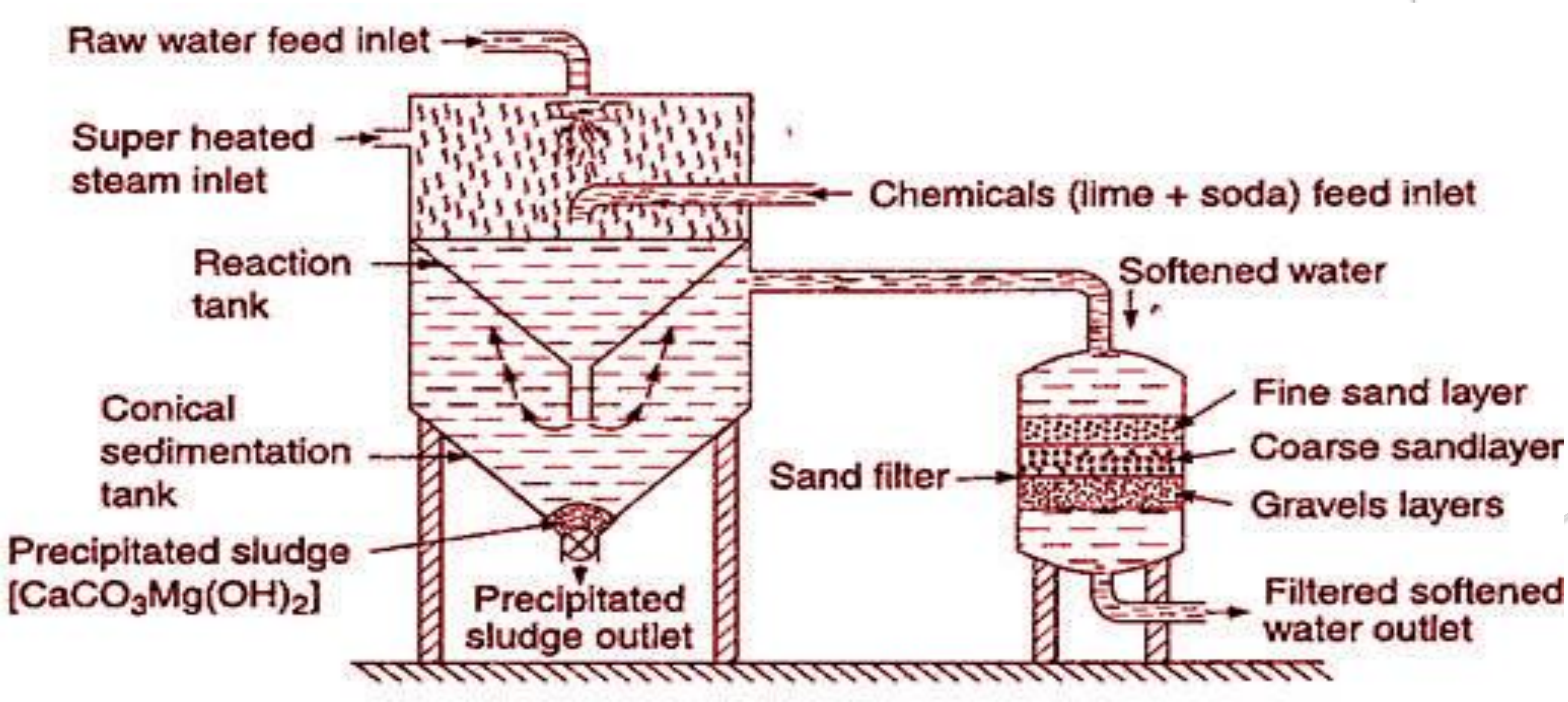
- Softened water is passed by filteration unit and finally filtered soft water flows out through outlet at the top.
- Cold lime soda provides residual hardness of 50-60 ppm.

- Limitations : In this process , reaction occurs at room temperature due to which partial softening of water occurs.

