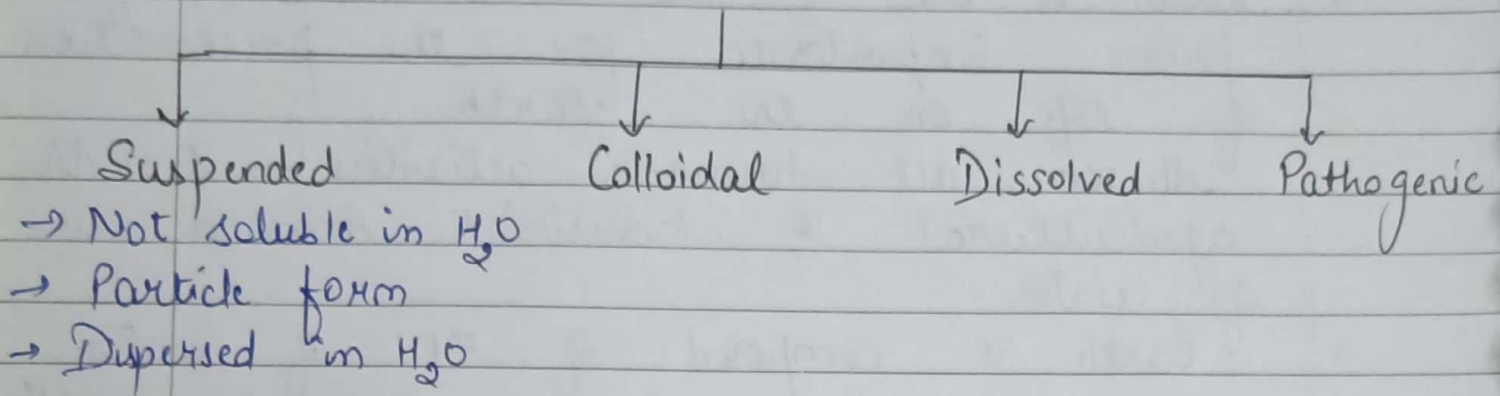


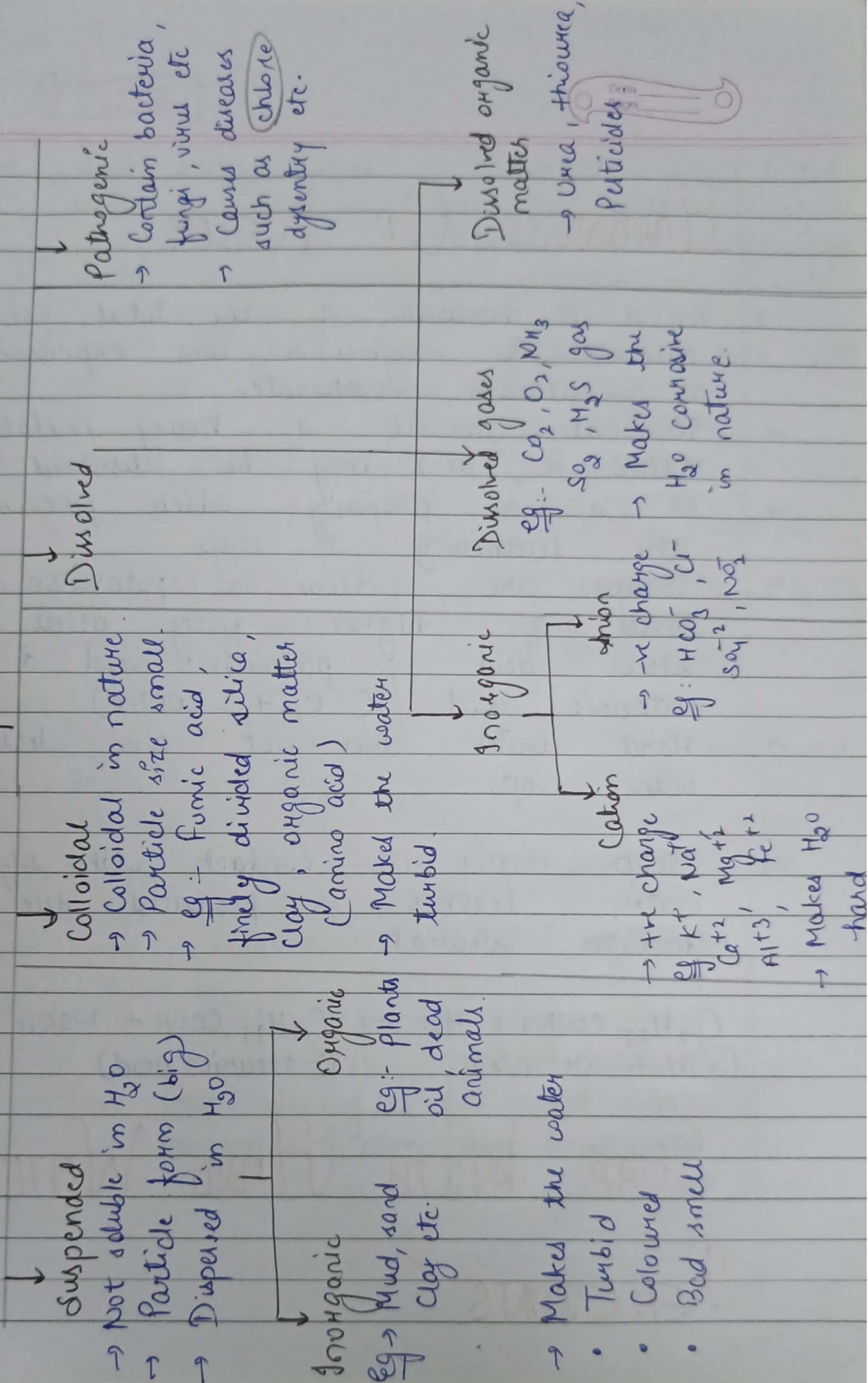
WATER

- Water is one of the basic materials of prime importance for the preservation of life on the Earth.
- Almost all human activities - domestic, agricultural & industrial demand use of water.
- Earth is composed of 71% of water but only less than 1% of world's water resources are available for the ready use.
- It is known as the universal solvent.
- Pure water is composed of 2 parts of hydrogen & 1 part of oxygen by volume and dissolved many substances.
- These dissolved salts are the impurities of water.
- As engineering material water is used for producing steam in boilers to generate hydroelectric power, furnishing steam for engines, for refrigeration and A.C.
- It is used for construction of concrete structures for manufacturing purposes.

IMPURITIES OF WATER :-

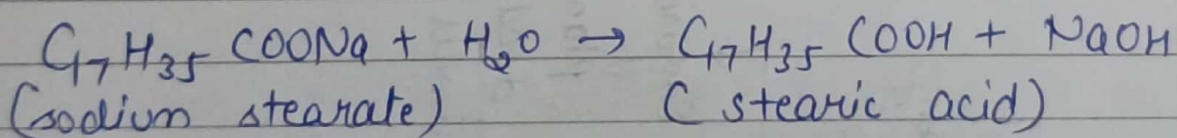


Impurities of water



HARDNESS OF WATER

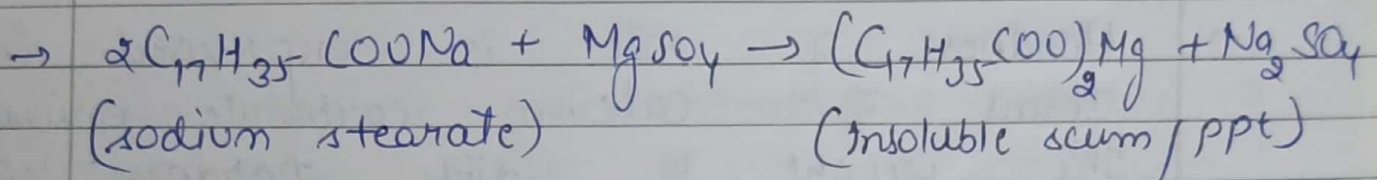
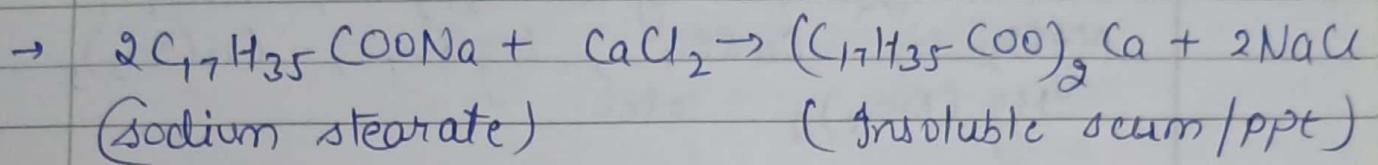
- It is a measure of the total concⁿ of calcium & magnesium ions expressed as calcium carbonate.
- Nominal amount of heavy metals (like Fe, Al) may be dissolved too.
- It is a property which prevents the lathering of soap.
- Soaps are sodium or potassium salts of higher fatty acids like oleic acid, palmitic acid & stearic acid ($C_{17}H_{35}COONa$).
- Hard water does not give lather with soap.
- ⇒ Soap comes in contact with soft water, lather is produced due to sodium stearate.



SOAP WITH HARD WATER

REACTIONS :-

→ When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white ppt. This insoluble white ppt prevents lathering of soap.



→ Different types of water have different degree of hardness. These are classified on the basis of degree of hardness as follows:-

Hardness	Name of water
0 - 70 mg/L	Soft water
70 - 150 mg/L	Moderate hard water
150 - 300 mg/L	Hard water
300 mg/L & above	Very hard water

DEGREE OF HARDNESS

- The total hardness of water is caused by 8 diff. dissolved salts of calcium & magnesium $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ etc.
- Hardness of water is expressed in terms of calcium carbonate equivalents. The weight of diff. hardness salts causing hardness are converted to weight equivalent to that of calcium carbonate.
- CaCO_3 is selected for expression of hardness because the molecular weight of CaCO_3 is 100, which is easy for calculation & it is the most insoluble salt & all the dissolved salts of calcium are precipitated as CaCO_3 .

Name of salt	Molecular wt.
$\text{Ca}(\text{HCO}_3)_2$	162
$\text{Mg}(\text{HCO}_3)_2$	146
CaCl_2	111
MgCl_2	95
CaSO_4	136
MgSO_4	120
CaCO_3	100

The method for calculating degree of hardness will be clear from the following formula :-

$$\text{Hardness of water in terms of } \text{CaCO}_3 \text{ equivalents} = \frac{\text{Amount of hardness using salt}}{\text{M.w. of hardness causing salt}} \times 100$$

here 100 = molecular wt. of CaCO_3 .

EXPRESSION OF HARDNESS -

UNITS :-

a) 1 ppm (parts per million)
→ Parts of CaCO_3 equivalent hardness per 10^6 parts of water.
1 ppm → 1 part of CaCO_3 equivalent hardness present in 10^6 parts of water.

b) Milligram per litre
→ No. of milligrams of calcium carbonate equivalent hardness tot in 1 litre of water.
1 mg/L = 1 mg of CaCO_3 equivalent hardness tot in 1 litre of H_2O .
1L = 1kg = 1000 g = 1000 × 1000 mg = 10^6 mg.
1 mg/L = 1 mg of CaCO_3 eq. per 10^6 mg of H_2O = ppm.

c) Degree Clark ($^\circ\text{Cl}$)
→ No. of grains (1/7000 lb) of CaCO_3 equivalent hardness per 70,000 parts of H_2O .
→ 1 Clark = 1 grain of CaCO_3 equivalent hardness per gallon of H_2O .
= 1 part of CaCO_3 of hardness per 70,000 parts of H_2O .

d) Degree French ($^\circ\text{Fr}$)
→ Parts of CaCO_3 equivalent hardness per 10^5 parts of water.
1° French = 1 part of CaCO_3 per 10^5 parts of hard H_2O .

- e) Milliequivalent per litre
 → No. of milliequivalents of hardness +ve per litre of H_2O .
 $1 \text{ meq/L} = 1 \text{ meq of } CaCO_3 \text{ per /lit. of } H_2O = 50 \text{ mg/L of } CaCO_3 \text{ eq} = 50 \text{ ppm.}$

RELATION BETWEEN VARIOUS UNITS OF HARDNESS

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1^\circ \text{F}_H = 0.07^\circ \text{C}_H = 0.02 \text{ meq/L}$$

Suppose total hardness of water sample =
 $121 \text{ ppm} = 121 \text{ mg/L}$
 $121 \times 0.07 = 8.47^\circ \text{C}_H$ & $121 \times 0.1 = 12.1^\circ \text{F}_H$

Permanent hardness = 101 mg/L , 101 ppm ,
 7.07°C_H , 10.1°F_H

Temporary hardness = 20 mg/L , 20 ppm ,
 1.4°C_H & 2°F_H .

