

Unit 3waterSources of water

- Surface water
- under ground water
- Rain water
- Sea water

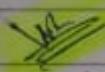
~~Impurities in water~~1) Dissolved impurities

Dissolved salts  $\rightarrow$  Carbonate, Bicarbonates

Dissolved gases  $\rightarrow$   $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{S}$

2) Suspended impurities  $\rightarrow$ 

clay, sand, vegetable Matter (easily seen by eye)

3) Colloidal impurities  $\rightarrow$  Organic waste4) Micro organisms  $\rightarrow$  Bacteria, virus, fungi etc.Hard water

- Contain dissolved salts of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$
- Does not form lather with soap
- Large quantity of soap is required during washing

Soft water

- Does not contain this salts
- Forms lather with soap
- Soap is not wasted at all.

Water Quality StandardsPhysical characteristics

Colour

odour

electrical conductivity

Temperature

Chemical characteristics

pH (6.5 to 8.5)

Total Dissolved solid (500 ppm)

Dissolve  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ Residual  $\text{Cl}_2$  (250 ppm)Biological characteristics

Bacteriological

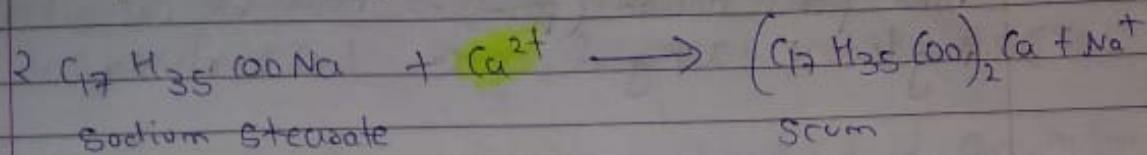
Virological

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Valency}}$$

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## Hardness of water

Soap consuming capacity of water



## Hardness of water

Temporary Hardness  
(carbonate hardness) (CH)

## Calcium & Magnesium Bicarbonate

It can be removed  
by Bel Boiling

$\text{O} \rightarrow \text{HCO}_3^-$  of  
 $\text{Ca}^{2+}/\text{Mg}^{2+}$  salt

B	S	C
T	P	

Permanent Hardness  
(Non-carbonate hardness)  
( $\text{KCH}$ )

calcium sulphate,  
Magnesium sulphate  
Calcium & magnesium  
chlorides.

It is not removed

Due to  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$  ions

WZ Reason of choosing Caco<sub>3</sub> as the standard for calculating hardness of cements

- ① Its Molecular weight exactly 100 which makes Mathematics calculation easier.
  - ② It is the most insoluble salts that can be precipitated in water treatment

$$\text{Equivalent of } \text{CaCO}_3 = \frac{\text{Mass of substance}}{\text{eq wt of substance}} \times \text{eq wt of } \text{CaCO}_3$$

If divalent ions present in salt (+2)

$$\text{Equivalent of } \text{CaCO}_3 : \frac{\text{mass of substance}}{\text{Molecular mass of substance}} \times 100$$

$$\text{Equivalent tonnes of } \text{CaCO}_3 = \frac{\text{Amount of hardness causing salt}}{\frac{\text{Mol Mass of } \text{CaCO}_3}{\text{Mol Mass of hardness causing salt}}} \times \text{Multiplication factor}$$

### Units of Hardness.

- 1) Parts per Million (ppm)  $\rightarrow$  Parts of  $\text{CaCO}_3 / 10^6 \text{ parts of water}$
- 2) mg/L  $\rightarrow$  1 mg of  $\text{CaCO}_3 / 1 \text{ L of water}$
- 3) Degree Clark  $\rightarrow$  Parts of  $\text{CaCO}_3 / 70000 \text{ parts of water}$  ( ${}^\circ\text{C}$ )
- 4) Degree French  $\rightarrow$  Parts of  $\text{CaCO}_3 / 10^5 \text{ parts}$  ( ${}^\circ\text{F}$ )

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.07 {}^\circ\text{ Clark} = 0.1 {}^\circ\text{ French}$$

Equivalent weight  $\text{Al}_2(\text{SO}_4)_3 = \frac{342}{6}$

Salt	Molar Mass	Multiplication factor
$\text{Ca}(\text{HCO}_3)_2$	162	100 / 162
$\text{Mg}(\text{HCO}_3)_2$	146	100 / 146
$\text{CaCO}_3$	100	100 / 100
$\text{CaSO}_4$	136	100 / 136
$\text{CaCl}_2$	111	100 / 111
$\text{MgCO}_3$	84	100 / 84
$\text{MgSO}_4$	120	100 / 120
$\text{MgCl}_2$	95	100 / 95
$\text{Mg}(\text{NO}_3)_2$	148	100 / 148
$\text{Al}_2(\text{SO}_4)_3$	342	100 / 114
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	100 / 278
$\text{HCO}_3^-$	82	100 / 82 x 2
$\text{CO}_3^{2-}$	61	
$\text{OH}^-$	60	
	2	

a) calculate the total hardness of water sample

having following composition in ppm

$\text{CaCO}_3 = 20^\circ\text{Cl}$ ,  $\text{MgSO}_4 = 4^\circ\text{Cl}$ ,  $\text{CaSO}_4 = 2^\circ\text{Cl}$ ,  
 $\text{Fe}_2\text{O}_3 = 0.04^\circ\text{Cl}$ ,  $\text{MgCl}_2 = 0.4^\circ\text{Cl}$ ,  $\text{SiO}_2 = 0.09^\circ\text{Cl}$