Continous cold lime soda process



Continous hot lime soda process



Hot lime soda process

- Water treated with chemicals at temperature 94-1000˚C.
- Reaction much faster and precipitation is complete.
- Precipitate form quickly & settle rapidly.
- So no coagulants needed.
- Dissolved gases like O2 &CO2 also removed.
- Softened water is 15-30ppm of residual hardness in hot lime process.

Comparison between hot lime & cold lime process

cold lime process	hot lime process
Reaction occurs at room temperature	Temperature is 94-1000˚C
Coagulation, ppt settles	Coagulant not required
Slow process	Rapid process
No fuel consumption	Steam used
Temp. hardness- lime used	Temp. hardness- bioling, no lime used
Residual hardness-60 ppm	Residual hardness- 15-30 ppm
Dissolved gases not removed	Dissolved gases are removed-CO2 & 02

- Advantages
- Economical
- Hydrated lime increases ph , less corrossive tendency.
- Decreases hardness causing salts & minerals
- Removes Fe & Mn also to some extent.

- Disadvantages
- Skilled person
- Sludge disposal
- Zero hardness water not produced.

Zeolite or permutit process

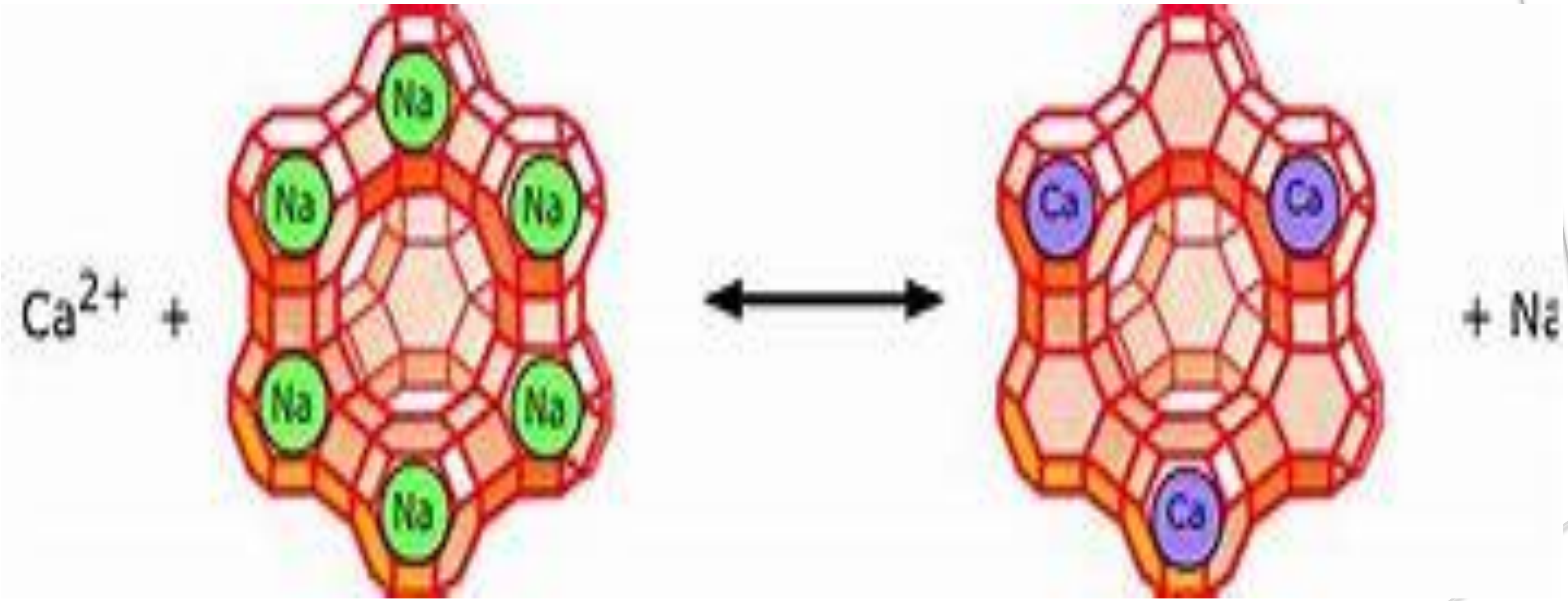
- It is a greek word meaning – Zein meaning to boil &
  Lithos meaning stone
- Minerals having microporous structure .
- Basically alumino silicate mineral with open structure that can accommodate a wide variety of cations such as $Na2+$, $K+$, $Ca2+$, $Mg2+$ and others.
- These positive ions are either loosely held or can be exchanged for others in contact solutions.
- Zeolites- aluminosilicate members of the family of microporous solids known as 'molecular sieves'.

