

Chemistry - Syllabus

Unit - 1 Water :-

Common impurities, Hardness, determination of Hardness by complexometric [EDTA method], Degree of Hardness, Units of Hardness.

Municipal water supply, Requisite of drinking water, Purification of water, sedimentation, filtration, disinfection, breakpoint, chlorination, methods, priming and foaming. Boiler troubles: Scale and sludge formation, Internal treatment methods, priming and foaming, Boiler corrosion and caustic embrittlement.

Water softening: lime-soda process, zeolite (Permutit) process, Detrineralization process.

Numerical problems based on Hardness, EDTA, Lime-Soda, zeolite process.

2. Organic fuels:-

Solid fuels: Coal, classification of coal, Proximate & ultimate analyses of coal & its significance, Gross & Net calorific value, Determination of calorific value of coal by Bomb calorimeter, Metallurgical coke, carbonization processes, Otto-Hoffmann by product oven method.

Liquid fuels: Advantages of liquid fuels, Mining, Refining and Knocking, octane number, Reforming, Synthetic petrol, Cracking, Composition of Petroleum, Anti-knocking agents, Cetane number.

Gaseous fuels: Advantage, manufacturing, composition, Calorific value of coal gas and oil gas, Determination of calorific value of gaseous fuels by Junker's calorimeter.

Unit - 3 Corrosion and Its control :-

Definition and significance of corrosion, Mechanism of chemical (Dry) and electrochemical (wet) corrosion, galvanic corrosion, concentration corrosion & pitting corrosion.

protection from corrosion, protective coatings - galvanization and tinning, cathodic protection, sacrificial anode and modifications in design.

Unit - 4 Engineering Materials :-

Portland cement: definition, Manufacturing by Rotary kiln, Chemistry of setting and Hardening of cement.

Role of gypsum.

Glass: Definition, Manufacturing by tank furnace, Signification of annealing, Types & properties of soft glass, hard glass, borosilicate glass, glass wool, safety glass.

Lubricants: Classification, Mechanism properties, viscosity and viscosity index, flash and power fire point, cloud and pour point, Emulsification and steam emulsion number.

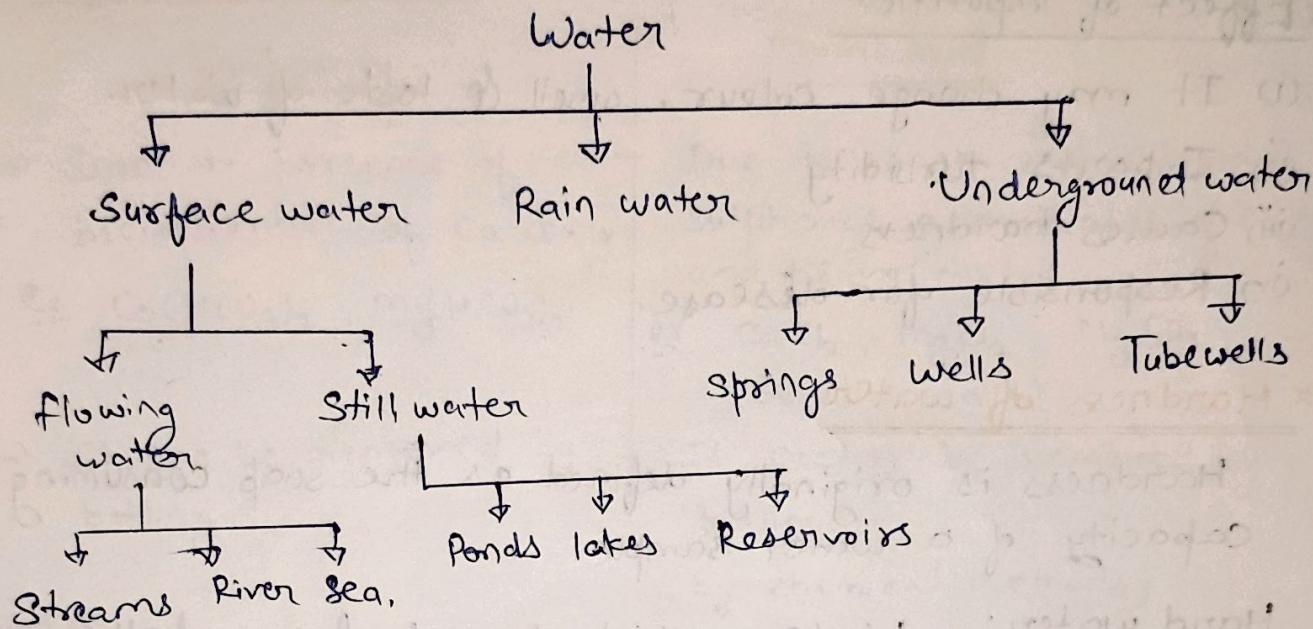
Unit - 5 Organic Reaction mechanism & Introduction of drugs

Organic Reaction mechanism: Substitution: S_N1 , S_N2 , electrophilic aromatic substitution in benzene, free radical, Halogenations of alkenes, Elimination; elimination in alkyl halides, dehydration of alcohols, Addition: electrophilic and free radical addition in alkenes nucleophilic addition in aldehyde and ketones, Rearrangement; carbocation, and free radical rearrangements.

Drugs: Introduction, synthesis, properties and uses of Aspirin, paracetamol.

* Unit - 1 Water *

- Sources of water:- (Universal solvent)



* Common Impurities of water :-

(i) Dissolved impurities -

(a) Inorganic salt $\Rightarrow \text{MgCl}_2, \text{CaCl}_2, \text{Mg}(\text{HCO}_3)_2$ etc.

(b) Organic salt \Rightarrow

(c) Dissolved gases $\Rightarrow \text{CO}_2, \text{N}_2, \text{O}_2, \text{N}_2\text{O}$ etc.

(ii) Suspended impurities -

(a) Inorganic \Rightarrow clay, sand

(b) Organic \Rightarrow oil globules, vegetable etc.

(iii) Colloidal impurities - finally divided silica & clay, amino acids etc.

(iv) Micro-organisms - fungi, bacteria etc.

* Soap Sodium salt of Higher fatty acids.

ex. Sodium stearate, sodium palmitate
 RCOONa (Soap)

* Effect of impurities

- (i) It may change colour, smell & taste of water.
- (ii) Imparts turbidity
- (iii) Causes hardness
- (iv) Responsible for disease.