Sol)	Constituents	Quantity ( $^\circ\text{Cl}$ )	Multiplication factor	$\text{CaCO}_3$ equivalent
	$\text{CaCO}_3$	20	100/100	20
	$\text{CaSO}_4$	2	100/136	1.47
	$\text{MgCl}_2$	4	100/95	1.21
	$\text{MgSO}_4$	4	100/120	3.33
Total Hardness	$\text{Fe}_2\text{O}_3$	0.04		
	$\text{SiO}_2$	0.09		

$$\begin{aligned} \text{Total hardness} &= 29.01^\circ\text{C} \\ &= 29.01 \times 14.3 \text{ ppm} \\ &= 414.84 \text{ ppm} \end{aligned}$$

$$1^\circ\text{Cl} = 14.3 \text{ ppm}$$

Multiplication factor =  $\frac{\text{Eq. weight of } \text{CaCO}_3}{\text{Eq. weight of compound substance}}$

(e) Calculate the total hardness of water in °F and °C.

$$\text{Mg(HCO}_3)_2 = 20.8 \text{ mg/L}, \text{Mg(NO}_3)_2 = 28.8 \text{ mg/L}$$

$$\text{MgCl}_2 = 21 \text{ mg/L}, \text{MgSO}_4 = 20 \text{ mg/L}$$

$$\text{CaCO}_3 = 21.2 \text{ mg/L} \quad \text{KCl} = 73.2 \text{ mg/L}$$

Equivalent of mg

Salt	Amount (mg/L)	Multiplication factor	Equivalent of mg Mg/L
Mg(HCO <sub>3</sub> ) <sub>2</sub>	20.8	100 / 146	14.2
Mg(NO <sub>3</sub> ) <sub>2</sub>	28.8	100 / 148	19.45
MgCl <sub>2</sub>	21	100 / 95	22.10
MgSO <sub>4</sub>	20	100 / 120	16.67
CaCO <sub>3</sub>	21.2	100 / 100	21.2
KCl	73.2		

$$\text{Total hardness} = 93.62 \text{ mg/L}$$

$$\text{Total Hardness} = 93.62 \times 0.1^\circ \text{Fr}$$

$$= 9.362^\circ \text{ Fr}$$

$$\text{Total Hardness in } {}^\circ\text{C} = 93.62 \times 0.07 {}^\circ\text{C}$$

$$= 6.55 {}^\circ\text{C}$$

~~W.C.~~ A water sample analysis

$$\text{Mg(HCO}_3)_2 = 83 \text{ mg/L}, \quad \text{Ca(HCO}_3)_2 = 134 \text{ mg/L}$$

~~$$\text{CaCO}_3, \text{CaSO}_4 = 124 \text{ mg/L}$$~~

$$\text{MgCl}_2 = 84 \text{ mg/L}$$

$$\text{CaCl}_2 = 94 \text{ mg/L}$$

calculate temporary & permanent hardness in Clark.

NaCl, Na<sub>2</sub>CO<sub>3</sub>, KCl, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> is not cooated  
it is not formed Hardness.

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For	Constituent	Quantity mg/l	Multiplication factor	(CaCO <sub>3</sub> equivalent) mg/l
8 mg/l	Mg(HCO <sub>3</sub> ) <sub>2</sub>	83	100 / 146	56.8
1 of CaCO <sub>3</sub> /L	Ca(HCO <sub>3</sub> ) <sub>2</sub>	137	100 / 102	82.7
5	CaSO <sub>4</sub>	124	100 / 13.6	91.2
0	MgCl <sub>2</sub>	84	100 / 95	88.4
2	CaCl <sub>2</sub>	94	100 / 111	84.7
93.62 1 g/l <sup>2</sup>	NaCl	50		
not cooated				

Temporary Hardness = Hardness due to Mg(HCO<sub>3</sub>)<sub>2</sub> + Ca(HCO<sub>3</sub>)<sub>2</sub>

$$= \text{82.7} \times 139.5 \text{ mg/l}$$

$$= 139.5 \text{ ppm}$$

$$= 139.5 \times 0.9^\circ\text{C} = 9.77^\circ\text{C}$$

Permanent = CaSO<sub>4</sub> + MgCl<sub>2</sub> + CaCl<sub>2</sub>

$$= 264.3 \text{ mg/l}$$

$$= 264.3 \text{ ppm} \times 0.07^\circ\text{C}$$

$$= 18.50^\circ\text{C}$$

Classification of water with respect to hardness

	ppm or mg/l
Soft	0 - 12
Slightly Hard	12 - 60
Moderately Hard	60 - 120
Hard	120 - 180
Very Hard	180 & above
4 ppm = 1 mg/l	

Q) No of coordination sites in EDTA

Ans) 6, Hexa dentate (Poly dentate)