TYPES OF HARDNESS :-

There are 2 types of hardness.

- 1) Temporary Hardness
- 2) Permanent Hardness

1) Temporary Hardness :-

- It is caused mainly due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals.
- The salts mainly responsible for temporary hardness of H_2O are $Ca(HCO_3)_2$ & $Mg(HCO_3)_2$.
- When bicarbonates are decomposed, yielding insoluble carbonates (by boiling), that can be removed by filtration.

2) Permanent Hardness :-

- It is due to the presence of dissolved chlorides and sulphates of Ca, Mg, Fe & other metals.
- The salts responsible for permanent hardness are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$.
- Permanent hardness can't be removed by boiling but it can be removed by the use of chemical agents.

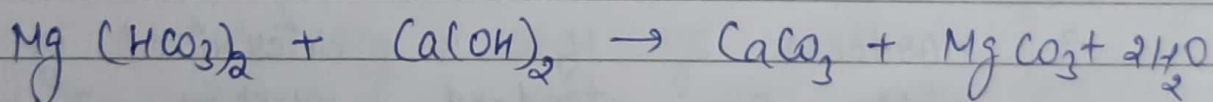
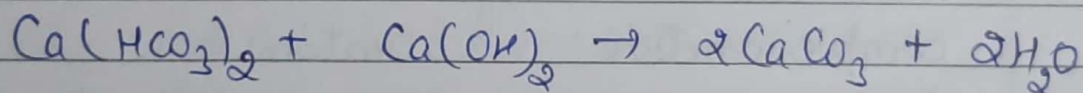
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Total hardness of water $\Rightarrow$ $T.H + P.H$

$T.H \Rightarrow$ Temporary hardness
 $P.H \Rightarrow$ Permanent hardness.

DETERMINATION OF HARDNESS By CLARK'S TEST :-

- $\rightarrow$ This method or test is for removal of temporary hardness.
- $\rightarrow$ In this, impurities of $Ca(HCO_3)_2$, $Mg(HCO_3)_2$ present.
- $\rightarrow$ In this, slaked lime $(Ca(OH)_2)$ is added with hard water then insoluble $CaCO_3$ is formed, which is removed by filtration.

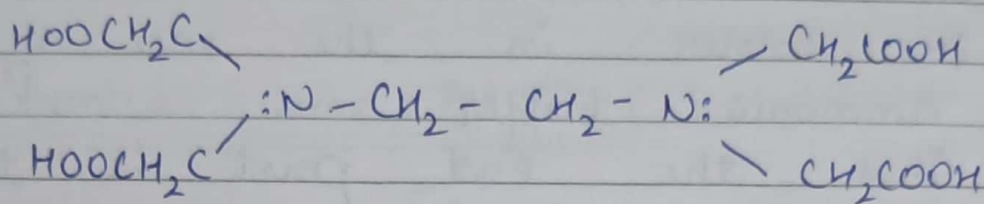


ESTIMATION OF HARDNESS OF WATER BY EDTA METHOD (COMPLEXOMETRIC TITRATION):-

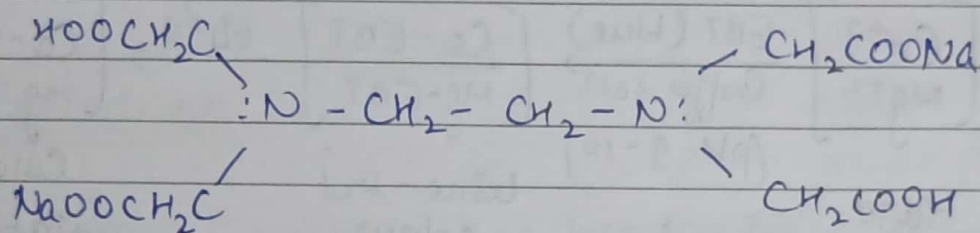
- Hardness in water is due to the presence of dissolved salts of Ca & Mg. It is unfit for drinking, bathing, washing & it also forms scales in boilers.
- Hence it is necessary to estimate the amount of hardness producing substance present in the water sample.
- The estimation of hardness is based on complexometric titration.
- Hardness of H_2O is determined by titrating with a standard solution of ethylenediamine tetraacetic acid (EDTA) which is a complexing agent.
- EDTA is a reagent that forms EDTA-metal complexes with many metal ions.

→ In alkaline condition ($\text{pH} > 9$) it forms stable complexes with the alkaline earth metal ions Ca^{+2} & Mg^{+2}

→ EDTA is insoluble in water, its disodium salt is used as complexing agent.



EDTA



Disodium salt of EDTA

Basic Principle :-

→ Total hardness is due to the trace of bicarbonates, chlorides and sulphates of Ca & Mg ions.

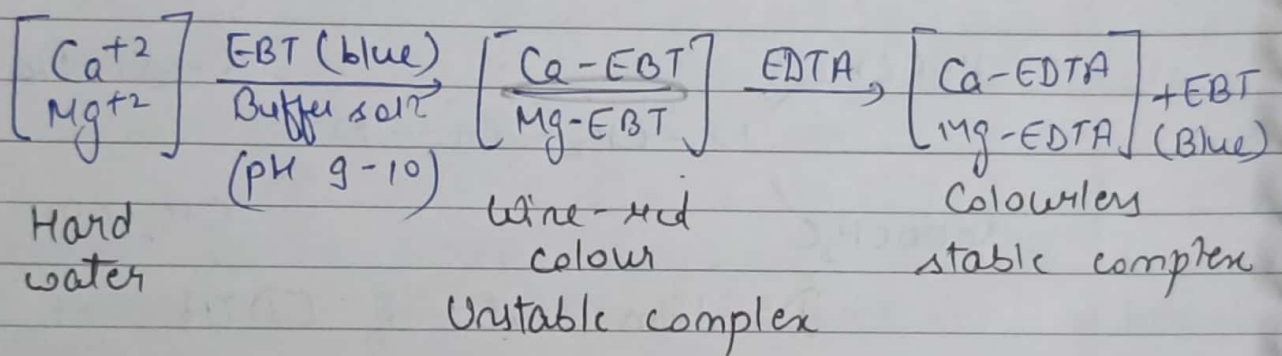
→ The total hardness of water is estimated by titrating the water sample against EDTA using Eriochrome black - T (EBT) Indicator.

→ Initially Ca^{+2} / Mg^{+2} forms a weak EBT - wine red coloured

Complex with $\text{Ca}^{+2}/\text{Mg}^{+2}$ ions + tit in the hard water.

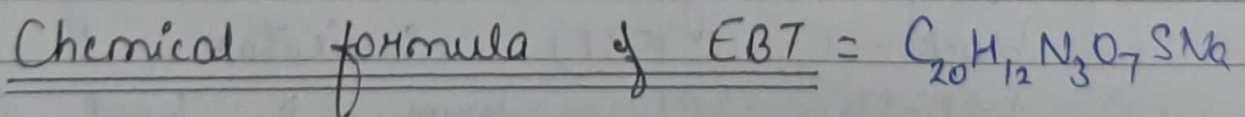
→ On addition of EDTA solⁿ, $\text{Ca}^{+2}/\text{Mg}^{+2}$ ions preferably form a stable EDTA - $\text{Ca}^{+2}/\text{Mg}^{+2}$ complex with EDTA leaving the free EBT indicator in solution which is steel blue in colour in the trace of ammonia buffer.

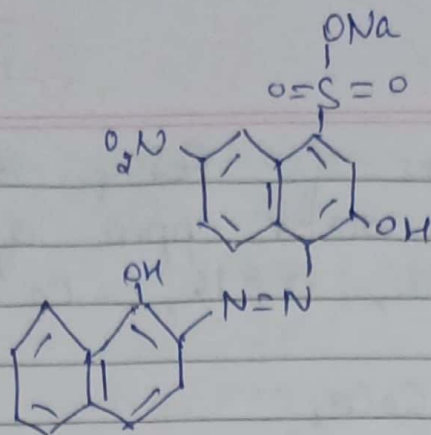
→ Thus the end point is the change of colour from wine red to blue.



→ In EDTA methods, the known water sample is titrated against standard EDTA solⁿ using EBT as indicator in the presence of basic buffer solⁿ. (pH = 10)

→ At the end point the wine red colour changes to blue.





EBT (structure)

⇒ Chemical name of EBT :-

sodium; (4Z)-4-[(1-hydroxynaphthalen-2-yl)hydrazinylidene]-7-nitro-3-oxonaphthalene-1-sulphate.

⇒ Procedure :-

- A known volume of hardwater sample is titrated against about 3 ml. of buffer soln.
- Add 4-5 drops of EBT indicator.
- This soln is titrated against a standard EDTA soln.
- The end point is colour change from wine-red to blue.

- NUMERICALS

Q.1) How many grams of FeSO_4 dissolved per litre gives 210.5 ppm of hardness?
 $[\text{Fe} = 56, \text{S} = 32, \text{O} = 16, \text{Ca} = 40, \text{C} = 12]$

solⁿ $\Rightarrow$

$$\begin{aligned} \text{FeSO}_4 &= \text{CaCO}_3 \\ 56 + 16 + 32 + (16 \times 3) &= 100 \\ 152 \text{ g} &= 100 \text{ g} \end{aligned}$$

$\therefore 100 \text{ ppm of hardness} = 152 \text{ g (ppm) of FeSO}_4$

$$210.5 \text{ ppm of hardness} = \frac{152}{100} \times 210.5$$

$$= 319.96 \text{ ppm of FeSO}_4$$

$$= 319.96 \text{ mg/L}$$

or

$$= 0.31996 \text{ g/L of FeSO}_4$$

Hence, 0.31996 g of FeSO_4 dissolved per litre gives 210.5 ppm of hardness.

= * =

Q.2) Calculate the temporary hardness & permanent hardness of a sample of water containing $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$, $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$, $\text{MgCl}_2 = 9.5 \text{ mg/L}$, $\text{CaSO}_4 = 13.6 \text{ mg/L}$. (Atomic wt. of Mg & Ca are 24 & 40 respectively.)

solⁿ

$$\text{Mg}(\text{HCO}_3)_2 = \frac{7.3}{146} \times 100 = 5 \text{ mg/L}$$

$$\rightarrow \text{Ca}(\text{HCO}_3)_2 \Rightarrow \frac{16.2}{162} \times 100 = 10 \text{ mg/L}$$

$$\rightarrow \text{MgCl}_2 \Rightarrow \frac{9.5}{95} \times 100 = 10 \text{ mg/L}$$

$$\rightarrow \text{CaSO}_4 \Rightarrow \frac{13.6}{136} \times 100 = 10 \text{ mg/L}$$

Temporary hardness due to $\text{Mg}(\text{HCO}_3)_2$ & $\text{Ca}(\text{HCO}_3)_2 \Rightarrow (5+10) \text{ mg/L} = 15 \text{ ppm}$

Permanent hardness due to MgCl_2 & $\text{CaSO}_4 \Rightarrow (10+10) \text{ mg/L} = 20 \text{ ppm}$
 $= x =$

MUNICIPAL WATER SUPPLY:-

Requisite (Requirements) for potable water:-

- 1) It should be sparkling clear and odourless.
- 2) It should be pleasant in taste.
- 3) It should be perfectly cool.
- 4) Its turbidity should not exceed 10 ppm.
- 5) It should be free from objectionable dissolved gases like hydrogen sulphide.
- 6) It should be free from objectionable minerals such as Pb, arsenic, Cu & Mg salts.
- 7) Its alkalinity should not be high. Its pH should be about 8.0.

- 8) It should be reasonably soft.
- 9) Its total dissolved solids should be less than 500 ppm.
- 10) It should be free from disease-producing micro-organisms.

STEPS INVOLVED IN PURIFICATION OF WATER :-

Natural water from rivers, canals etc. does not conform to all the required specifications of drinking H_2O . For removing various types of impurities, the foll. treatment processes are employed :-

- 1) Sedimentation
- 2) Coagulation
- 3) Filtration
- 4) Sterilization
- 5) Break point chlorination.

① Sedimentation :- It is a process of allowing water to stand undisturbed in big tanks, about 5 m deep, when most of the suspended particles settle down at the bottom.