* Hardness of water

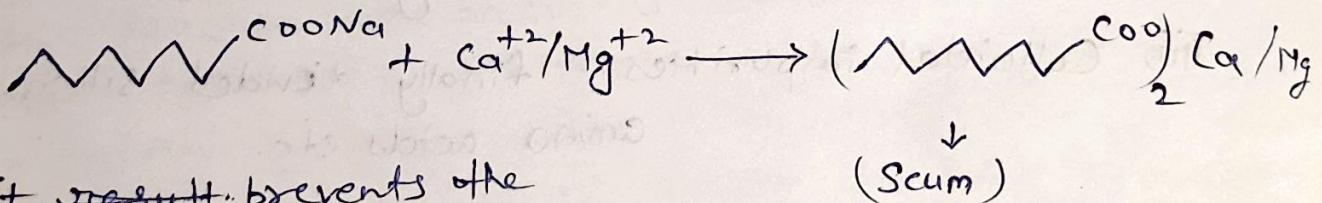
Hardness is originally defined as the soap consuming capacity of a water sample.

Hard water:- Water which doesn't form lather or foam with soap is known as hard water.

Causes of hardness \rightarrow Presence of $\text{Ca}^{+2}/\text{Mg}^{+2}$ ions in along with metals Fe^{+2} , Mn^{+2} or Al^{+2} and soluble salts.

Soft water:- Water which easily produce lather or foam with soap is known as soft water.

Note when hard water is treated with soap -
it forms scum



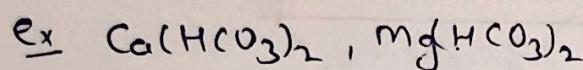
\rightarrow It ~~result~~ prevents the formation of foam & result the wastage of soap.

\rightarrow Insoluble, sticky
 \rightarrow Calcium or magnesium salt of higher fatty acid.

* Types of Hardness :-

Temporary

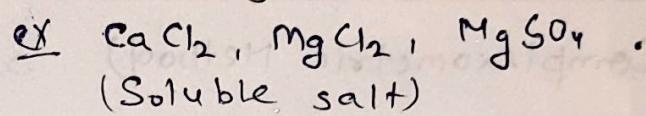
→ Due to presence of bicarbonate of Ca & Mg



→ It can be removed by boiling.

Permanent

Due to presence of chlorides, sulphates and nitrates of Ca & Mg and heavy metal.



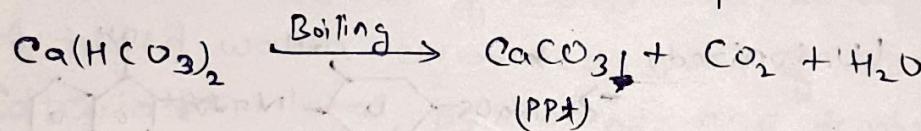
It cannot be removed by boiling.

(by chemical methods)

Note

During boiling

bicarbonate decompose into carbonates which are insoluble and can be separated.



Degree of Hardness :-

It is expressed as equivalent of CaCO_3 .

Reason

(a) It is completely insoluble in water.

(b) It's molecular weight is 100 and so calculation becomes easier.

$$\text{Hardness} = \frac{(\text{Mass of hardness producing substance})}{(\text{Chemical eq. of hardness producing substance}) \times n} \times 100$$

here n is valency of Metal.

Units of hardness

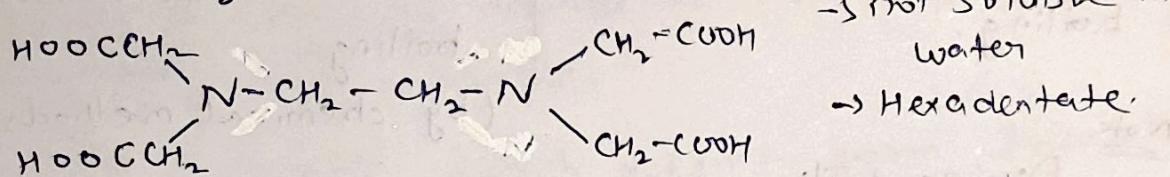
$$1 \text{ mg/liter} = 1 \text{ ppm} = 0.1^\circ \text{Fr} = 0.07^\circ \text{Cl}$$

- * ppm \Rightarrow number of parts of CaCO_3 per million parts of H_2O
- ${}^\circ\text{Cl}$ \Rightarrow Degree Clarke & ${}^\circ\text{Fr}$ = Degree french.

Determination of Hardness of water in Lab:-

(Complexometric Method)

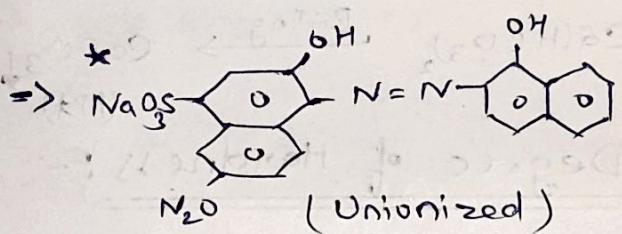
EDTA \Rightarrow Ethylene diamine tetra acetic acid.



- \rightarrow Using indicator \Rightarrow EBT (Eriochrome-black T)
- \rightarrow Sodium salt of EDTA is used in this titration.

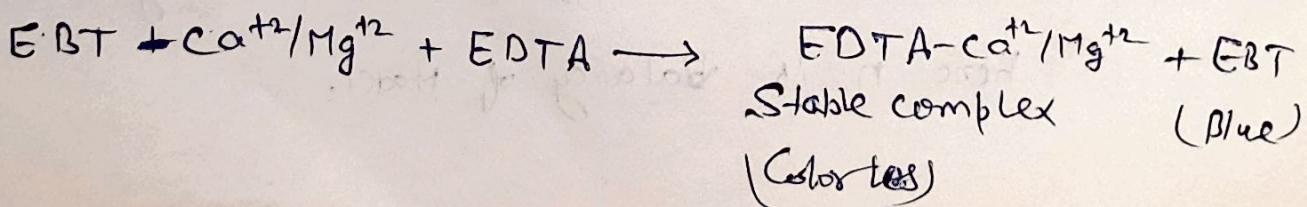
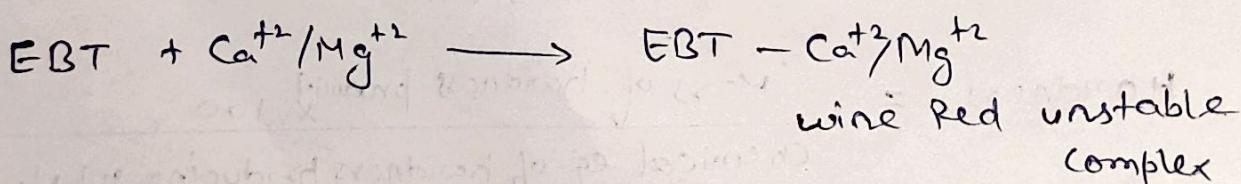
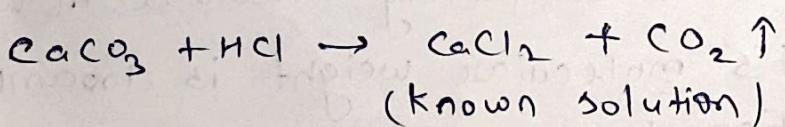
EBT \rightarrow Blue (Unionized)