Q) What is Degree of Hardness of water

Ans) Degree of hardness means expressing hardness in terms of  $\text{CaCO}_3$

because  $\text{CaCO}_3 \rightarrow$  Molar mass = 100

Equi. Mass =  $100/2 = 50$

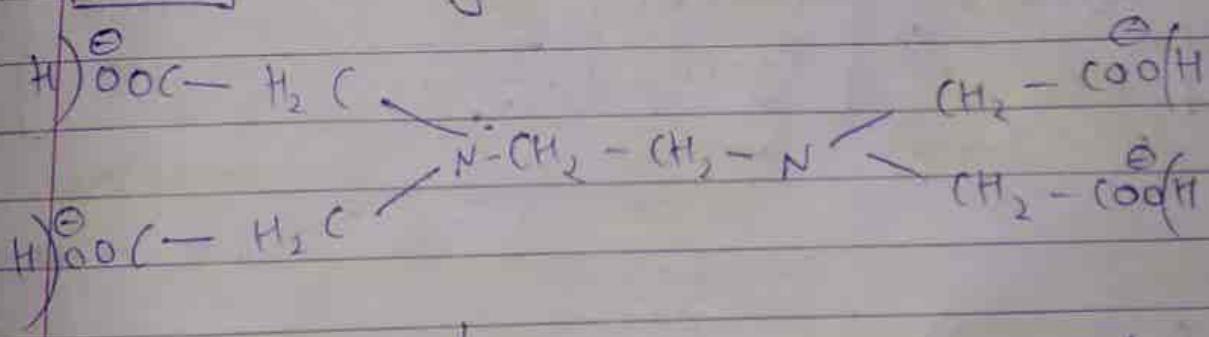
& it is most insoluble salt.

$$\begin{aligned}\text{Total hardness} &= \text{Permanent hardness} + \text{Temporary Hardness} \\ &= \text{CH} + \text{NCH}\end{aligned}$$

Determination of Hardness of water by  
EDTA Method

i) complexometric titration of water sample  
with EDTA as titrant & EBT as Indicator

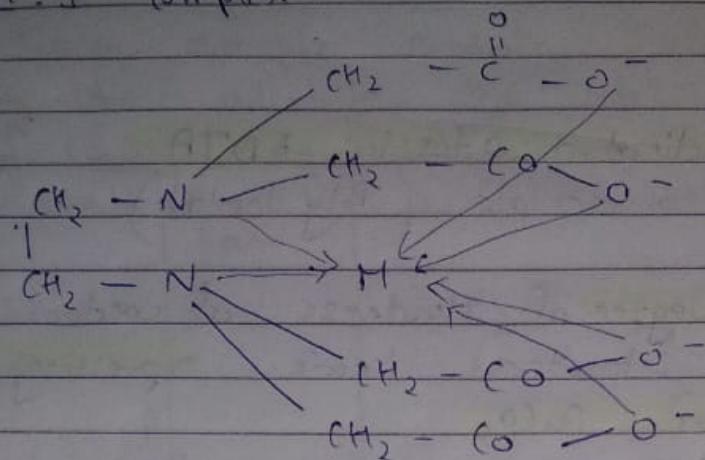
EDTA  $\rightarrow$  Ethylene Diamine Tetra Acetic acid



Tetra / Hexa dentate compound

When EDTA is mixed with metal

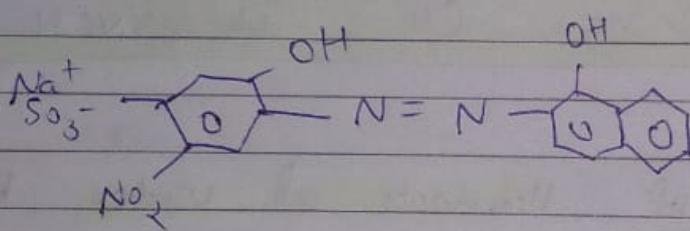
1:1 complex



$M = Ca, Mg$  metal EDTA complex

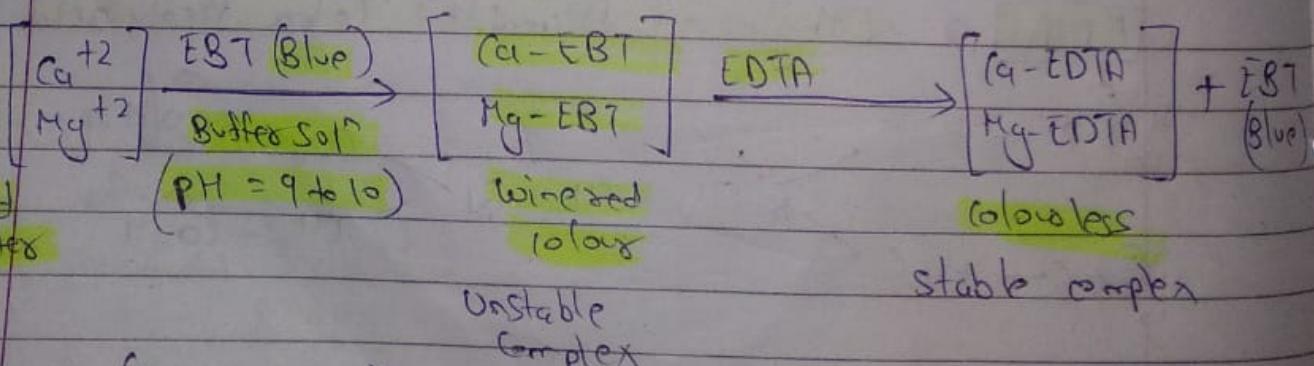
### ii) Complexometric Titration

Eriochrome Black T (EBT)



Blue wine red colour

### iii) Principle of complexometric titration



$$\text{Buffer soln} = \text{NH}_4^+(\text{Cl} + \text{NH}_4\text{OH})$$

is used to maintain pH 9 to 10

## Experimental calculation

- 1) Standard Hard water preparation
- 2) Standardization of EDTA
- 3) Total Hardness of Sample water
- 4) Hardness of water after boiling
- 5) Temporary Hardness

### Observation

Let volume of water taken each titration: 50ml

Volume of EDTA used when titrated against

Standard Hard water =  $V_1$  ml

" " " " " " " "

Sample Hard water =  $V_2$  ml

" " " " " " " "

Water having permanent hardness =  $V_3$  ml

### Calculation

- i) Molarity of standard Hard water

$$= \frac{\text{No of Moles}}{\text{vol of sol}^n (\text{L})} = \frac{1\text{gm} / 100\text{gm}}{1\text{L} / \text{of sol}^n} = 0.01\text{M}$$

1 liter of sol<sup>n</sup> = 1gm of CaCO<sub>3</sub>

1 ml of sol<sup>n</sup> = 1 mg CaCO<sub>3</sub>

- ii) Standardization of EDTA sol<sup>n</sup>.