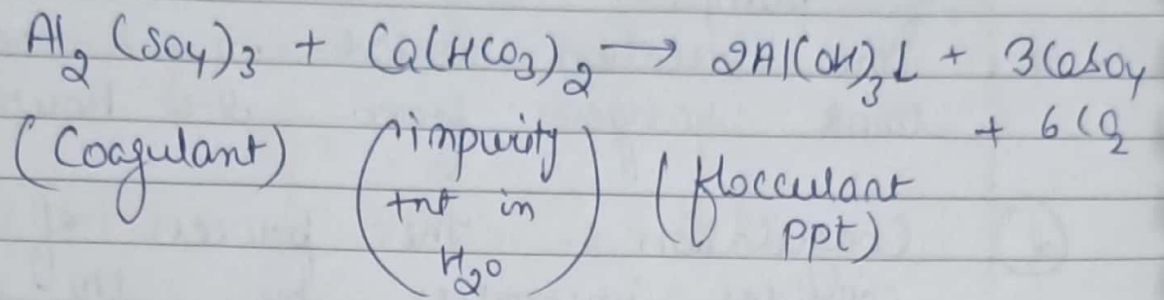
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- due to force of gravity. The clear supernatant water is then drawn from tank with the help of pumps.
 - The retention period in a sedimentation tank ranges from 2-6 hours.

② Coagulation :- The process of removing colloidal impurities by the addition of required amount of chemicals (called coagulants).

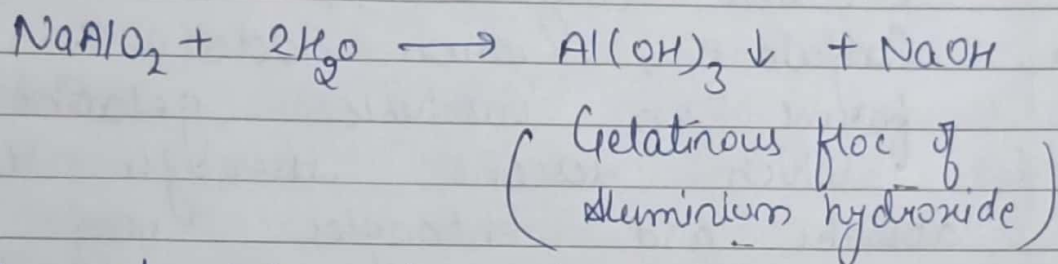
- Coagulant, when added to water, forms an insoluble gelatinous, which descends through the H_2O , absorbs and entangles very fine suspended impurities forming bigger ~~flock~~ flocs, which settle down easily.
- Coagulants like alum or ferrous sulphate provide Al^{+3} or Fe^{+3} ions w/h neutralize -ve charge on colloidal particles.
- After losing their charge, the tiny clay particles come nearer to one another and combine to form bigger particles which settle down.
- For proper mixing of coagulants with water, mixers are employed.

Chemical Coagulants :-

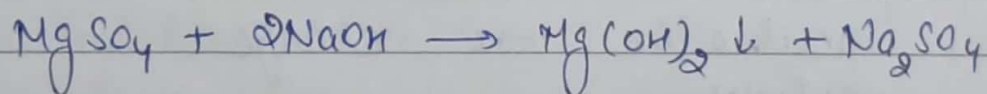
i) Alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$]



ii) Sodium aluminate ($NaAlO_2$)



The aluminium hydroxide floc causes sedimentation. The NaOH thus produced, ppt of $Mg(OH)_2$ salt is produced.

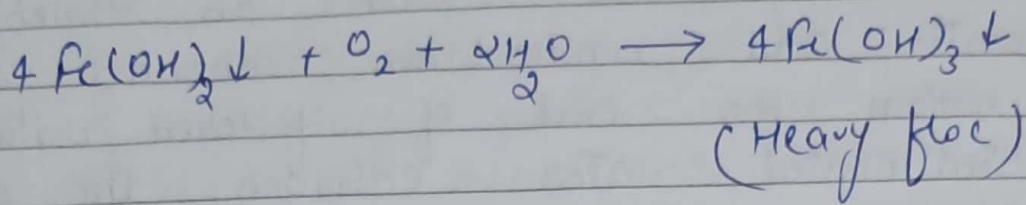
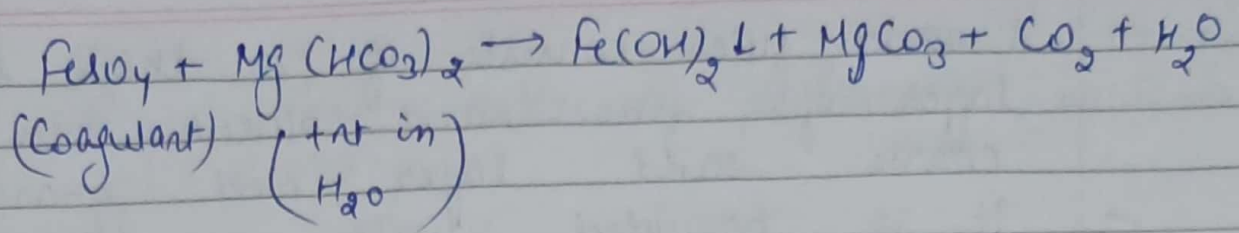


iii) Ferrous Sulphate [$FeSO_4 \cdot 7H_2O$]

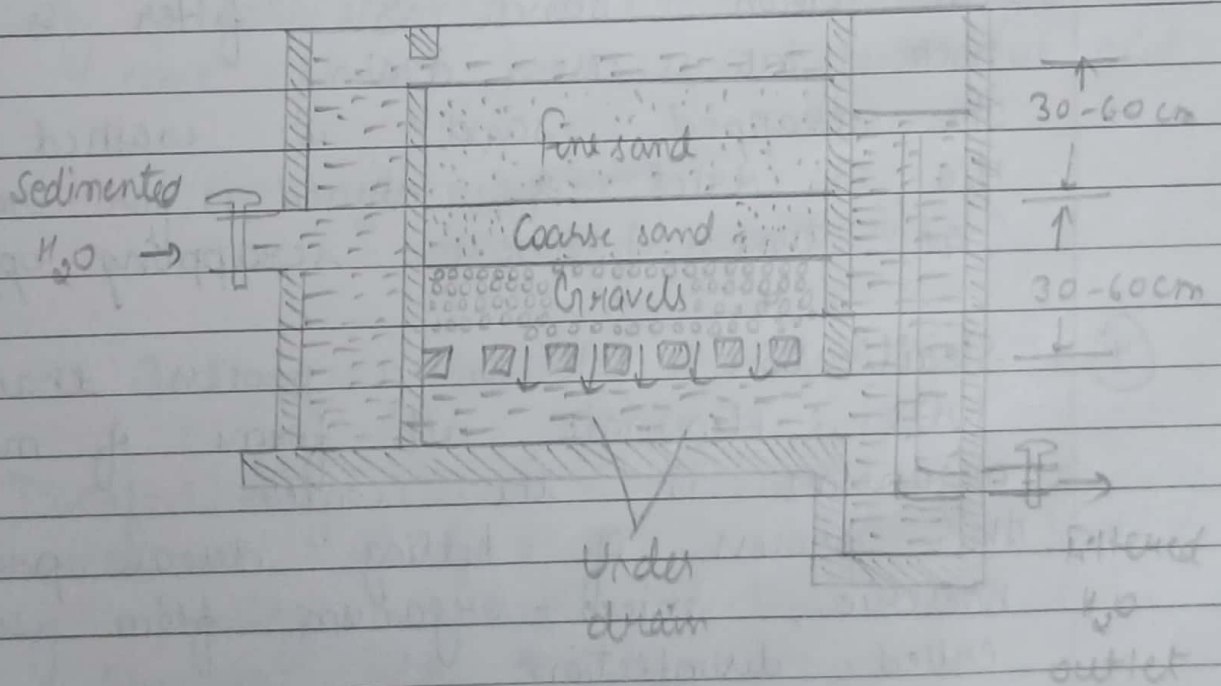
→ It gives good result above pH value of 8.5.

→ It reacts in the pres of alkality.

→ If alkality is not pres, sufficient lime is also added.



- (3) Filtration :- It is the process of removing colloidal matter & most of the bacteria, micro-organisms by passing H_2O through a bed of fine sand and other proper sized granular material.
- It is carried out by using sand filter.



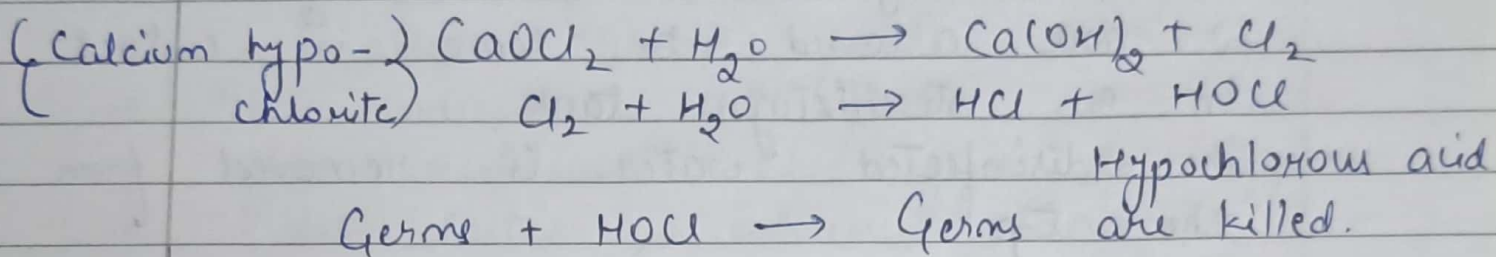
Sand Filter

- A sand filter consists of a thick top layer of fine sand placed over coarse sand layer and granules.
- It is provided with an inlet for water and underdrain channel at bottom for exit of filtered water.
- Sedimented water entering the sand filter is uniformly distributed over entire fine sand bed.
- During filtration, sand pores get clogged, due to retention of impurities in pores.
- When rate of filtration become slow, working of filter is stopped & about 2-3 cm of top fine sand layer is scrapped off & replaced with clean sand & filter is put back into use again.
- The scrapped sand is washed with H_2O , dried & stored for reuse at time of next scrapping operation.

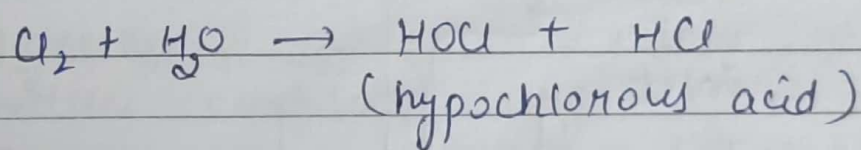
- (4) Sterilization :- It is a process that kills, eliminate all forms of micro-organisms in the water.
- The process of killing disease producing bacteria, micro-organism from water called disinfection.
 - The chemicals which are added to H_2O for killing bacteria called disinfectants.

(i) By boiling :- By boiling for 10-15 min, all the disease producing bacteria are killed.

(ii) By adding bleaching powder :- About 1 kg of bleaching powder per 1000 kilolitres of H_2O is mixed & H_2O allowed to stand undisturbed for several hours.
→ The chemical action produces hypochlorous acid (powerful germicide)

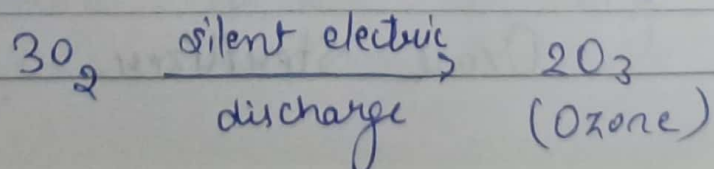


(iii) By Chlorination :- Cl (either gas or in concⁿ. form) produces hypochlorous acid

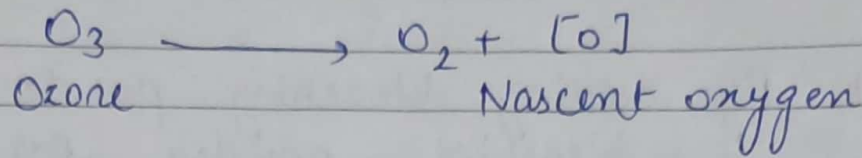


Bacteria + $HOCl \rightarrow$ Bacteria are killed.