\downarrow
wine red
(Ionized)

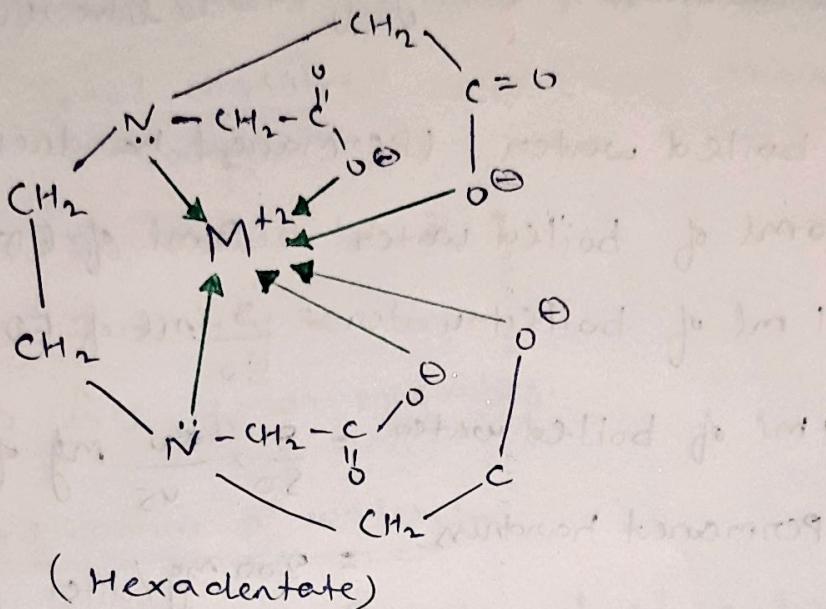


less stable & easily replaced by [EBT]

Standard solution \Rightarrow 1 g CaCO_3 per liter water.



EDTA - metal ion complex



E 1 gm of calcium carbonate is dissolved in 1 liter of water. 50 ml of standard hard water consumed 45 ml of EDTA solution. 50 ml of sample water consumed 18 ml of EDTA solution. After boiling 50 ml of boiled water consumed 9 ml of EDTA solution. Calculation total, permanent and temporary hardness.

$$\text{Sol}^n = \underline{\text{Step 1}} \quad 50 \text{ ml of std w} = 45 \text{ ml of EDTA}$$

$$1 \text{ ml of EDTA} = \frac{50}{45} \text{ ml of std. w.}$$

$$* \text{ Strength of EDTA} = \frac{50}{45} \text{ mg of } \text{CaCO}_3$$

Step 2 Total hardness.

$$50 \text{ ml of std w} = 18 \text{ ml of EDTA}$$

$$1 \text{ ml of std w} = \frac{18}{50} \text{ ml of EDTA}$$

$$1 \text{ ml of std w} = \frac{18}{50} \times \frac{50}{45} \text{ mg of } \text{CaCO}_3$$

$\frac{1}{2}$ liter of sample water = 400 mg per litre.

Total hardness = 400 mg of CaCO_3 / litre H_2O

Step III with boiled water (Permanent hardness)

50 ml of boiled water = 9 ml of EDTA

1 ml of boiled water = $\frac{9}{50}$ ml of EDTA

1 ml of boiled water = $\frac{9}{50} \times \frac{50}{45}$ mg of CaCO_3

* Permanent hardness = 200 mg/liter As

Temporary hardness = Total - Permanent

= 200 mg/l.

* Disadvantage of Hardwater:-

- (i) Dissolved salt increase boiling point and it wastes the large amount of heat.
- (ii) Scum is sticky and stick to body.
- (iii) Lot of soap is wasted in cleaning.
- (iv) creates problems in boiler.
- (v) In industries.

* Municipal water Supply

Water supplied by govt agency. It contains large number of impurities and unfit for drinking.

Potable water \Rightarrow which is fit for drinking.

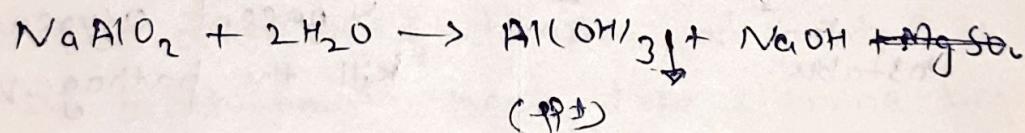
* Requisites of drinking water:-

- (i) Water should be clear, od· pleasant and odourless.
- (ii) Total dissolved solid (TDS) should be less than 500 ppm.
- (iii) pH should be 7-8.
- (iv) Turbidity < 10 ppm.
- (v) free from microbes.

* Purification of water:-

1. Screening → Removing floating particle by net.
2. Sedimentation → (Plain) heavy particles settle down at the bottom & they are removed.
- (3) Sedimentation with coagulation → Removing finely divided suspended impurities.

Coagulants like alum, $\text{NaAlO}_2 \text{Al}_2(\text{SO}_4)_3$ are used.



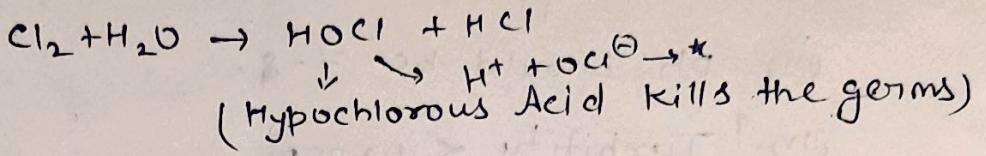
- (4) Filtration → Removing colloidal impurities & larger organisms.

by ~~the~~ passing through the layer of sand & pebbles

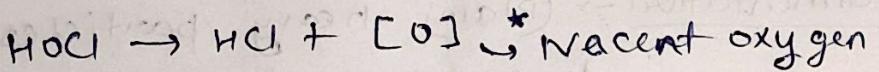
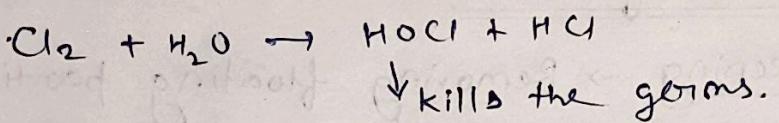
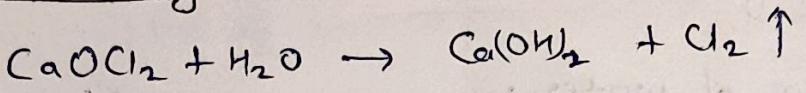
5. Disinfection:- kills microbes (Pathogen)

(a) boiling \Rightarrow by boiling water for 20-30 mins.