10 ml std Hard water + 1 ml Buffer (Wine Red) + 2-3 drops EBT

↓ Titrate against EDTA

(Wine Red → Blue) ⇒ end point

Let volume of EDTA consumed =  $V_A$  ml

Standard Hard water = EDTA

$$M_1 V_1 = M_2 V_A$$

$$0.01 \times 10 = M_A V_A$$

$$\text{Molarity of EDTA soln} = \frac{0.1}{V_A}$$

(ii) Total Hardness of sample Hard water

1 ml of sample + 1 ml  
Hemocytometer Buffer + 1-2 drops + BT  
(Wine Red)

↓ Titrate against EDTA

(Wine Red  $\rightarrow$  Blue)  $\Rightarrow$  End point

Let volume of EDTA consumed =  $V_B$  ml

Sample Hard water = EDTA

$$M_{\odot} \times v_{\odot} = M \times v$$

$$M_w \times 10 = \frac{0.1}{v_p} \times v_B$$

MCQ 0.01 C 20

$$M_w = \frac{0.01}{V_A} V_B$$

~~Molarity  
of  
Sample  
H<sub>2</sub>O<sub>2</sub>~~

Sample HW  
volume of EDTA  
measured

Volume of EDTA  
consumed  
Standard KM

Strength in terms of  $\text{CaCO}_3$  equivalent

$$= 1000 \left( \frac{V_B}{V_A} \right)$$

iv) Permanent Hardness of sample Hard water  
 250 ml of water Boil  $\rightarrow \left(\frac{1}{5}\right)^{\text{th}}$  of volume  $\rightarrow$  Hard water 2 L

Sample HW = EDTA

$$\text{HW} \times V_D = \text{M}_\text{EDTA} \times V_C$$

$$\text{HW} \times 10 = \frac{0.1}{V_A} V_C$$

instead of sample HW

$$\boxed{\text{HW} = 0.01 \left( \frac{V_C}{V_A} \right)}$$

Volume of EDTA used for 250 ml of water containing permanent hardness

v) Temporary Hardness = Total Hardness - Permanent Hardness

(v) 50 ml of sample hard water was titrated against 0.01 M EDTA. It required 15 ml of EDTA for titration 50 ml of sample hard water after boiling & filtering required 5 ml of EDTA. calculate the total, permanent, & temporary Hardness.

(Ans) Molality of EDTA = 0.01 M

$$n \times 50 = 0.01 \times 15$$

$$M_1 = \frac{0.01 \times 15}{\phi^2} = 50$$

Total Hardness =  $H_1 \times 100 \times 1000$  ppm in terms  
of  $\text{CaCO}_3$  equivalent

Permanent hardness      EDTA  
Boiled water

$$1\text{m} \times 50 = 5 \times 0.01$$

$$M_w = \frac{0.01 \times S}{S_0}$$

Permanent Hardness =  $H_w \times 100 \times 1000$  ppm in terms  
of calcium.

$$= \frac{0.01 \times 5}{5_0} \times 100 \times 1000$$

$$\begin{aligned}\text{Temporary Hardness} &= \text{Total - Permanent} \\ &= 200 \text{ ppm.}\end{aligned}$$

a) 500 ml of a sample of water on EDTA titration with EBT as indicator consumed 18 ml of 0.045 EDTA till end point is reached  
 Calculate Hardness

Sq)

$$\text{EDTA} \quad \text{water sample}$$

$$0.045 \times 18 = 500 \times M_w$$

$$M_w = \frac{0.045 \times 18}{500} = 0.00162$$

$$M_w = \cancel{0.00162} \times 100 \times 1000$$

$$= 162 \text{ } \text{dL}^{-1}$$

### Alkalinity of water

Alkalinity is the measure of the ability of water to neutralize the acids.

#### Alkalinity

Caustic Alkalinity  
 due to  $\text{OH}^-$  and  
 $\text{CO}_3^{2-}$

Bicarbonate alkalinity  
 due to  $\text{HCO}_3^-$

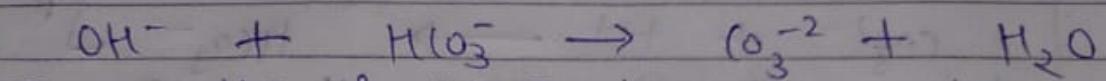
WZ  
 Causes of alkalinity in natural water / alkalinity in water

- a)  $\text{OH}^-$
- b)  $\text{CO}_3^{2-}$
- c)  $\text{HCO}_3^-$
- d)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$
- e)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$

Q) Why alkalinity of water cannot be due to the presence of  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ .

The possibility of  $\text{OH}^-$  &  $\text{HCO}_3^-$  together is ruled out

Sol) Because these two ions combine together form  $\text{CO}_3^{2-}$



Thus  $\text{OH}^-$  &  $\text{HCO}_3^-$  ions cannot exist together in water.

So all these ions ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  &  $\text{HCO}_3^-$ ) can not exist together.

### Determination of Alkalinity

Principle → Due to the help of titration of water sample against a standard acid,

Indicators → Phenolphthalein and Methylorange

#### Procedure

A known amount of water sample is titrated against a standard acid using phenolphthalein as indicator.

The end point is disappearance of pink colour is  $V_1$ . To the same solution add 2 or 3 drops of Methyl orange, continue the titration till the pink colour (slightly reddish) disappears, this end point at volume used acid is  $V_2$ .

10 WS + 1-2 drop phenolphthalein

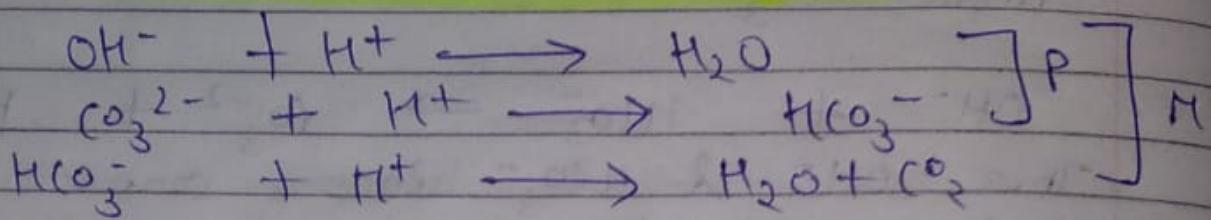


Titrated against  $\frac{N}{10}$  HCl  
pink to colourless

Pink to colourless

↓  
1-2 drops Methyl orange  
followed by titration  
↓

Yellow → Orange



where P is Phenolphthalein

M is Methyl orange

### Observation

let volume water sample taken for titration =  $V_1$  ml  
volume of acid used upto phenolphthalein  
end point =  $V_1$  ml.

Extra volume of acid used upto

Methyl orange end point =  $V_2$  ml

Total volume used upto Methyl

orange end point =  $(V_1 + V_2)$  ml

Normality of acid used for titration =  $\frac{N}{10}$

phenolphthalein Alkalinity (P)

writes

$N_w V_w$

$N_w \times 10$

acid

$N_A V_{A1}$

$\frac{N}{10} \times \cancel{10} V_{A1}$

$$N_w = \frac{V_{A1}}{100}$$

Strength in terms of  $\text{CaCO}_3$  =  
 $= \text{Nw} \times \text{Eq wt } \text{CaCO}_3$

$$= \frac{V_1}{100} \times 50 = \text{g/L}$$

$$\rho = \frac{V_1}{100} \times 50 \times 1000 \text{ ppm}$$

$$= \rho$$

Methyl orange Alkalinity (M)  
 acid water  
~~Nw~~  $\frac{1}{10} (V_1 + V_2) = \text{Nw} \times 10$

$$\text{Nw} = \frac{V_1 + V_2}{100}$$

Strength in terms of  $\text{CaCO}_3$

$$= \text{Nw} \times \text{Eq wt } \text{CaCO}_3$$

$$= \frac{V_1 + V_2}{100} \times 50 \text{ g/L}$$

$$M = \frac{(V_1 + V_2)}{100} \times 50 \times 1000 \text{ ppm}$$

- $\frac{N}{10}$
- (c) 100 ml of water sample on titration with N/50  $\text{H}_2\text{SO}_4$  gave a titre value 5.8 ml of phenolphthalein end point and another 100 ml sample on titration with some acid give a titre value of 11.6 ml to methyl orange end point. Calculate the alkalinity of water sample in terms of  $\text{CaCO}_3$  equivalents and comment the type of alkalinity.

acid

$$so) N_p \times 100 = \frac{1}{50} \times 5.8$$

$$N_p = 1.16 \times 10^{-3} N$$

$$P = N_p \times \frac{50 \times 1000}{10^3} \text{ ppm}$$

$$P = \frac{1.16 \times 10^{-3} \times 50}{10^3} \times 1000$$

$$P = 58 \text{ ppm}$$

acid

$$N_m \times 100 = \frac{1}{50} \times 116$$

$$N_m = 2.32 \times 10^{-3} N$$

$$M = N_m \times \frac{50 \times 1000}{10^3} \text{ ppm}$$

$$M = 116 \text{ ppm}$$

$$P = \frac{1}{2} M \quad \text{Hence } CO_3^{2-} \text{ present}$$

$$2P = M \quad CO_3^{2-} \text{ present}$$

Q) A sample During titration of water sample with  $\frac{N}{10}$  H<sub>2</sub>SO<sub>4</sub> using phenolphthalein indicator zero ml of H<sub>2</sub>SO<sub>4</sub> was used which type of alkalinity present in water.

Ans) When P=0 then alkalinity of OH<sup>-</sup> & CO<sub>3</sub><sup>2-</sup> are absent only HCO<sub>3</sub><sup>-</sup> present.

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~~WZ~~  
~~Audit~~

Alkalinity       $\text{OH}^-$        $\text{CO}_3^{2-}$        $\text{HCO}_3^-$

$P = 0$       X      X      M

$P = M$        $P = M$       X      X

$P = \frac{1}{2}M$       X       $2P$       X

$P > \frac{1}{2}M$        $2P - M$        $2(M - P)$       X

$P < \frac{1}{2}M$       X       $2P$        $M - 2P$

Boiler feed water (water for steam generation)  
A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. Water is mainly used in boilers for the generation of steam.