- Molecular sieves refers to the ability to selectively sort molecules on size exclusion principle.
- Eg- analcite, chabazite , heulandite , natrolite, phillipsite, stilbite.
- Natrolite is a tectosilicate mineral and is hydrated sodium & aluminium silicate.
- Zeolites form naturally when volcanic rocks and ash layers reacts with alkaline ground water.

Principle of softening by zeolite method

- Calcium or magnesium ions in water displace sodium ions from zeolite which are released into water (Na ion)
- As zeolite converts its Ca2+ forms , they loose effectiveness & must be regenerated
- Regenration: By passing conc. brine (NaCl) solution through them causing reaction to reverse.

Principle of softening by zeolite method



Process

- Steel tank has thick layer of permutit
- Hardwater percolated at specific rate through zeolite bed
- Calcium and magnesium retained by zeolite (CaZe & MgZe)
- Outgoing water contains Na salts.

- X represents zeolite, the exchange material

Removal of carbonate hardness:

- $Ca(HCO_3)_2 + Na_2X$ ------> $CaX + 2NaHCO_3$
- $Mg(HCO_3)_2 + Na_2X$ ------> $MgX + 2NaHCO_3$

Removal of non-carbonate hardness:

- $CaSO_4 + Na_2X$ ----- > $CaX + Na_2SO_4$
- $CaCl_2 + Na_2X$ ------> $CaX + 2NaCl$
- $MgSO_4 + Na_2X$ ------> $MgX + Na_2SO_4$
- $MgCl_2 + Na_2X$ ------> $MgX + 2NaCl$

Regeneration of zeolite

- After sometimes zeolite is converted into Ca & Mg zeolite & loses sodium exchange capacity and gets exhausted.
- To regulate exhausted zeolite , supply of water is stopped & reclaimed by treating bed with 10% sodium chloride solution.
- $CaX + 2NaCl \dashrightarrow Na_2X + CaCl_2$
- $MgX + 2NaCl \dashrightarrow Na_2X + MgCl_2$
- Washings containing $CaCl_2$ and $MgCl_2$ are led to drain & regenerated zeolite bed again used for softening purpose.

Advantages of zeolite process

- 10 ppm hardness water is produced.
- Equipment is compact & occupies less space.
- Hardness causing ions are exchanged with Na ions , No ppt or sludge formation occurs.
- Running, maintenance is less.
- Less skilled workers can also operate.
- Adjusts automatically according to hardness of water.

Disadvantages of zeolite process

- Sodium salt simply gets flushed out of the system, usually released to drain or soil causing damaging consequences to environment specially arid regions. Therefore many jurisdictions prohibit such release & disposal of spent brine should be done at approved sites.
- Not suitable for turbid water since it clogs the pores of bed & makes bed inactive.
- Mn & Fe should be removed beforehand because they form MnZe & FeZe which is difficult to regenerate.
- Water used should be free from acid because acid destroys zeolite bed.
- Hot water cannot be used since it dissolves zeolite bed.
- Treated water contains more sodium salt than lime soda process.
- Only cations are removed.

Ion exchange or Deionization or Deminerelization process

- A reversible exchange of ions takes place between the stationary ion exchange phase and external liquid mobile phase.
- Ion exchange resin consist of an insoluble polymer matrix that is permeable.
- Such resin consist of cross-linked , long chain organic polymers with a microporous structure.
- Functional group attached to polymer causes ion exchange.
- Most typical resin is cross-linked polysterene .
- Required active/ functional group can be added after polymerisation or substituted monomer can be used.