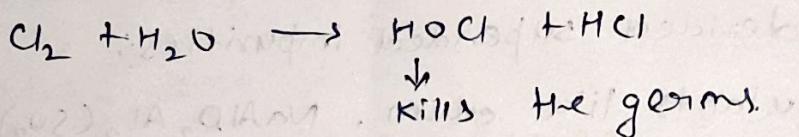
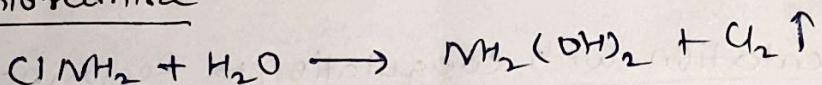
(b) Chlorination



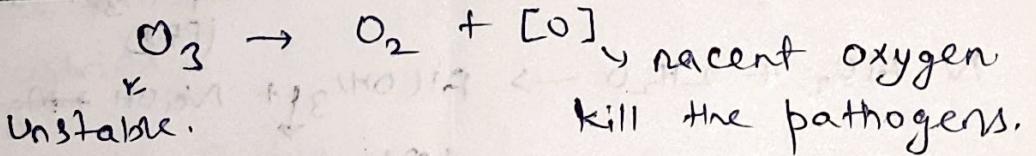
(c) By bleaching power



(d) By Chloramine



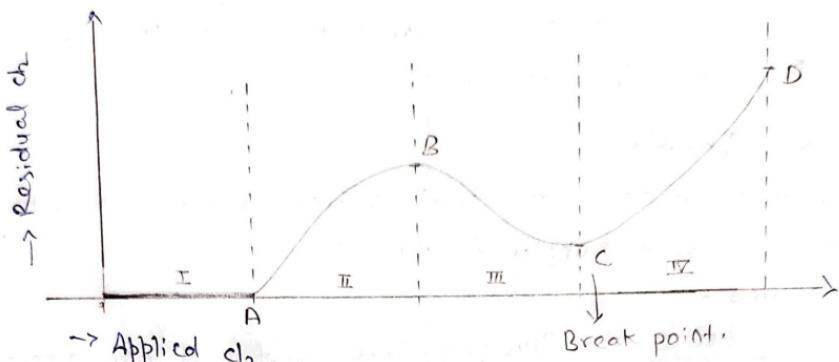
(e) By Ozone



(f) By Using KMnO₄

(g) Uv radiation

* Break Point chlorination



I \Rightarrow Added chlorine is consumed immediately due to oxidation.

II \Rightarrow formation of chloro-organic & chloramine

III \Rightarrow further increased amount of Cl_2 responsible for oxidation of chloro-organic compounds & decrease in amount of residual chlorine at point c.

IV \Rightarrow After break point chlorination, added is not used in any reaction.

Note The addition of chlorine at point c is known as break point where free chlorine begins to appear and all the colour, odour & taste at break points.

Definition The chlorination of water to such an extent that living organism as well as other organism impurities in water are destroyed.

- * Significance of chlorination :-
 - It ensures complete destruction of organic compounds.
 - and micro-organisms and prevents the growth of weeds in water.

- * Boiler Trouble :-

Boiling means to heat water & convert into steam and supply to turbine.

problems -

(i) Sludge ⇒ Sludges are soft and non-adherent deposits. (Insoluble)

- It can be removed easily.
- It can transfer heat to some extent & are less dangerous.

→ formed by substance like $MgCl_2$, $CaCl_2$ etc
 $CaCl_2$, $MgSO_4$

(ii) Scale ⇒ formation of hard, tight adhere to surface.

It can't be removed easily.

Causes ⇒ $CaSO_4$, $Mg(OH)_2$



Sludge

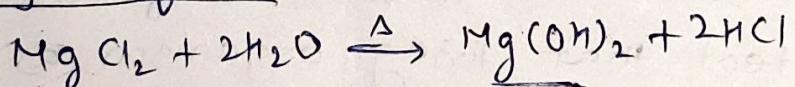


Scale

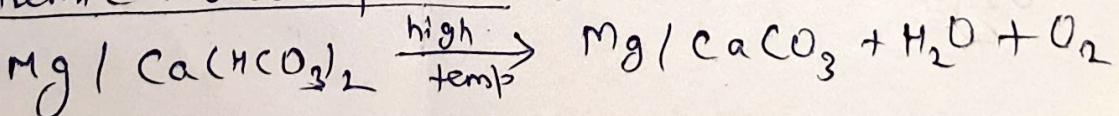
- * Causes of formation of Sludge & scale -

(i) Decrease in solubility ⇒ like $CaSO_4$
 when temp increases then solubility decrease and gets precipitated as hard scale.

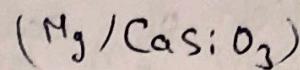
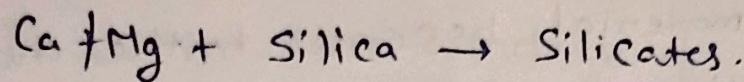
(ii) Hydrolysis of salts ⇒



(iii) Chemical decomposition ⇒



(iv) formation of Silicates



hard to remove.

(v) Disadvantage

- (i) Wastage of fuel.
- (ii) Distortion of boiler. (Begging)
- (iii) Danger of explosion due to uneven expansion of scale.

→ ~~Rem.~~ Soft Scale can be removed by brush.

→ brittle sludge can be removed by sudden heating and sudden cooling.

(iii) Priming water droplets carried with steam.
harmful for blades of ~~scale~~ boiler.

Cause ⇒ changing in boiling point & high heating.

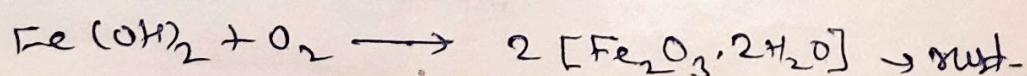
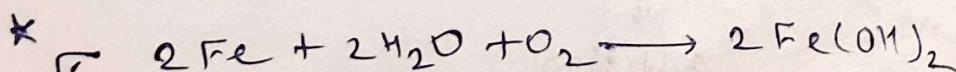
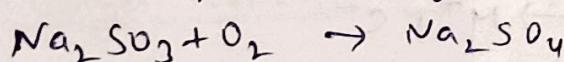
(iv) Foaming Due to surface tension bubbles are carried with steam and it may create to rotate the turbine.

(v) Boiler corrosion:-

The decay of boiler corrosion material due to chemical reaction.

It Reduce boiler strength.

Cause ⇒ presence of CO_2 , O_2 , dissolved salts or acid

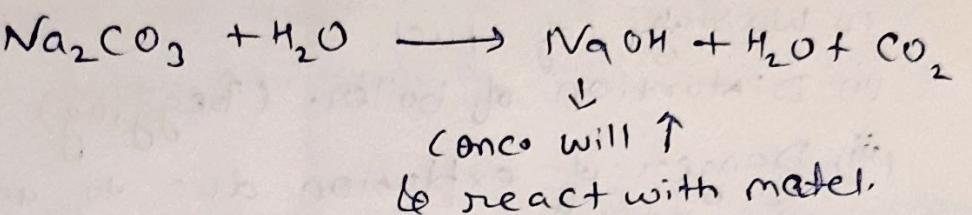


(v) Caustic embrittlement :-

Boiler material becomes brittle due to the accumulation of caustic substance.