~~for steam~~

- Boiler Feed should have following
- i) Hardness should be below 0.2 ppm
  - ii) Caustic alkalinity (due to OH<sup>-</sup> ion) should be 0.15 to 0.45 ppm
  - iii) Soda alkalinity (due to Na<sub>2</sub>CO<sub>3</sub>) should be 0.45 to 1 ppm.

Untreated water containing impurities may lead to following problems in boiler

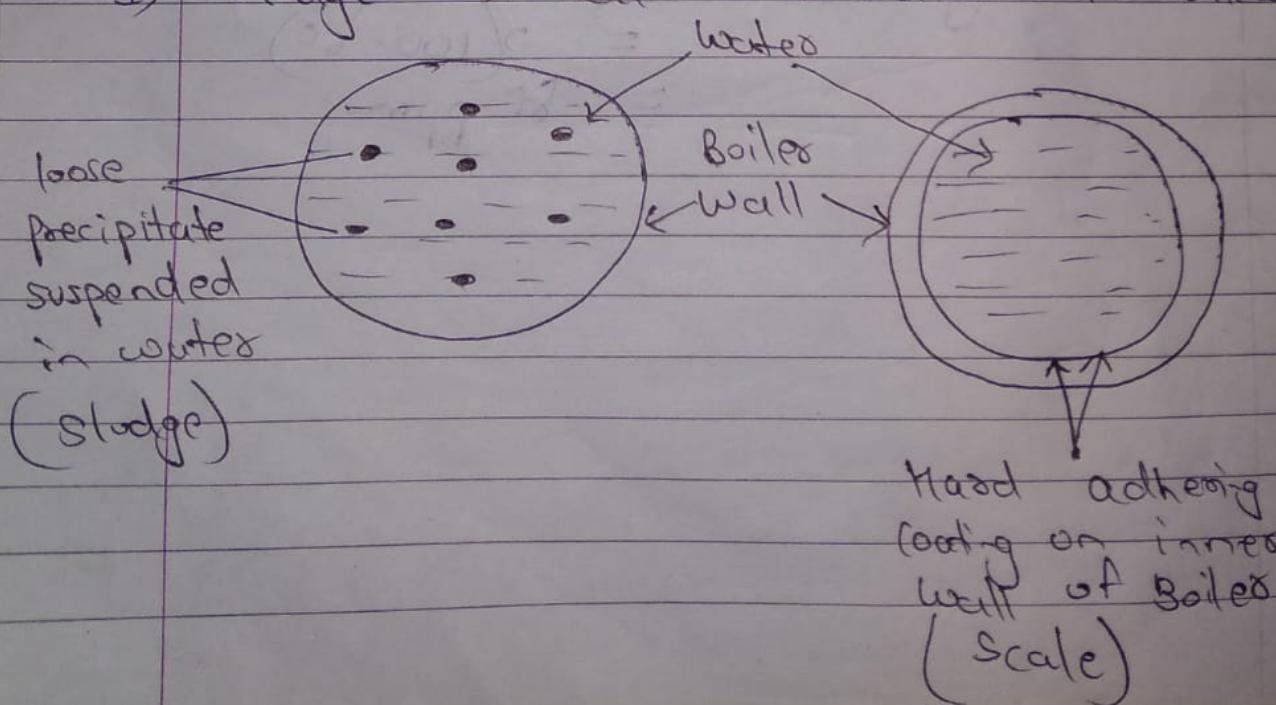
i) Scale & sludge formation

Boiler ~~rust~~ corrosion

Caustic embattlement

~~Rust~~ Boiling & foaming

i) Sludge & scale formation in boilers



### Sludge formation

Sludge are formed by the substance having greater solubilities in hot water than in cold water.

e.g.  $Mg(OH)_2$ , Calk,  $MgSO_4$

Disadvantages

- i) wastage of fuel
- ii) decrease efficiency of Boiler
- iii)

### Prevention of sludge formation

- i) can be prevented by using soft water
- ii) cleaning operation should be done - means removal of portion of concentrated water and replacing it by fresh water collected (blow down operation)

### Removal of sludge

sludge can easily be removed by scrapping off with a brush

### Scale formation

Scale are formed through

the

- ① Decomposition of Bicarbonates
- ② Hydrolysis of salt
- ③ Deposition of  $CaSO_4$
- ④ presence of Silica

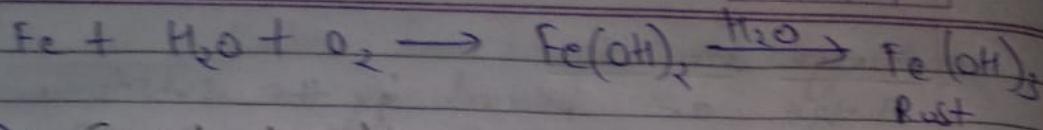
Disadvantages (Same as Sludge d/t)

### Prevention

- i) External treatment
- ii) Internal treatment

Removal → (Same as ~~sludge~~ Sludge d/t)

- i) Boiler corrosion is decay of boiler material due to attack of certain ~~che~~ chemicals on its surface & formed compound like oxides Sulphide etc.