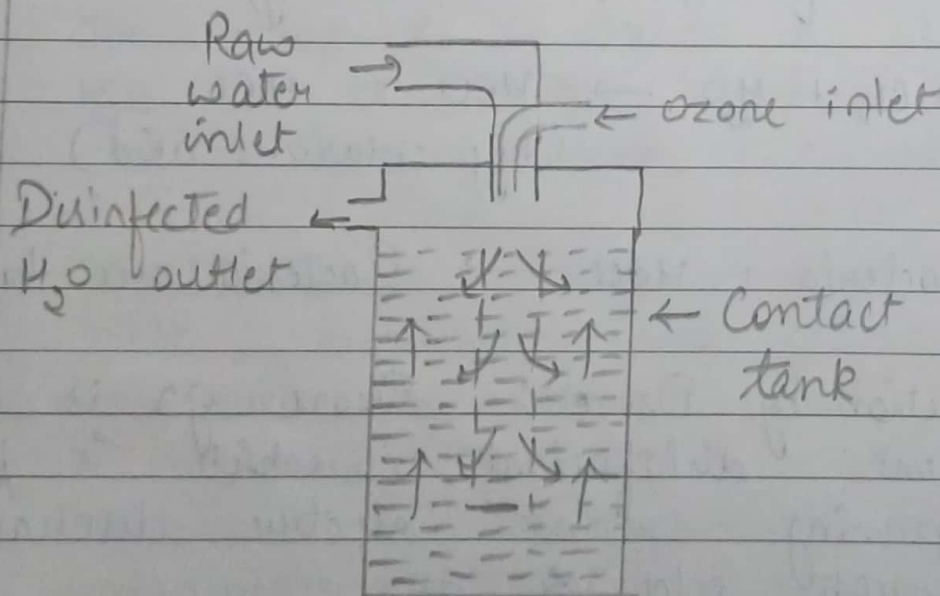
(iv) Disinfection by Ozone :- Ozone (O_3) is an excellent disinfectant, which is produced by passing silent electric discharge through cold & dry oxygen.



Ozone is highly unstable & breaks down, liberating nascent oxygen.



- The nascent oxygen is very powerful oxidising agent & kills all the bacterial as well as oxidises the organic matter + it in H_2O .
- Ozone is injected into the H_2O & the 2 are allowed to come in contact in a sterilizing tank.
- The disinfected water is removed from the top.
- The contact period about 10-15 min. & the usual dose strength 2-3 ppm.



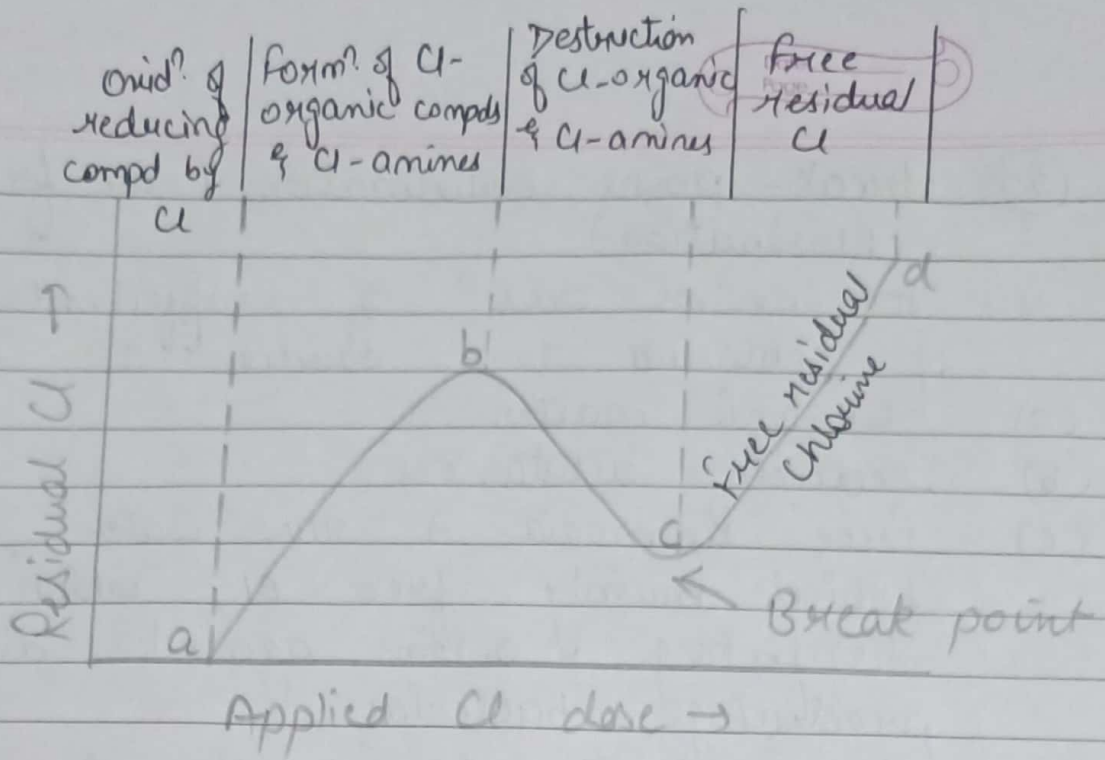
Ozone Sterilizer

(5) Break-point chlorination (or free-residual chlorination)

- It involves addiⁿ of sufficient amount of chlorine to oxidise :-
 - (a) Organic matter
 - (b) reducing substances
 - (c) Free ammonia in raw water, leaving behind mainly free Cl, which possess disinfecting action against disease-producing bacteria.
- The addⁿ of Cl at the dip or break is called break-point chlorination.
- This indicates the point at which free residual Cl begins to appear.
- All tastes, odours disappear at break-point, resulting in appearance of H₂O free from bad tastes & odours.

Advantages :-

- It oxidises completely organic compounds, NH₃ & other reducing compounds.
- It removes colour in H₂O, due to trace of organic matters.
- It destroys 100% all disease-producing bacteria.
- It removes both odour & taste from the H₂O.
- It prevents growth of any weeds in H₂O.



Break - Point Chlorination Curve

SOFTENING METHODS :-

- 1) Lime - Soda Process $\leftarrow$ Cold lime soda
Hot lime soda
- 2) Zeolite or Permutit Process.
- 3) Ion Exchange / de-ionisation / de-mineralisation process.

Q LIME - SODA PROCESS :-

$\rightarrow$ Water used for industrial purposes (such as steam generation) should be sufficient pure. It should be free from hardness-producing salt before put to use.

→ The process of removing hardness - producing salts from water is known as softening of water.

In Lime - soda process :-

→ The soluble Ca^{+2} & Mg^{+2} salts in H_2O are chemically converted into insoluble compounds, by adding calculated amount of lime $[\text{Ca}(\text{OH})_2]$ & soda $[\text{Na}_2\text{CO}_3]$.

→ CaCO_3 & $\text{Mg}(\text{OH})_2$ are precipitated, filtered off.

→ It is slow process.

→ For accelerating process, hot lime soda process is used.

→ Substance that bring down fine particles of ppt called accelerators like activated charcoal are added.

100 parts by mass of CaCO_3 are equivalent to :-

(i) 74 parts of $\text{Ca}(\text{OH})_2$

(ii) 106 parts of Na_2CO_3

Lime requirement for softening

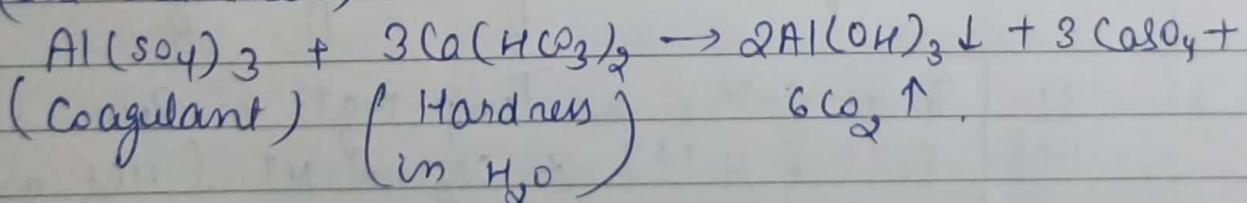
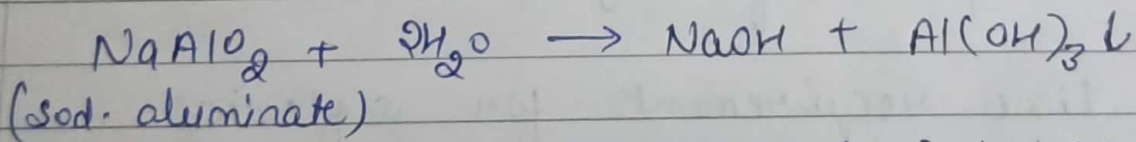
$$\frac{74}{100} \left[\text{Temp. Ca}^{+2} + 2 \times \text{Temp. Mg}^{+2} + \text{Perm. (Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3}) + \text{CO}_2 + \text{N}^+ (\text{HCl or } \frac{1}{2}\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \text{ all in terms of CaCO}_3 \right]$$

Soda requirement for softening

$$\frac{100}{100} \left[\text{Perm.} (Ca^{+2} + Mg^{+2} + Al^{+3} + Fe^{+2}) + H^+ (HCl \text{ or } H_2SO_4) - HCO_3^- \text{ all in terms of } CaCO_3 \text{ eq.} \right]$$

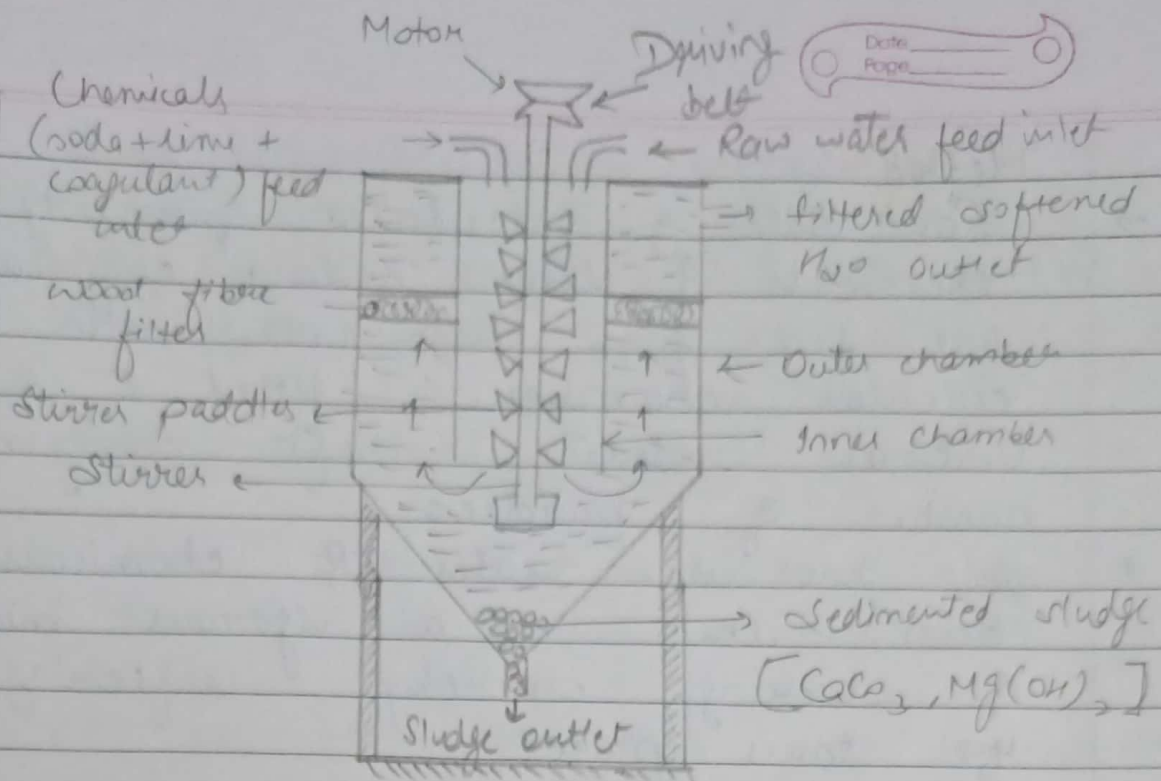
(i) Cold Lime - Soda Process :-

- In this, calculated amount of chemicals (lime & soda) are mixed with H_2O at room temp.
- At room temp., the ppt formed are finely divided so they do not settle down easily & can't be filtered easily.
- It is essential to add small amount of coagulants (like alum, aluminium sulphate, sod. aluminate) which form ppt (flocs), gelatinous ppt of $Al(OH)_3$ & entraps the fine ppt.
- It provides H_2O containing a residual hardness of 50-60 ppm.