Cause \Rightarrow highly alkaline water.

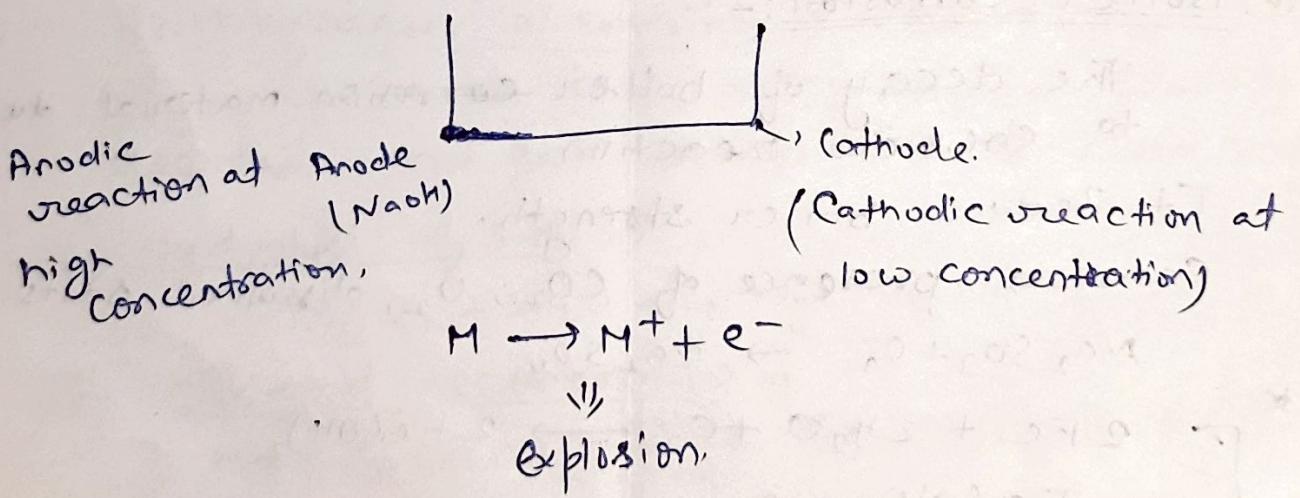
It takes place joint, bends and material become brittle.



Cause \rightarrow High concentration of NaOH
 \rightarrow presence of sodium silicate.
 \rightarrow

Disadvantages

- (i) Damaging the boiler
- (ii) Efficiency will be decrease.
- (iii) Dissolved salt carried to the blade & harmful for it.
- (iv) Can't judge the level of water.
- (v) Chances of explosion will increase.



* Water Softening :-

To remove the hardness of water,
Removing Ca^{+2} and Mg^{+2} ions.

There are two methods -

(I) External method :-

Water introduced to the boiler first and then softening the water.

Methods

(i) Colloidal conditioning :-

At low pressure, scale formation can be avoided by adding kerosene, tannin, agar-agar.

It will ~~make~~ make loose deposition of ppt.

(ii) Phosphate conditioning :-

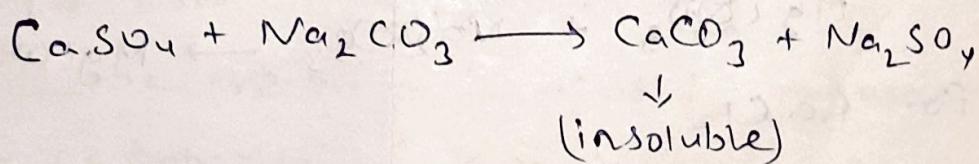
At high pressure boiler,

Sodium phosphate reacts with Mg^{+2} and forms soft sludge.



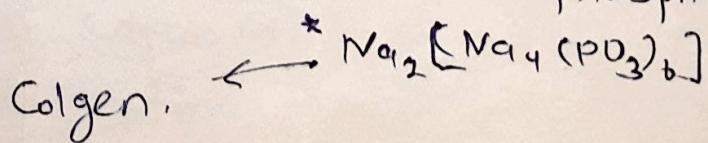
(Sludge deposit)

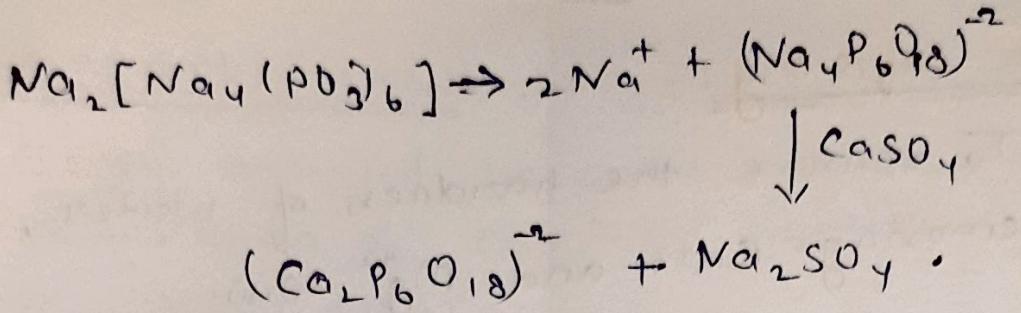
(iii) Carbonate conditioning :-



easy to remove.

(iv) Colgen conditioning :- Adding of Sodium hexameta phosphate.





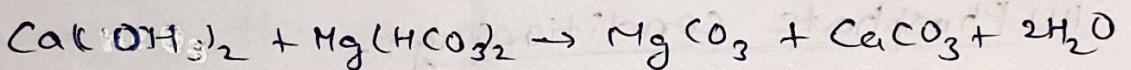
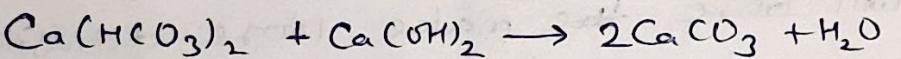
* External methods

(i) Lime Soda Process:-

Hydrated lime $[\text{Ca}(\text{OH})_2]$ + Soda ash $[\text{Na}_2\text{CO}_3]$ are added in hard water.

(i) For temporary hardness -

Only lime is required.
reacts with bicarbonate.