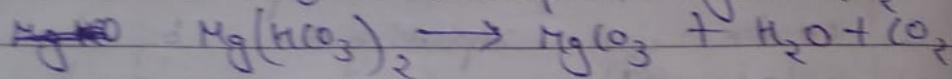
Caused due to

- Dissolve O<sub>2</sub>
- Dissolve CO<sub>2</sub>
- Mineral acids

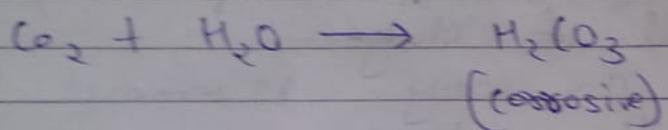
Its Prevention

- i) Adding Na<sub>2</sub>SO<sub>3</sub> / Na<sub>2</sub>S + O<sub>2</sub> → Na<sub>2</sub>SO<sub>4</sub>
- ii) Hydrazine
- iii) Mechanical

Dissolved CO<sub>2</sub> Mainly present as dissolved CO<sub>2</sub> & bicarbonate on decomposition gives CO<sub>2</sub>



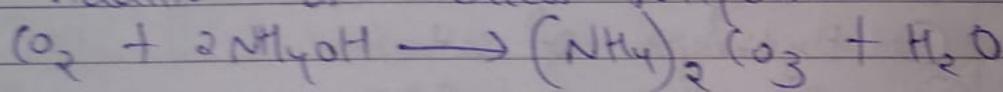
~~WZ~~



It is removed by (CO<sub>2</sub>)

→ Mechanical de aeration along with oxygen

→ Addition of excess NH<sub>4</sub>OH



### iii) Caustic Embrittlement

(NaOH) Caustic is used for Base, Embrittlement → easily broken

Boiler किसी water oil steam जैसे कोई नहीं होता

Caustic की वजह से बहुत आसानी से ब्रेक होता है

Boiler corrosion causes due to highly alkaline water in the boilers. Boiler Material become brittle

due to the accumulation of caustic substance

Then this

It is mainly corrosion caused by a high concentration of NaOH in the boiler feed water. It is characterized by the cracks on boiler material particularly at places of high local bends such as bend cause caustic embrittlement.

### Causes

Water evaporates in boiler,  $\text{Na}_2\text{CO}_3$  increases in boiler. In high pressure boilers  $\text{Na}_2\text{CO}_3$  is used for softening of lime soda water, some  $\text{Na}_2\text{CO}_3$  left in water. Then  $\text{Na}_2\text{CO}_3$  increases it under geo. Hydrolysis  $\downarrow$  from  $\text{NaOH}$

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$$

$\text{NaOH}$  make (caustic) alkaline water. This alkaline water enters minute cracks present inner wall of boiler by capillary action.

Inside  $\Rightarrow$  cracks water evaporates, volume hydroxide rising.

The concentrated area with high stress works as anode ~~the~~ diluted area works as cathode.

At anode  $\text{NaOH}$  attack the surrounding material and dissolves the boiler iron as Sodium ferrate forming rust.

### Prevention

- 1) By controlling Temperature
- 2) By controlling Hardness
- 3) By avoiding alkalis
- 4) adding  $\text{Na}_2\text{SO}_4$  to boiler water
- 5) By using sodium phosphate in place of  $\text{Na}_2\text{CO}_3$  as softening agent to the Boiler water.

#### iv) Priming

due to rapid boiling the steam may carry some water droplets along with it. This is called wet steam. The process of wet steam production is called priming.

It causes corrosion in pipelines

#### Causes

- i) Sudden boiling
- ii) High water level in boiler
- iii) High steam velocities

#### Prevention

- i) Proper boiler design
- ii) Reduce steam velocities
- iii) Maintaining proper water level

#### Foaming

If oils and greases are present they produce stable bubbles on water surface.

This is known as foaming.

#### Prevention

- i) Anti foaming agents such as Castor oil etc.
- ii) Oil and grease can be removed by adding coagulants like Sodium aluminate.

#### Note

The phenomenon of carrying water along with impurities by steam is called carry over, this is mainly due to priming and foaming.

Foaming and Priming are collectively known as "Carry over".

- i) Disadvantages of priming and foaming  
Dissolved salts may enter the parts of other machinery thereby decreasing their life.
- ii) It decrease the efficiency of Boiler  
The Maintenance of boiler pressure becomes difficult.

### Desalination of brackish water

Desalination  $\rightarrow$  means desalting of water, water containing high concentration of dissolved solids with a peculiar salty or brackish (Salty) taste is called brackish water

### Desalination define

Desalination means desalting of water (Removal of salts from water is known as desalination)

Fresh water (having  $< 1000 \text{ ppm}$  of dissolved solids)  
Brackish water (having  $> 1000 \text{ ppm}$  but  $< 3500$ )  
Sea water (having  $> 3500 \text{ ppm}$ )