Method :-

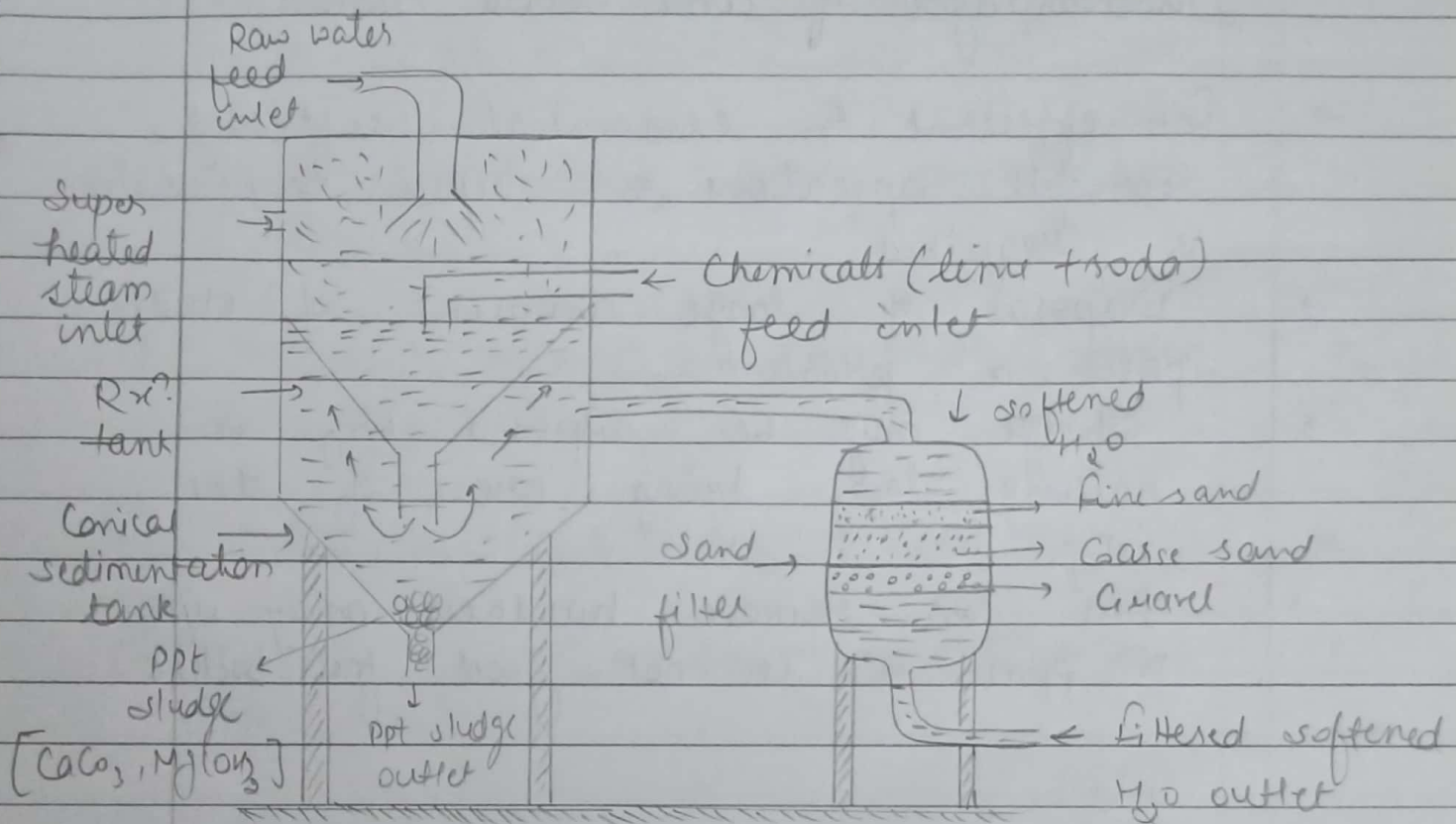
- Raw water & calculated quantity of chemicals (lime + soda + coagulant) are fed from top into inner vertical circular chamber, fitted to a vertical rotating shaft carrying a number of paddles.
- As the raw water & chemicals flows down, there is a vigorous mixing & stirring whereby softening of H_2O takes place.
- As the softened H_2O comes into outer chamber it rises upward.
- The heavy sludge (ppt) settle down in outer chamber by time softened H_2O reaches up.
- The softened H_2O then passes through a filtering media (made up of wood fibres) to ensure complete removal of sludge.
- Filtered soft H_2O finally flows out through outlet at the top.
- Sludge settling at the top bottom of outer chamber is drawn off.



(ii) Hot Lime-Soda Process :-

- It involves treating H_2O w/ softening chemicals at temp. of $80 - 150^\circ C$.
- Hot process is operated at a temp. close to the B.P. of H_2O . so
 - a) rxn. proceed faster.
 - b) softening capacity ↑
 - c) ppt / sludge settle down easily, hence
 - d) no coagulants are added.
 - e) much of dissolved gases (such as CO_2 & air) driven out of H_2O .
 - f) Viscosity of softened H_2O is lower, so filtration of H_2O becomes much easier, it ↑ filtering capacity of filters.
 - g) It produces H_2O of lower residual hardness of $15 - 30$ Ppm.

- It consists of 3 parts :-
- a 'relaxation tank' in w/h raw H_2O , chemicals, steam are mixed.
 - a 'conical sedimentation vessel' in w/h sludge settle down.
 - a 'sand filter' w/h ensures complete removal of sludge from softened H_2O .



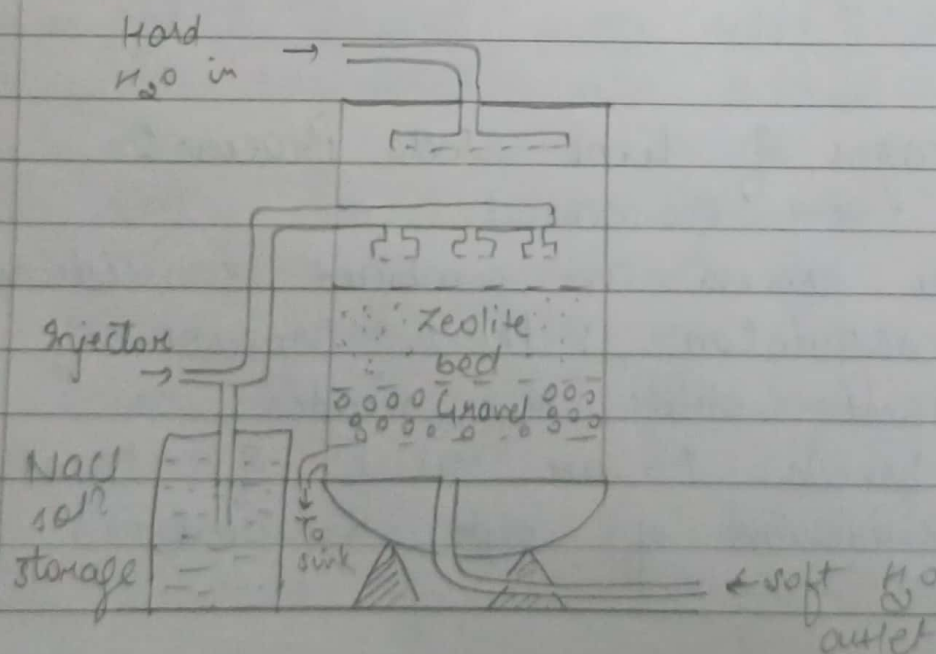
Advantages of Lime - Soda Process :-

- It is very economical.
- If the process is combined w/ sedimentation & coagulation, lesser amount of coagulant shall be needed.
- The process ↑ pH value of treated H_2O so corrosion of pipe is reduced.

- Besides the removal of hardness, quantity of minerals in H_2O are reduced.
- To certain extent Fe, Mn also removed.
- Due to alkaline nature of H_2O , amount of pathogenic bacterial in H_2O also reduced.

Disadvantages of Lime-soda Process :-

- For efficient & economical softening, careful operations & skilled supervision is required.
- Disposal of large amount of sludge poses a problem.
- Sludge may be disposed off in raising low lying area of the city.
- This can remove hardness only upto 15 ppm w/h is not good for boilers.



(Lime-soda)

Table - Calculation of L-S requirement

Constituents	Reaction	Need
(1) Ca^{+2} (Perm. Ca)	$\text{Ca}^{+2} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	S
(2) Mg^{+2} (Perm. Mg)	$\text{Mg}^{+2} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{+2}$	L + S
(3) HCO_3^- (eg NaHCO_3)	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_3^{+2}$	L - S
(4) $\text{Ca}(\text{HCO}_3)_2$ (Temp. Ca)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	L
(5) $\text{Mg}(\text{HCO}_3)_2$ Temp. Mg	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
(6) CO_2	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
(7) H^+ (HCl / H_2SO_4)	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{+2} + 2\text{H}_2\text{O}$	L
(8) Coagulants FeSO_4	$\text{Fe}^{+2} + \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 + \text{Ca}^{+2}$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe}(\text{OH})_3$	L
(9) $\text{Al}_2(\text{SO}_4)_3$	$2\text{Al}^{+3} + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{Ca}^{+2}$	L
(10) NaAlO_2	$\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$	-L
2NaOH is eq. to $\text{Ca}(\text{OH})_2$		

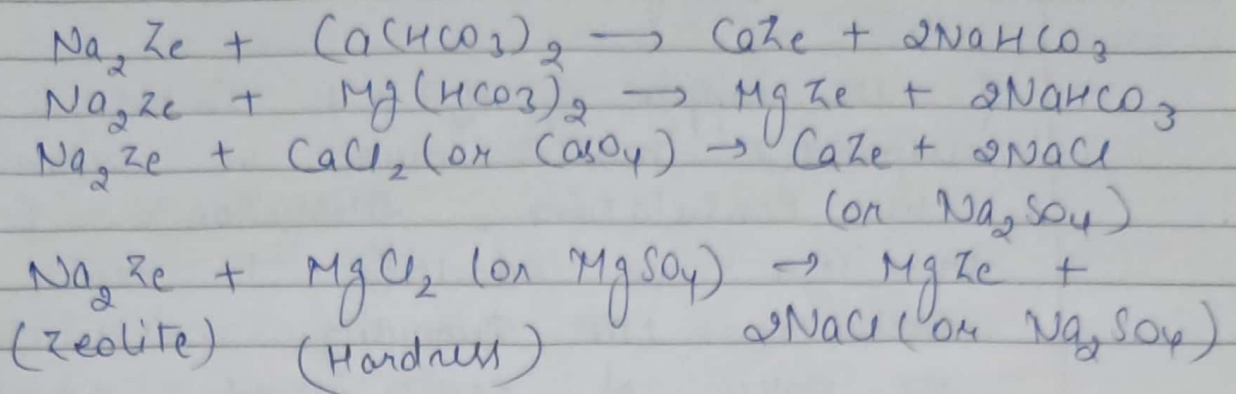
② ZEOLITE OR PERMUTIT PROCESS:-

- Chemical formula of Zeolite is $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ (crystalline aluminosilicate)
- It is hydrated sodium aluminosilicate capable of exchanging reversibly by its Na^+ ions for hardness producing ions in H_2O . ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$)
- It is also known as permutite.
- Zeolites are of 2 types :-
- a) Natural zeolite are non-porous → eg:- natrolite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- b) Synthetic zeolite are porous & possess gel structure. They are prepared by heating china clay, feldspar & soda ash, eg:- Beta (BEA), Linde Type F (EDI).

Process :-

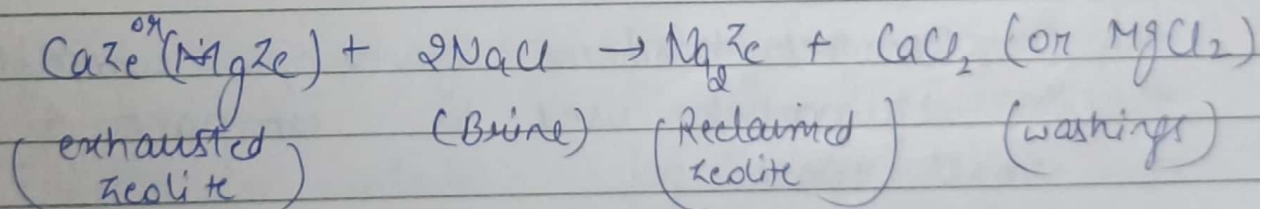
- Hard H_2O is percolated at a specified rate through a bed of zeolite, kept in a cylinder.
- The hardness causing ions (Ca^{+2} , Mg^{+2}) etc. are retained by zeolite as CaZe & MgZe , while outgoing H_2O contains Na salts.