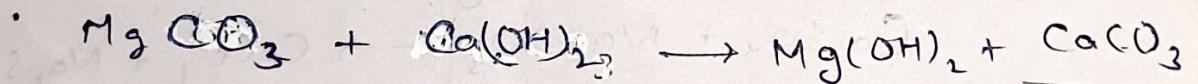
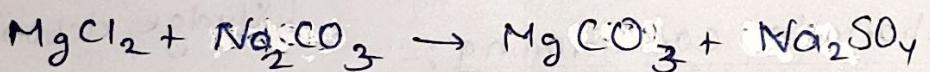


(ii). For permanent hardness-

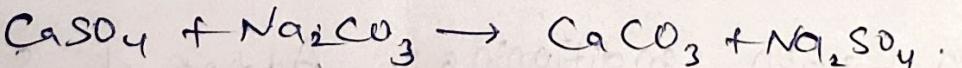
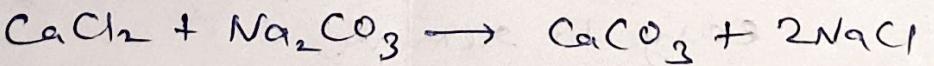
lime & Soda both are required:

for $\text{MgCl}_2, \text{MgSO}_4 \rightarrow$ both

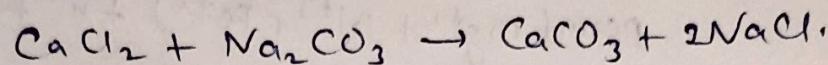
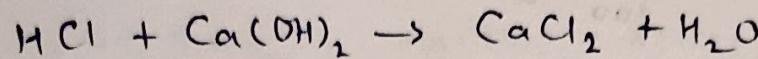
for $\text{CaSO}_4, \text{CaCl}_2 \rightarrow$ Only Soda.



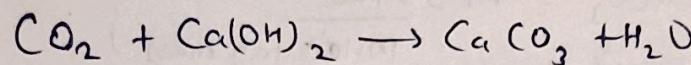
for CaCl_2



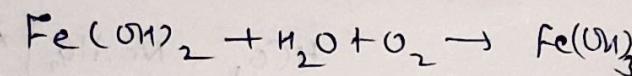
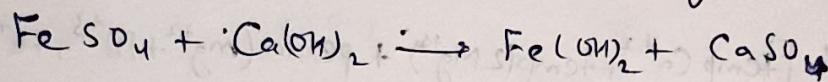
* if Acid (H^+ ion) is present in Hard water
then both are required.



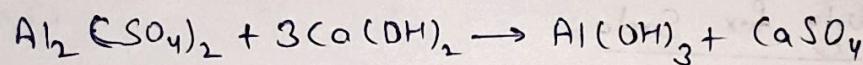
* In presence of CO_2 only $\text{Ca}(\text{OH})_2$ is required.



* In presence of dissolved Salt of Al, Fe, Na



* Al =

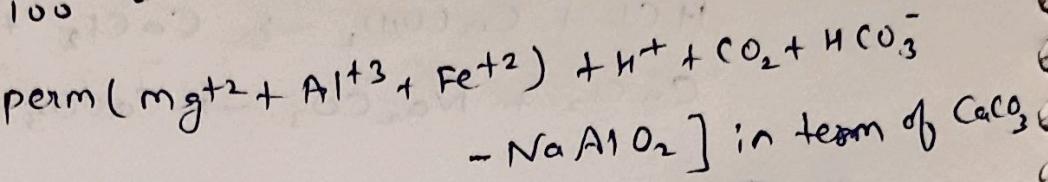


This whole process is carried out either in cold or hot water.

	Cold Soda-lime	Hot Soda-lime
(i)	at normal temp	at $80 - 150^\circ\text{C}$
(ii)	less efficient	Very efficient
(iii)	Reaction is slower	Fast and complete.
(iv)	Filteration slow	Filteration fast.
(v)	Couglants are essential	No need of couglants.
(vi)	low softening capacity	High softening capacity.
(vii)	large quantity of lime is required	less lime is required.
(viii)	No steam required	Required.
(ix)	Cheap	Costly.

Formula for Hardness

$$\text{For lime} = \frac{74}{100} [\text{temp } \text{Ca}^{+2} + \text{temp } (2\text{Mg}^{+2})] +$$



$$(\text{In term of } \text{CaCO}_3 = \text{HPS} \times \frac{100}{\text{molecular mass}})$$

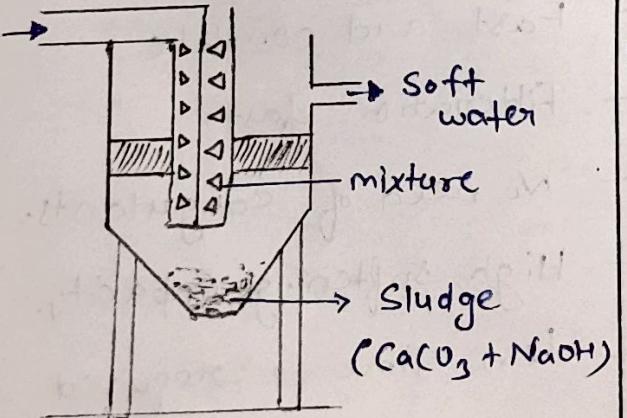
If per % of purity or volume is given -

$$\text{lime} = \frac{74}{100} [\text{temp } \text{Ca}^{+2} + \text{temp } (2\text{Mg}^{+2}) + \text{perm } (\text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2}) + \text{H}^+ + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2] \times \frac{100}{\% \text{ purity}} \times \text{volume.}$$

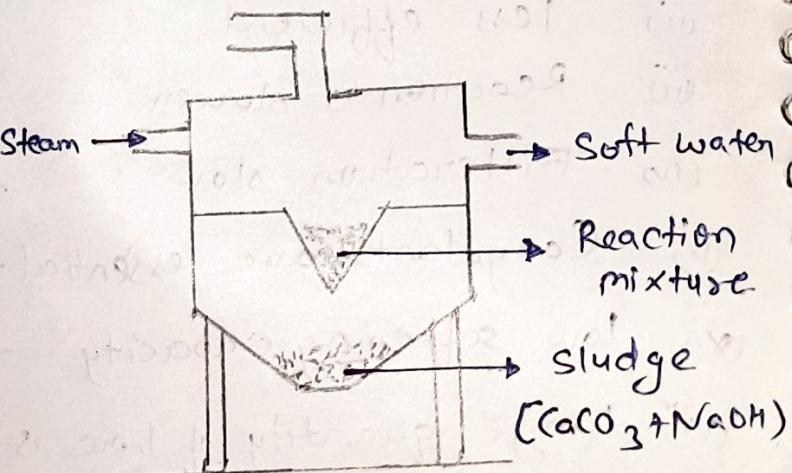
Similarly for Soda

$$\text{Soda} = \frac{106}{100} [\text{perm } (\text{Mg}^{+2} + \text{Ca}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3}) + \text{H}^+ - \text{HCO}_3^-] \text{ in terms of } \text{CaCO}_3 \times \text{Volume} \times \frac{100}{\% \text{ purity.}}$$

Cold lime-Soda



Hot lime Soda



Q A Sample water has the Analytical report -

$$\text{MgCO}_3 = 84 \text{ mg/l}, \text{CaCO}_3 = 40 \text{ mg/l}$$

$$\text{CaCl}_2 = 55.5 \text{ mg/l}, \text{Mg}(\text{NO}_3)_2 = 37 \text{ mg/l}$$

$$\text{KCl} = 20 \text{ mg/l}$$

Calculate the amount of lime (86% pure) & Soda (83% pure) needed for the treatment of 800000 l of water.