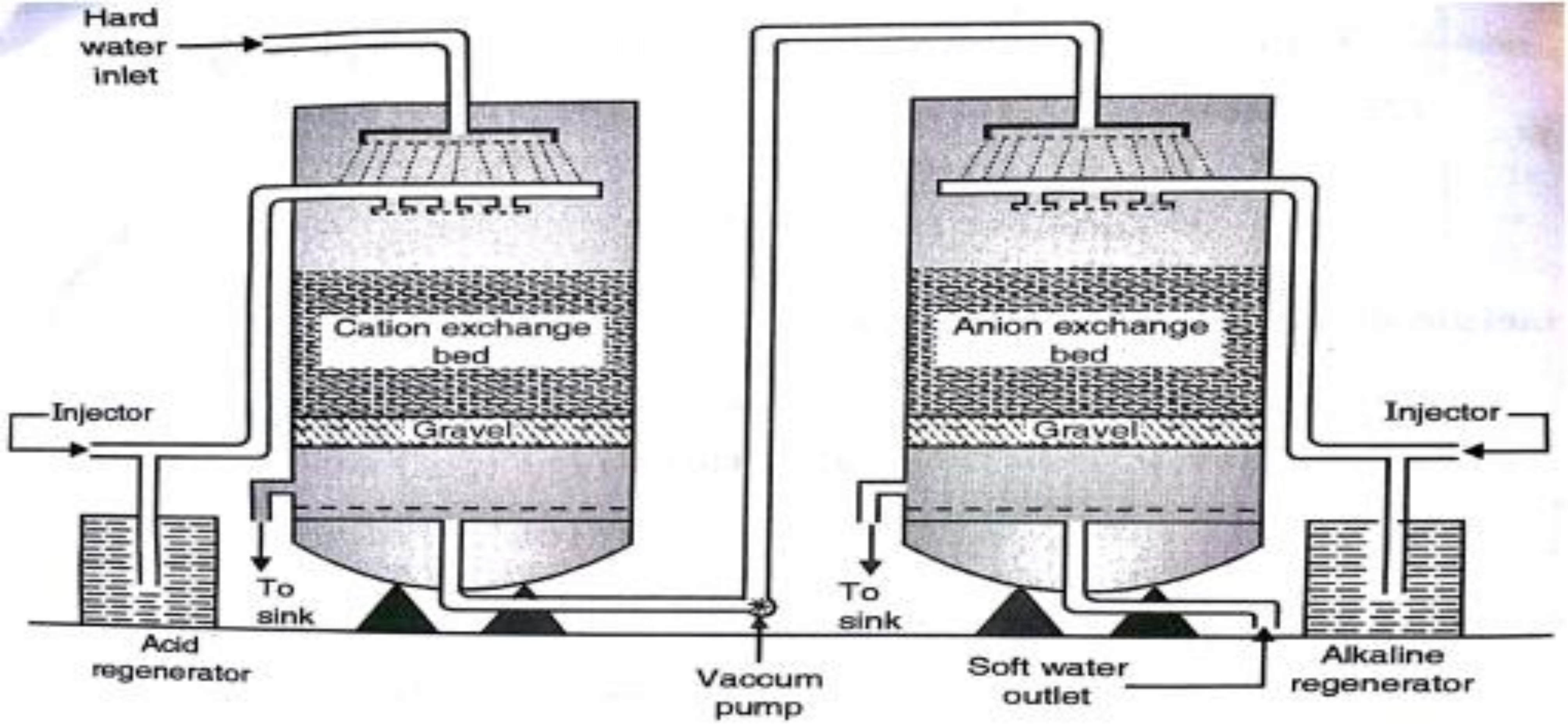
Cation exchange resin (RH+)

- H+ ions are exchanged with the cations of the solution.
- Usually styrene divinyl benzene copolymer is used which on carboxylation or sulphonation become capable of exchanging their H+ ions with cations of the solution.
- Cation exchange resin – Amberlite IR-120 and Dowex -50

Anion exchange resin (ROH-)

- OH- ions are exchanged with anions of the solution.
- Usually styrene divinyl benzene or amine formaldehyde copolymer which on treatment with dilute NaOH solution become capable of exchanging their OH- ions with anions of the solution.
- Anion exchange resin- Amberlite-400 and Dowex-3

Ion exchange process diagram



Demineralisation Diag. 2

Ion exchange process

- Water passes through column containing hydrogen ion exchanger (cation exchanger) .
- Then water passes through second column containing hydroxyl ion exchanger (anion exchanger) .
- H+ and OH- ions released from cation exchanger and anion exchanger column gets combined to produce water molecule.