→ Rxn takes place as follows :-



Regeneration :-

- After some time, zeolite is completely converted into Ca & Mg zeolite & it ceases to soften H_2O i.e. it gets exhausted.
- At this stage, supply of hard H_2O is stopped & exhausted.
- At this stage, zeolite is reclaimed by treating the bed w/ a concⁿ. 10% brine (NaCl) solⁿ.



The washing are led to drain & the regenerated zeolite bed thus obtained is used again for softening purpose.

Limitations of Zeolite Process :-

- If the supply of H_2O is turbid, the suspended matter must be removed (by coagulation, filtration), before the H_2O is admitted to zeolite bed, otherwise the turbidity will clog the pores of zeolite bed, making it inactive.
- If H_2O contain large quantities of coloured ions such Mn^{+2} & Fe^{+2} then they must be removed first, becoz these ions produce Manganese & iron zeolites w/h can't be easily regenerated.
- Mineral acids like (HCl, HF, HBr, H_2SO_4) if +ve in H_2O , destroy zeolite bed, so they must be neutralised w/ soda before admitting H_2O to zeolite bed.

Advantages :-

- It removes hardness of 10 ppm completely.
- The equipment used is compact & occupying small space.
- No impurities are precipitated so there is no danger of sludge formation.
- The process automatically adjusts itself for variation in hardness of H_2O .

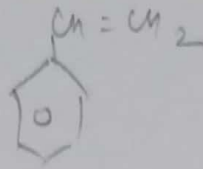
- It is quite clean.
- It requires less time for softening.
- It requires less skill for maintenance as well as operations.

Disadvantages :-

- Water contains more Na salt than in Lime-soda process.
- It only replaces Ca^{+2} & Mg^{+2} ions by Na^+ ions but leaves all acidic ions like HCO_3^- & CO_3^{-2} as such in softened H_2O .
- High turbidity H_2O can't be treated efficiently by this method, bcoz fine impurities get deposited on zeolite bed, creating problem for its working.

* Comparison of Permutit process with lime soda process :-

Permutit Method	Lime - soda Method
1) H_2O of 10-15 ppm hardness is obtained.	1) H_2O of 15-50 ppm hardness is obtained.
2) Treated H_2O contains larger amount of Na^+ salts than in original raw water.	2) Treated H_2O contains lesser amount of Na^+ salts.
3) Cost of plant & material is higher.	3) Capital cost is lower.

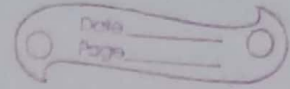


- | | |
|--|--|
| 4) Operation expenses are lower. | 4) These are higher. |
| 5) It can't be used for treating acidic H_2O , bcoz permutit material undergoes disintegration. | 5) There is no such limitation. |
| 6) Plant occupies less space. | 6) Plant occupies more space. |
| 7) The raw water to be softened must be free from suspended matter otherwise pores of permutit material are blocked & bed loses its exchange capacity. | 7) There are no such limitation. |
| 8) It can operate under pressure & can be made fully automatic. | 8) It can't operate under pressure. |
| 9) It involves no problem of settling, coagulation, filtration & removal of sludge. | 9) It involves difficulty in settling, coagulation, filtration & removal of ppt. |
| 10) Treated H_2O contains more dissolved salts. | 10) Contains lesser dissolved salts. |

③ ION EXCHANGE / DE -

IONISATION / DE-MINERALISATION Process

Resins are solid viscous substance that are convertible to polymers



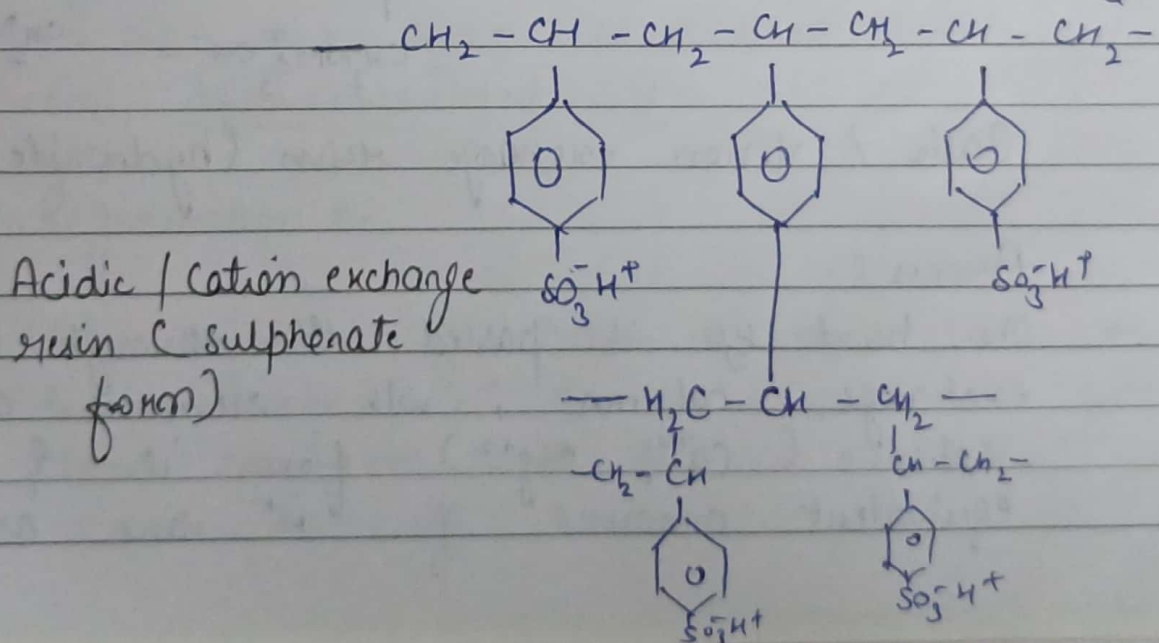
- Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure & the "functional groups" attached to the chain are responsible for ion-exchanging properties.
- Resins containing acidic functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$) are capable of exchanging their H^+ ions with other cations.
- Basic functional groups ($-\text{NH}_2$, $=\text{NH}$) are capable of exchanging their anions with other anions.

2 types:-

cation exchange resin (RH^+)
anion " " (R^-an^-)

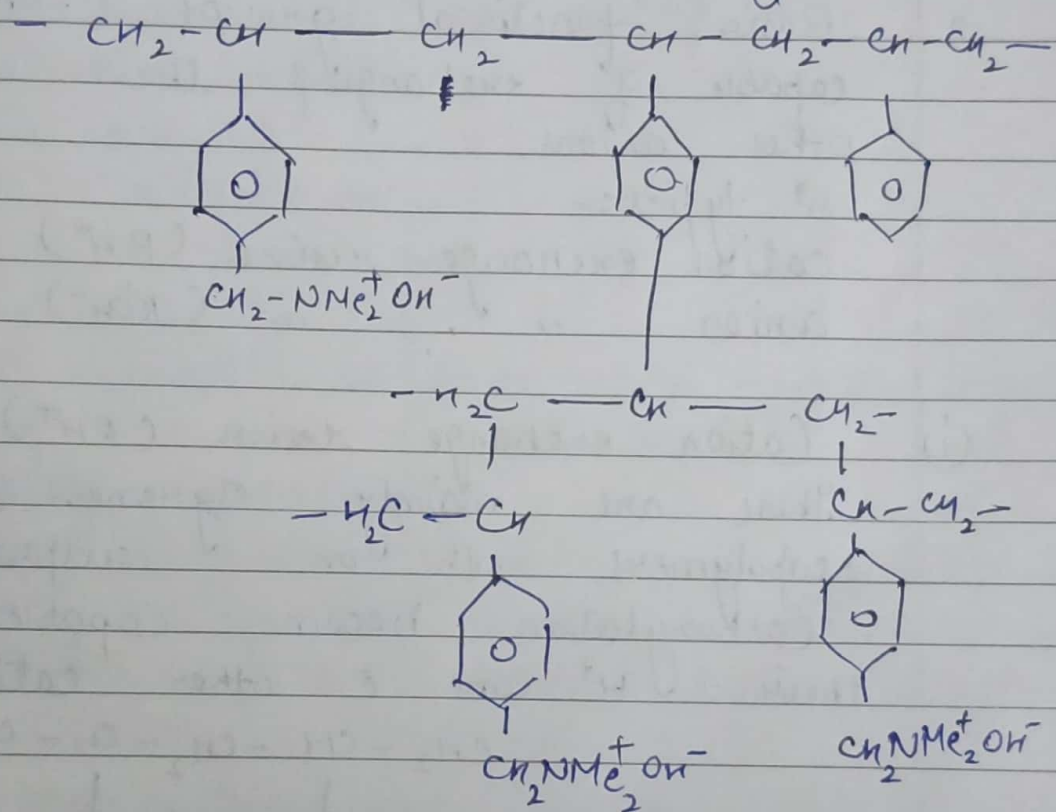
(i) Cation exchange resin (RH^+)

- These are mainly styrene-divinyl benzene copolymers which on sulphonation or carboxylation become capable to exchange their H^+ ions with other cations in H_2O .



(ii) Anion exchange resin ($R'OH^-$)

- These are styrene-divinyl benzene or amine-formaldehyde copolymers w/h contain amine or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of their resin matrix.
- After treatment w/ dil. NaOH solⁿ it become capable of exchange their OH^- w/ other anions in H_2O .

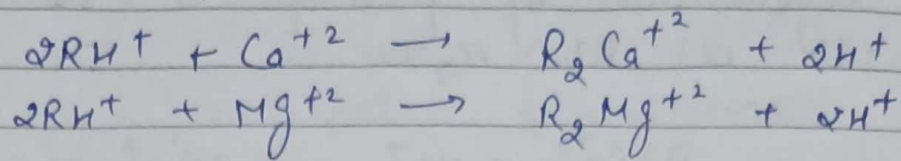


Basic / Anion exchange resin (hydroxide form)

Process :-

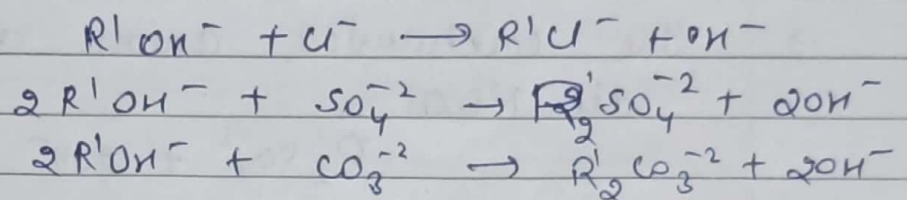
- The hard H_2O is passed 1st through cation exchange column, w/h removes all cations (Ca^{+2} , Mg^{+2}) from it & equivalent amount of H^+ ions are

released from this column to H_2O :-

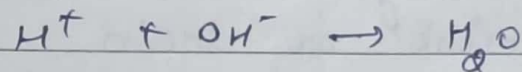


→ Then hard H_2O passed through anion exchange column, w/h remove all the anions (SO_4^{-2} , Cl^-) & equivalent amount of OH^- ions are released from this column to H_2O :-

→ x



→ H^+ & OH^- ions get combined to form H_2O molecule.



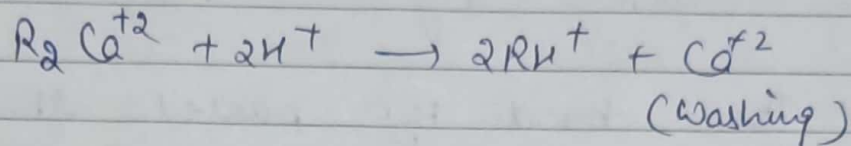
→ H_2O coming out from exchangers is free from cations as well as anions.

→ In free H_2O is k/as deionized or de-mineralised H_2O .

Regeneration :-

→ When capacities of cation & anion exchangers to exchange H^+ & OH^- ions are lost, then they are said to be exhausted.

- The exhausted cation exchange column is regenerated by passing a soln. of dil. HCl or dil. H_2SO_4 .