Soln

	Amt	Molar factor	Amt x m.f. = eq
MgCO_3	84 mg/l	$100/84$	100
CaCO_3	40 mg/l	$100/100$	40
CaCl_2	55.5 mg/l	$100/110$	50
$\text{Mg}(\text{NO}_3)_2$	37 mg/l	$100/148$	25.17
KCl	20 mg/l	$100/75.5$	Not perform in hardness.

for lime

$$= \frac{74}{100} [2 \times 100 + 40 + 25.17 + 50] \times \frac{100}{86} \times 800000$$

$$= \frac{74}{86} \times 315.17 \times 800000$$

$$= 21.69 \times 10^6 \text{ mg}$$

$$= 21.69 \text{ Kg} \quad \underline{\text{Answer}}$$

for Soda

$$= \frac{106}{100} \times [100 + 40] + 0 - 0 \times \frac{100}{83} \times 800000$$

$$= 14.30 \times 10^6 \text{ mg}$$

$$= 14.30 \text{ Kg} \quad \underline{\text{Answer}}$$

Note CaCO_3 as well as MgCO_3 is considered in temporary hardness.

Q A sample of water was analyzed & found contains the following -

$$\text{Mg}(\text{HCO}_3)_2 = 20 \text{ mg/l} \quad \text{CaCl}_2 = 12 \text{ mg/l}$$

$$\text{CaSO}_4 = 25 \text{ mg/l} \quad \text{SiO}_2 = 2 \text{ mg/l}$$

$$\text{CaCO}_3 = 5 \text{ mg/l} \quad \text{NaCl} = 1 \text{ mg/l}$$

$$\text{MgCl}_2 = 10 \text{ mg/l}$$

Calculate the amount of lime & Soda.

<u>Soln</u>	<u>Given</u>	<u>amt</u>	<u>molar mass eq.</u>	<u>molar f x mole. = eq.</u>
	$\text{Mg}(\text{HCO}_3)_2$	20	$100/146$	$20 \times 100/146 = 13.7$
	CaSO_4	25	$100/136$	$25 \times 100/136 = 18.3$
	CaCl_2	12	$100/111$	$100/111 \times 12 = 10.8$
	CaCO_3	5	$100/100$	$100/100 \times 5 = 5$
	MgCl_2	10	$100/95$	$100/95 \times 10 = 10.5$
	SiO_2			Do not responsible for hardness.
For	NaCl			

for lime temp = $\text{Mg}(\text{HCO}_3)_2 + \text{CaCO}_3$
 perm = MgCl_2

$$\text{lime} = \frac{74}{100} [13.69 \times 2 + 5 + 10.5]$$

$$\text{lime} = \frac{74}{100} \times 42.7$$

$$\text{lime} = 31.59 \text{ mg/l}$$

for Soda perm = $MgCl_2$, $CaCl_2$, $CaSO_4$

$$\text{Soda} = \frac{106}{100} [13.6 + 10.8 + 10.5]$$

$$\text{Soda} = 45.2 \text{ mg/l} \quad \underline{\text{Answer}}$$

Q A water sample on analysis give the following data -

$$(i) Ca^{+2} = 20 \text{ ppm} \quad (iv) HCO_3^- = 150 \text{ ppm}$$

$$(ii) Mg^{+2} = 25 \text{ ppm} \quad (v) K^+ = 10 \text{ ppm}$$

$$(iii) CO_2 = 30 \text{ ppm}$$

& v. purity of lime is 87%, & for Soda is 91%. then calculate amount of lime & Soda for 1 million water.

Soln	Given data is	amt	molar eq. = molat. f. x amt	eq. = molat. f. x amt
	Ca ⁺²	20 ppm	100/H ₂ O	104.16
	Mg ⁺²	25 ppm	100/24	104.16
	CO ₂	30 ppm	100/44	68.18
	HCO ₃ ⁻	150 ppm	100/61	245.9
	K ⁺	not responsible for hardness		

R Note ions are responsible for permanent hardness

$$\text{for lime} = \frac{74}{100} [\text{perm}(20\text{g}^{+2}) + \text{CO}_2 + \text{HCO}_3^-] \times V \times \frac{100}{V.p}$$

$$= \frac{74}{100} [104.16 + 68.18 + 245.9] \times 10^6 \times \frac{100}{87}$$

$$= 355.6 \times 10^6 \text{ mg/l} = 355.6 \text{ kg/l (lime)}$$

for Soda

$$\begin{aligned} &= \frac{106}{100} [\text{perm}(\text{mg/l}) + \text{Ca}^{2+} - \text{HCO}_3^-] \times \frac{100}{91} \times 10^6 \\ &= \frac{106}{100} [50 + 104.16 - 245.9] \times \frac{100}{91} \times 10^6 \\ &= 106 \times 10^6 \text{ mg/l} \\ &= 106 \text{ kg/l Soda } \underline{\text{Answer}} \end{aligned}$$

Adv → economical

→ less corrosion tendencies.

→ it removes hardness as well as minerals.

→

Disadvantage

→ Sludge disposal problem

→ It cannot be used in high pressure boilers.

→ Requires careful operation & skilled supervision.

Regeneration ⇒ No need.

(ii) Zeolite or Permutit Process :-

(Base exchange)

both for (temporary & permanent)

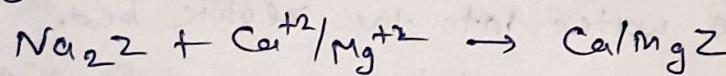
Zeolite \Rightarrow Sodium aluminium silicate $[Na_2Al_2Si_2O_8 \cdot nH_2O]$
(Hydrated)

It can be represent as Na_2Z .

Zeolite \rightarrow Natural \Rightarrow non porous, amorphous, durable.
Hard.

Synthetic \Rightarrow porous, crystalline structure.
(Jelly like)

When it comes to contact to Ca^{+2}/Mg^{+2} ions, it exchanges Na with ions.