- Cation removal:

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

$2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$

- Anion removal:

$R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-$

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

$2R'OH^- + CO_3^{2-} \rightarrow R_2CO_3^{2-} + 2OH^-$

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

Regeneration of resins

- Cation and anion resin loose capacity to exchange , then they are called as exhausted.
- An exhausted cation exchange resin is regenerated by passing a solution of dil. HCl or H2SO4.
- An exhausted anion exchange resin is regenerated by passing a solution dil. NaOH.
- The columns are washed by deionized water & washings (Ca2+, Mg2+, SO4^{2-}, Cl-) are drained or sinked.
- Freshly regenerated resin is again used.

Regeneration of resins

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

- $R_2' SO_4^{2-} + 2\,OH^- \rightarrow 2R'OH^- + SO_4^{2-}$

- Washings (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-) are drained or sinked.

Ion-exchange advantages & disadvantages

- Advantages

1. Produces 2 ppm water which can be used in boilers.
2. Highly acidic or highly alkaline water can be softened.

- Disadvantages

1. Costly equipment & chemical for regeneration.
2. Turbid water cannot be used, it decreases life of resin.

Internal treatment / Sequestration

- Water is treated inside the boiler is called internal treatment.
- In this process , also called sequestration, an ion is prohibited to exibit its original character by complexing or converting it with more soluble salt by adding appropriate reagent.
- In this process certain chemicals are added which either convert the scale forming impurity in the form of sludge , which can be removed easily via blow down operation or by converting into dissolved salts which do not cause any harm.

- To remove accumulated sludge , following procedures are performed-

1. Colloidal conditioning
2. Carbonate conditioning
3. Phosphate conditioning
4. Calgon conditioning
5. Treatment with sodium meta aluminate($NaAlO_2$)
6. Complexometric technique

Colloidal conditioning

- Scale formation is avoided by introducing colloidal substances like kerosene , tannins, glue, agar-agar, etc to boiler water.
- These substances get adsorbed over scale forming impurities forming non-sticky & loose deposits which can be removed via blow down operation.
- This is beneficial for low pressure boiler only.

Carbonate conditioning

- In low pressure boilers scale formation is avoided by adding sodium carbonate to boiler water , when salts like $CaSO_4$ get convert to $CaCO_3$.
- $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$
- So the deposition of $CaSO_4$ hard scale is prevented & $CaCO_3$ formed is removed via blow down operation.

Phosphate conditioning

- In high pressure boiler , to avoid scale formation sodium phosphate is mixed with hardness causing agent or salt causing hardness.
- This forms non-adherent & easily removable sludge which is removed via blow down operation.

- $3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$
- Selection of salt depends upon alkalinity of water:

1. Tri-sodium phosphate Na_3PO_4 for **low alkaline water**.
2. Di-sodium hydrogen phosphate Na_2HPO_4 for **sufficiently alkaline water**.
3. Sodium di-hydrogen phosphate NaH_2PO_4 for **highly alkaline water.**

Calgon conditioning

- Sodium hexa meta phosphate $Na_6(PO_3)_6$ is called calgon.
- It is a coordinate compound.
- Prevents scale & sludge formation by forming soluble complex compound with $CaSO_4$.
- In high pressure boiler, calgon combines with scale forming salts and forms non-adherent & easily removable sludge which is removed via blow down operation.

Calgon conditioning

- $Na_2[Na_4(PO_3)_6] \rightarrow [Na_4P_6O_{18}]^{2-} + 2Na^+$

  calgon

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

  calgon soluble complex

Invitation of query from students:

Name:

Email:

Other contact details:

QUESTIONS

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Thank You

Great God, Medi-Caps, All the attendees

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