- The column is washed w/ deionised H_2O & washing contain (Ca^{+2} , Mg^{+2}) is passed to sink or drain. (Cl^- , SO_4^{2-})
- The exhausted anion is washed by dil. NaOH.
- $$R'_2SO_4^{-2} + 2OH^- \rightarrow 2R'OH^- + SO_4^{-2}$$
- (washing)
- The column is washed w/ deionised H_2O , washing containing (Na^+ , SO_4^{-2} , Cl^-) is passed to sink or drain.

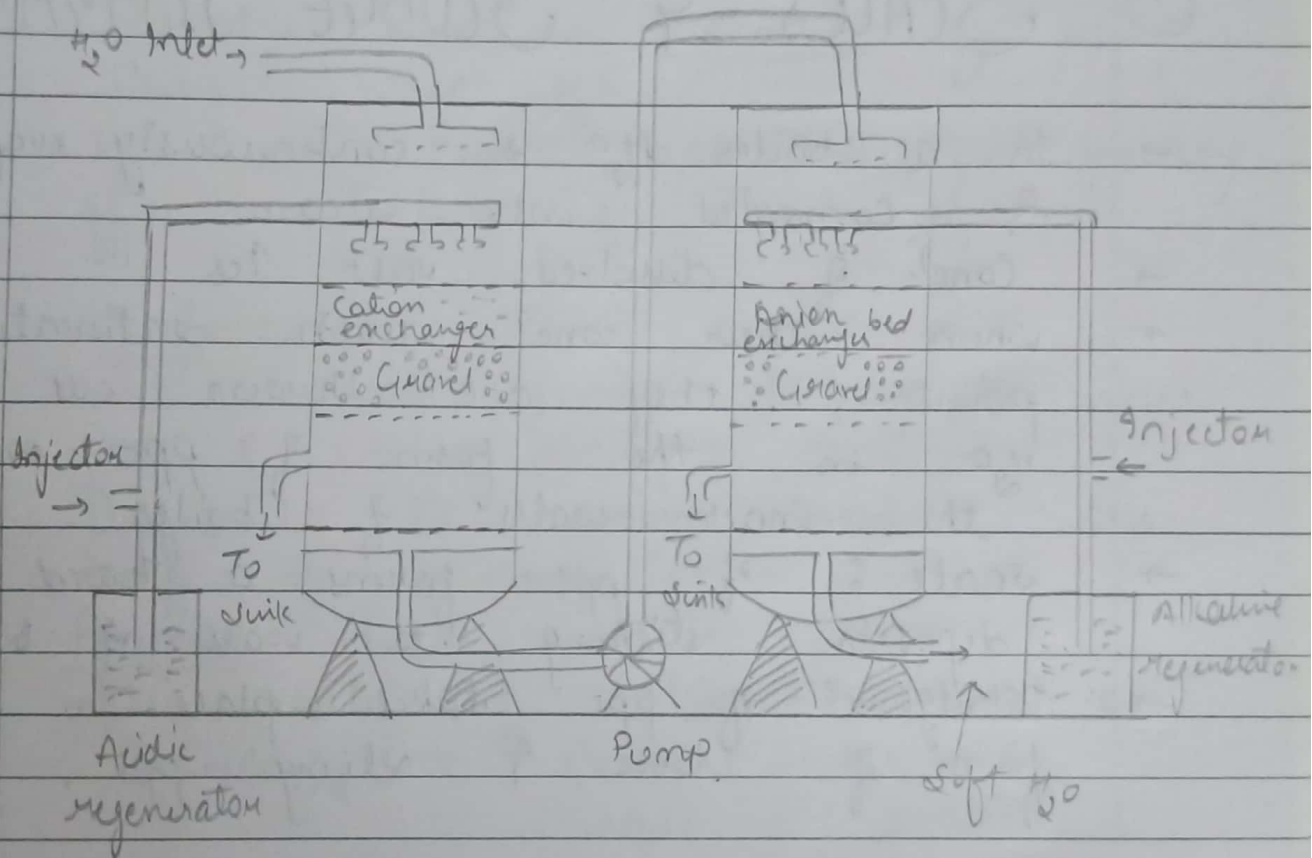
Advantages:-

- The process can be used to soften highly acidic / alkaline H_2O .
- It produces H_2O of very low (2 ppm) of hardness.
- It is very good for boilers (high pressure)

Disadvantages:-

- The equipment is costly & more expensive chemicals are needed.
- If H_2O contain turbidity, output of

process is reduced.
→ Turbidity must be below 10 ppm. If it is more, it has to be removed 1st by coagulation & filtration.



Demineralisation of water

BOILER TROUBLES :-

Boiler troubles are :-

- 1) Scale & sludge formation
- 2) Caustic Embrittlement.
- 3) Priming & foaming.

① SCALES & SLUDGE FORMATION :-

- In a boiler H_2O is continuously evaporated & converted into steam.
- Concⁿ of dissolved salt is.
- When their concⁿ reach saturation points, they are thrown out of H_2O in the form of ppt on the inner walls of boiler.
- Scale :- of ppt forms a hard deposits sticking to walls of boilers.
- Sludge :- of ppt takes place in the form of loose & slimy ppt.

Sludge :-

- soft, loose, slimy ppt formed in the boiler.
- Formed at comparatively colder portion of boiler & collected at bends (where flow rate is slow)

- Formed by substance w/h have greater solubility in H_2O (hot) than in cold H_2O . eg. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.
- Easily removed by wire brush.

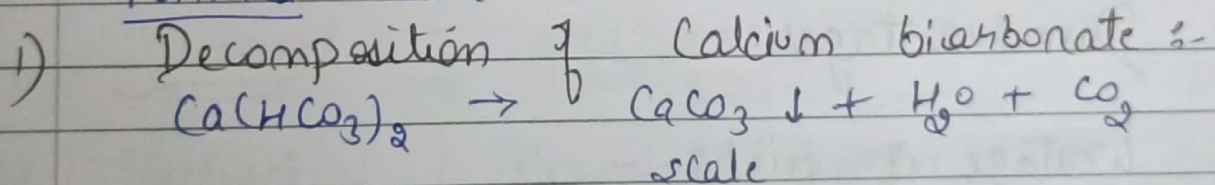
Disadvantages:-

- Poor conductor of heat so they tend to waste a portion of heat generated.
- Excessive sludge formation disturbs the working of boiler.
- Sludge can be removed by using:-
- Using soft H_2O
 - by blow down operation i.e. drawing off a portion of conc. H_2O .

Scales:-

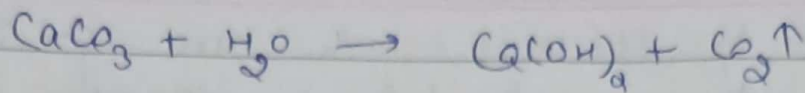
- Hard deposits firmly sticking to inner wall of boiler.
- Difficult to remove even $\bar{c}$ the help of hammer.

Formed due to:-



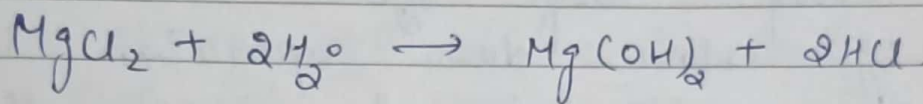
(soft, mainly formed in low pressure boiler)

In high pressure boiler, $CaCO_3$ is soluble due to formation of $Ca(OH)_2$



- ii) Deposition of CaSO_4 .
- Solubility of CaSO_4 dec $\bar{c}$ $\uparrow$ in temp.
 - It is completely insoluble in super heated H_2O .
 - Hard scale formation takes place in high pressure boiler.

- iii) Hydrolysis of Magnesium salt :-
- It is performed in high pressure boiler.



- iv) Presence of silica (SiO_2) :-
- Even very small amounts of silica leads to deposits of Ca/Mg silicates (CaSiO_3 & MgSiO_3) w/h adheres firmly to inner boiler water walls.
 - It is difficult to remove.

Disadvantages :-

- i) Wastage of fuel :-
- Rate of flow of heat transfer is greatly reduced due to poor conductivity of scales.
 - Overheating is required for steady supply of heat hence fuel consumption inc.

- ii) Lowering of boiler safety :-
 → To steady supply heat overheating is required, wh makes boiler material soft, weak.
 → Results in distortion of boiler tube & makes the boiler unsafe to bear high pressure.
- iii) ↓ in efficiency of boiler :-
 → Deposits of scales in valves & condensers choke them partially & ↓ the efficiency of boiler.
- iv) Danger of Explosion :-
 → Due to uneven expansion the thick scales get cracked, results in form of large steam & develop high pressure.
 → It may cause explosion of boiler.

Removal of scales :-

- Mechanical / Chemical method
- Loosely adhering scales are removed in the help of scraper / wire brush.
- Brittle scales are removed by giving thermal shocks.
- Loosely adhering scales are removed by frequent blow down operation (frequently removing ppt)

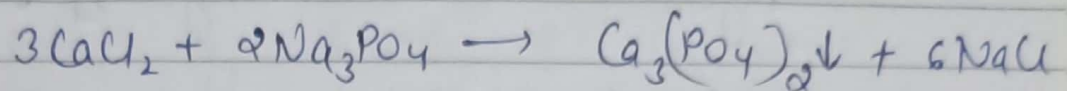
- Adherent & hard scales are removed by dissolving salts by adding chemicals.
- CaCO_3 scales → 5-10% HCl
- CaSO_4 scales → EDTA.

Prevention of Scale formation :-

- 1) External treatment :- Use of soft H_2O .
- 2) Internal treatment :- Also called sequestration
 - In this addition of chemical to boiler H_2O either to
 - a) To ppt scale forming impurities in form of sludge w/h can be removed by blow down operation.
 - b) To convert them into compounds, w/h will stay in dissolved form in H_2O & do not harm.
- i) Colloidal Conditioning :-
 - In low pressure boilers, scale form? can be avoided by adding organic substance like kerosene, tannin, agar-agar (gel).
 - These gel-coated over scale yielding non-sticky, loose deposits w/h can be removed by blow down process.

ii) Phosphate Conditioning :-

→ In high pressure boilers, scale formation can be avoided by adding sod. phosphate w/h form soft sludge of Ca & Mg phosphate w/h can be removed by blow down operation.

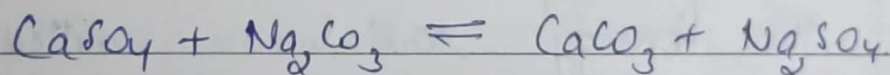


Main phosphates are :-

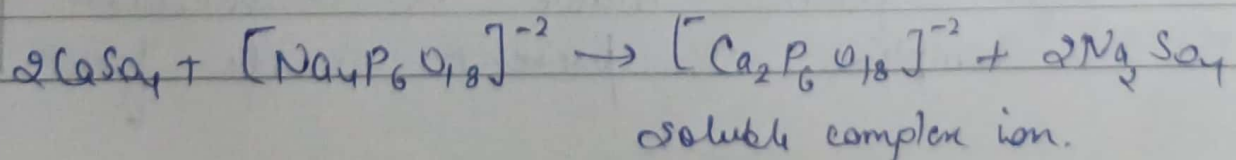
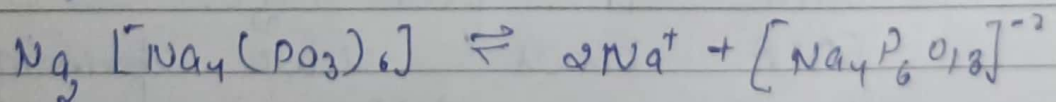
- NaH_2PO_4 (sod. hyd. phosphate) (acidic)
- Na_2HPO_4 (disod. hyd. ") (weakly alkaline)
- Na_3PO_4 (trisod. phosphate) (alkaline)

iii) Carbonate Conditioning :-

In low pressure boiler, scale formⁿ can be avoided by adding sod. carbonate then it will convert into Ca / MgCO_3 in equilibrium.

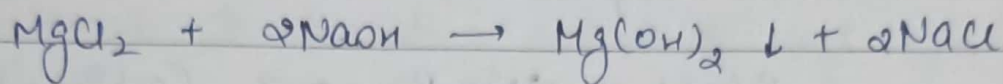
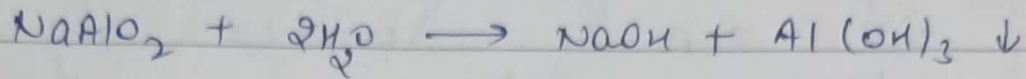


iv) Calgon Conditioning :- ^{$[\text{NaPO}_3]_6$} (sod. hexametaphosphate)
Addⁿ of Calgon prevent scale formⁿ by forming soluble complex.



v) Treatment = sod. aluminate (NaAlO_2)

→ sod. aluminate gets hydrolysed yielding NaOH & a gelatinous ppt of $\text{Al}(\text{OH})_3$



vi) Electrical conditioning :-

→ sealed glass bulb, containing Hg , connected to a battery, are set rotating in boiler.