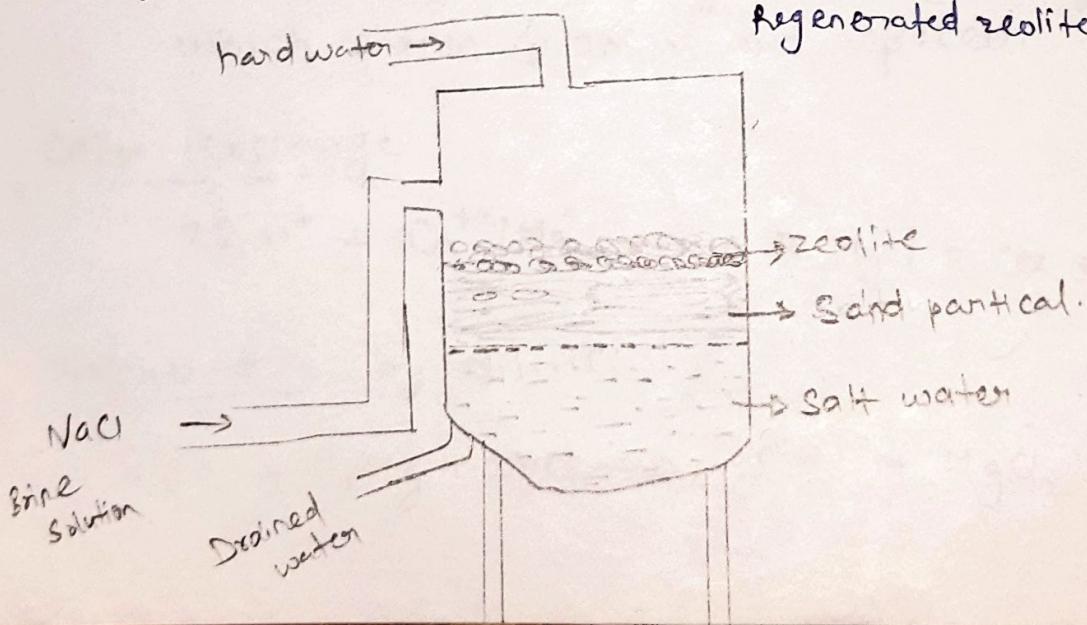


Note when all the sodium ions are replaced by Ca^{+2} or Mg^{+2} then zeolite is exhausted.

Regeneration by washing with conc. $NaOH$ solution
that is known as brine solution.



hard water \rightarrow regenerated zeolite.



$$\text{Hardness} = \frac{50 \times M \times V_2 \times 10^3}{58.5 \times V_1}$$

Here V_1 = Total volume of water

V_2 = volume of NaCl (regeneration)

m = amount of NaCl

Advantage

- (i) It requires less time for softening.
- (ii) less skill is required.
- (iii) Equipment is compact and less space is required.
- (iv) No danger of sludge formation.

Disadvantage

- (i) less efficient as compared to Ion exchange.
- (ii) Mineral acid must be neutralized before feeding the water into the zeolite bed.
- (iii) if water contains large amount of Mn^{+2} or Fe^{+2} they must be removed. (Regeneration is diff.)

(iii) **Ion Exchanger** :- [Demineralisation]

(Reversible reaction)

Properties of Ion exchanger (Crossed linked organic)

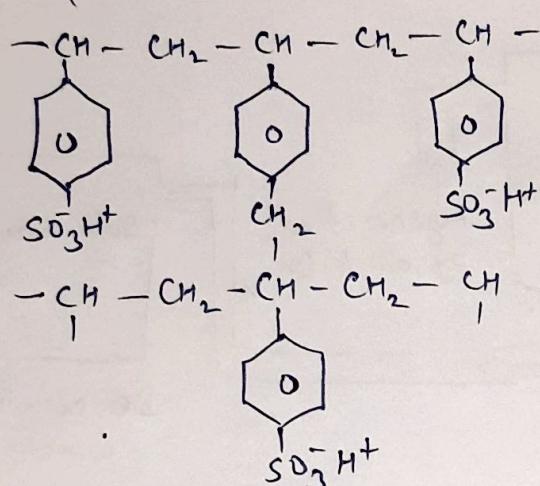
- (i) Complex and polymeric nature. (Regin)
- (ii) Insoluble in organic solvent & water.

These are of two types-

Cationic

Acidic ion exchanger

(R^-H^+)

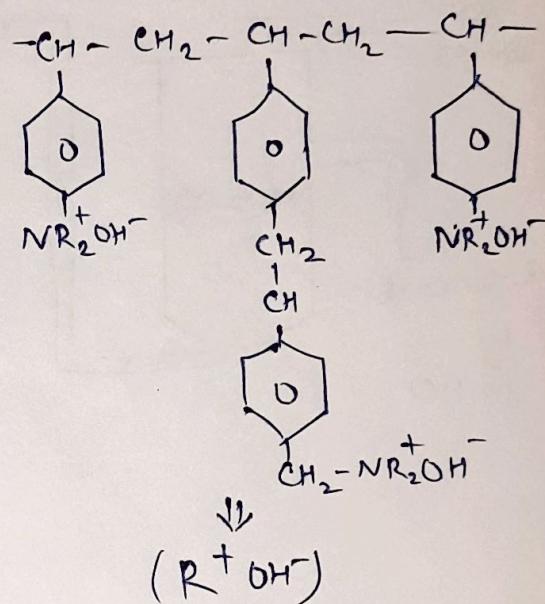


\Downarrow
 (R^-H^+)

Anionic

Basic ion exchanger

(R^+OH^-)



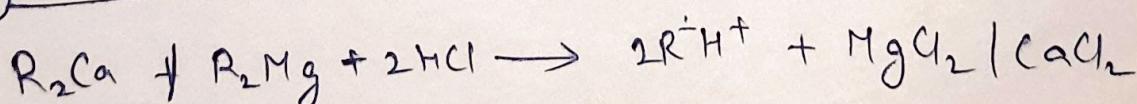
\Downarrow
 (R^+OH^-)

These have active functional group from which cation & anions are replaced.

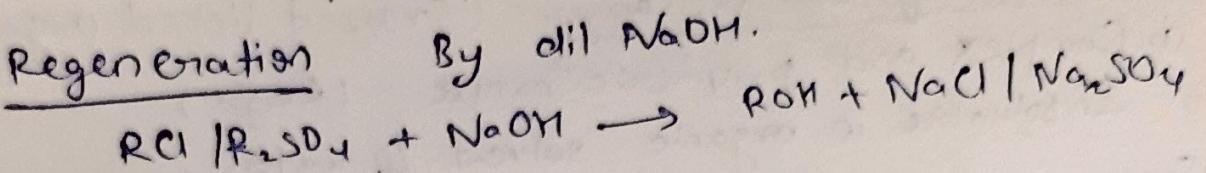
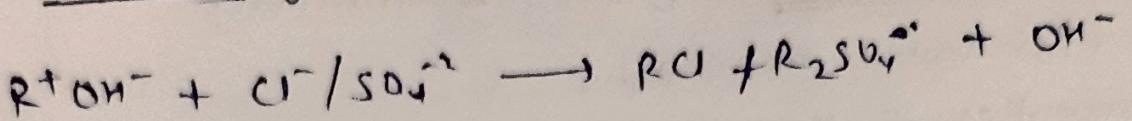
Cation exchange



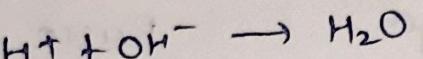
Regeneration by dil. HCl



Anion exchange



By these reactions,
H⁺ ion & OH⁻ ion combined to form water



cation
exchange

Anion exchange