→ When H_2O boils, Hg bulb emit electrical discharge w/h prevents scale form?

vii) Radioactive conditioning :-

→ Tablets containing radioactive salts are placed inside the boiler H_2O at a few points.

→ The energy radiations emitted by these salts prevent scale formation.

viii) Complexometric method :-

→ It involves 1.5% alkaline soln of EDTA to feed - H_2O .

→ EDTA binds scale forming cations to form stable & soluble complex & prevent scale form?

→ It prevents :-

a) deposition of iron oxides in boiler.

b) reduces carry over of oxides in steam

c) protects boiler unit from corrosion by wet steam.

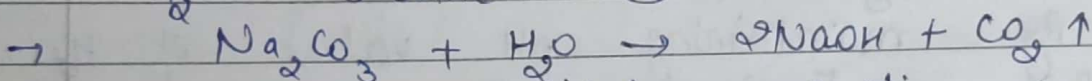
(2) CAUSTIC EMBRITTLEMENT

→ The formⁿ of brittle & intercrystalline cracks in the boiler shell is called caustic embrittlement.

→ It is a type of boiler corrosion, caused by highly alkaline water in boiler.

→ In lime-soda process, some residual Na_2CO_3 is still present in softened H_2O .

→ This Na_2CO_3 decomposes to give NaOH & CO_2 due to w/h boiler H_2O become "caustic".



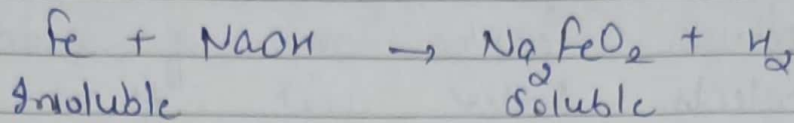
→ This very dilute caustic H_2O flows into minute hair cracks in boiler by capillary action.

→ On evaporation of H_2O , the dissolved caustic soda $\uparrow$ its concⁿ inside hair cracks.

→ This concⁿ alkali dissolves iron of boiler as sod. ferrate.

→ It causes embrittlement of H_2O boiler parts such as bends joints,

rivets etc., due to w/h boiler gets fail.



Electrochemical cell

(Anodic site) conc. NaOH || dil. NaOH (cathodic site)

Iron at joints & bends

Iron at Plane surface

→ Anodic portion undergoes corrosion & gets dissolved.

Prevention method :-

→ By using sod. phosphate as softening reagent in external treatment of boiler H₂O.

→ By maintaining pH value of H₂O & neutralization of alkali.

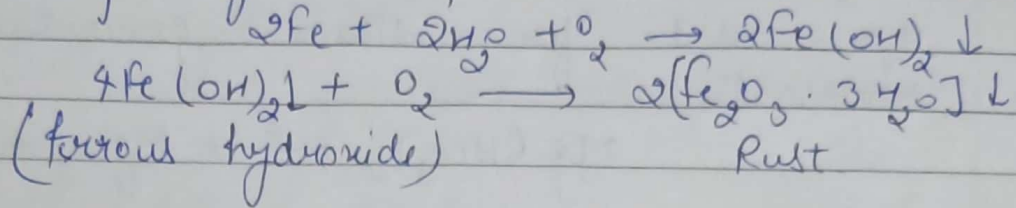
→ By adding Tannin or lignin or sod. sulphate to block the hair cracks thereby preventing the infiltration of caustic soda solⁿ.

③ BOTLER CORROSION :-

→ Boilers corrosion is decay of boiler material by a chemical attack by environment.
Main reasons are :-

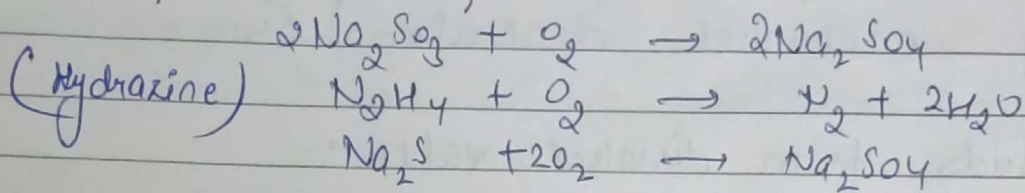
1) Dissolved oxygen :-

→ Dissolved oxygen in H_2O in trace of prevailing high temp attacks boiler material



Removal of dissolved O_2 →

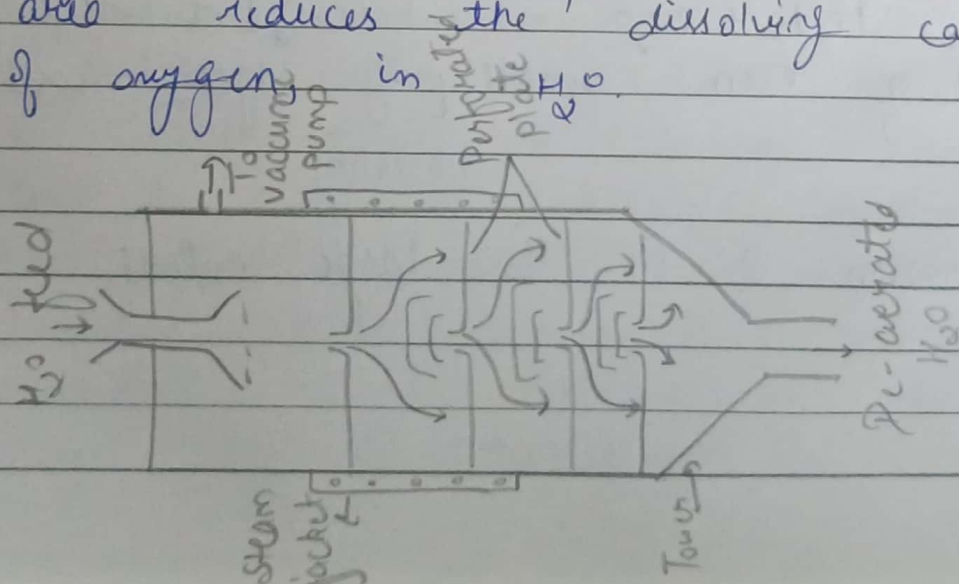
→ By adding calculated amount of sodium sulphite or hydrazine or sodium sulphide



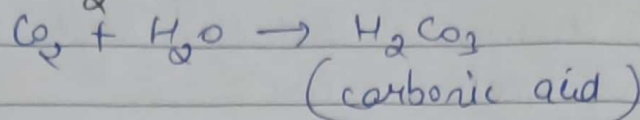
2) By mechanical de-aeration :-

→ Water spraying in a perforated plate - fitted tower, heated from side connected to vacuum pump

→ High temp, low pressure & large surface area reduces the dissolving capacity of oxygen in H_2O .

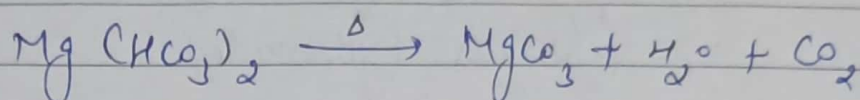


2) Dissolved CO_2 :-



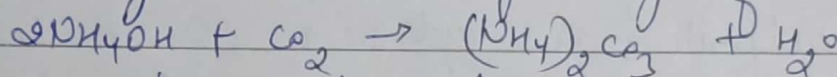
→ Carbonic acid has slow corrosion effect on boiler material

→ CO_2 is also released inside the boiler, if H_2O used for steam generation contains bicarbonates



Removal of CO_2

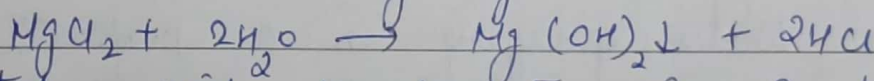
→ By adding calculated quantity of ammonia :-



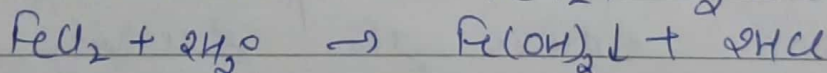
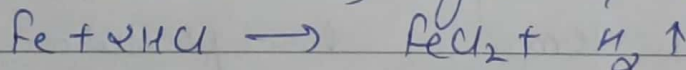
→ By mechanical deaeration process along CO_2

3) Acids from dissolved salts :-

→ H_2O containing dissolved magnesium salts liberate acids on hydrolysis.



→ The liberated acid react with Fe of boiler & produce acid (HCl) again & again.



→ trace of even small $\downarrow$ of MgCl_2 will cause amount

corrosion of Fe to large extent

④ PRIMING & FOAMING :-

- When ~~the~~ a boiler is steaming (i.e. producing steam) rapidly, some particles of liquid H_2O are carried along $\bar{c}$ steam.
- This process of 'wet steam' formⁿ called priming.
- It is caused by :-
 - a) trace of large amount of dissolved salts.
 - b) high steam velocities.
 - c) sudden boiling.
 - d) improper boiler design.
 - e) sudden $\uparrow$ in steam prodⁿ rate.

Foaming :-

- It is the prodⁿ of foam or bubbles in boiler wh don't break easily.
- Foaming is due to trace of oils

- Priming & foaming occurs together. They are objectionable because :-
 - a) dissolved salt are carried by wet steam to super-heated & turbine blades where they are deposited as H_2O evaporates. This deposits reduces their efficiency.
 - b) Dissolved salts may enter parts of other machinery where steam is being used, $\bar{c}$ ing life of machinery.

Priming can be avoided by :-

- i) Fitting mechanical steam purifier.
- ii) Avoiding rapid change in steaming rate.
- iii) Efficient softening & filtration of feed H_2O .

Foaming can be avoided by :-

- i) Adding anti-foaming chemicals like castor oil.
- ii) Addition of $NaAlO_2$ (Sod. aluminate)

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Q.1) Calculate quantity of lime & soda required for softening 50,000 litres of H_2O containing following salts per litre
 $Ca(HCO_3)_2 = 8.1 \text{ mg}$, $Mg(HCO_3)_2 = 7.5 \text{ mg}$,
 $CaSO_4 = 13.6 \text{ mg}$, $MgSO_4 = 12.0 \text{ mg}$, $MgCl_2 = 2 \text{ mg}$ & $NaCl = 4.7 \text{ mg}$

soln. $Ca(HCO_3)_2 = \frac{8.1}{162} \times 100 = 5 \text{ mg/L}$

$Mg(HCO_3)_2 = \frac{7.5}{146} \times 100 = 5.14 \text{ mg/L}$

$CaSO_4 = \frac{13.6}{136} \times 100 = 10 \text{ mg/L}$

$MgSO_4 = \frac{12}{120} \times 100 = 10 \text{ mg/L}$

$MgCl_2 = \frac{2}{95} \times 100 = 2.11 \text{ mg/L}$

Lime requirement for 50,000 L H_2O

$$= \frac{74}{100} \left[\begin{array}{l} \text{Ca(HCO}_3)_2 + 2 \text{Mg(HCO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as} \\ \text{CaCO}_3 \text{ eq.} \end{array} \right] \times \text{vol. of } H_2O$$

$$= \frac{74}{100} [5 + 2 \times 5.14 + 10 + 2.11] \text{ mg/L} \times 50,000 \text{ L}$$

$$= \frac{74}{100} [27.39 \text{ mg/L}] \times 50,000 \text{ L}$$

$$= 10,13,430 \text{ mg} \times 10^{-6} \text{ kg/mg} = \boxed{1.0134 \text{ kg}} \text{ Ans.}$$

Soda requirement for 50,000 L H_2O

$$= \frac{106}{100} \left[\text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ eq.} \right] \times \text{vol. of } H_2O$$

$$= \frac{106}{100} [10 + 10 + 2.11] \text{ mg/L} \times 50,000 \text{ L}$$

$$= \frac{106}{100} [22.11 \text{ mg/L}] \times 50,000 \text{ L}$$

$$= \frac{23.4366 \times 50,000}{100}$$

$$= 11,71,830 \text{ mg} \times 10^{-6} \text{ kg/mg} = \boxed{1.171830 \text{ kg}} \text{ Ans.}$$

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