### Techniques for desalination of brackish waters

Reverse Osmosis

Distillation

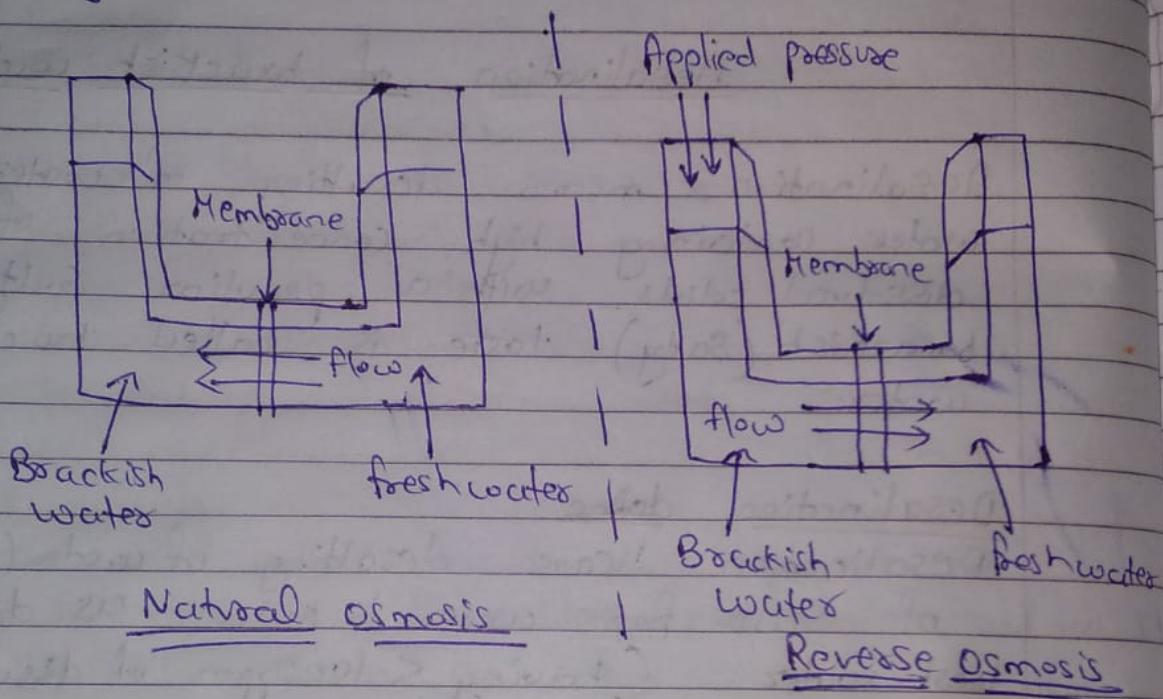
Freezing

Electrodialysis

#### 1) Reverse Osmosis $\rightarrow$

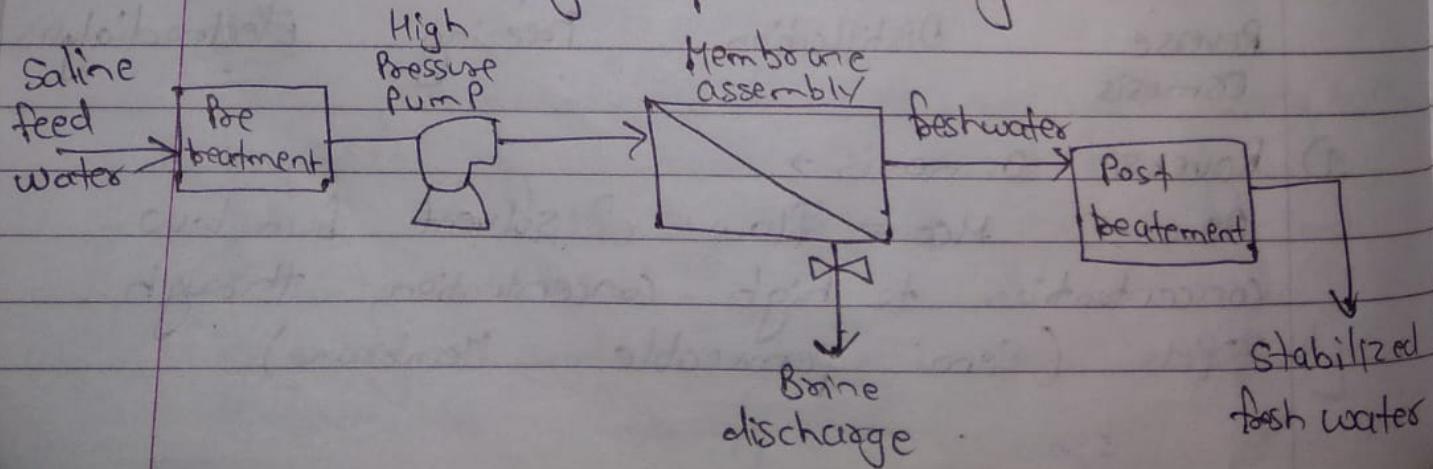
Osmosis Means flow of solvent from low concentration to high concentration through SPM (Semi permeable Membrane)

The flow is continuous till the concentration equal on both sides, the driving pressure for osmosis is **osmotic pressure**. If hydrostatic pressure is excess of osmotic pressure is applied on the concentration side the flow of solvent is reverse more from high concentration to low across SPM.



When applied pressure be more than osmotic pressure then flow of solvent from high concentration to low concentration through SPM is called **reverse osmosis**.

Water softening process using Reverse osmosis



### Application

- 1) Treatment of waste water
- 2) Purification of water
- 3) Desalination
- 4) Reclamation of Minerals.

### Advantages

- 1) The energy requirement is 30% lower than that of distillation process.
- 2) It is simple process
- 3) Purification through reverse osmosis removes ionic as well as non-ionic, colloidal matter.

### 3) Electrolytic Electrodialysis

This desalination process consist of the phenomenon by which an electric current is passed through an ion soln. The positive ions (cations) migrate toward the Negative electrode (cathode) while the Negative ion (anions) move to the positive electrode (anode). Semi permeable Membranes are placed b/w both electrodes so that only  $\text{Na}^+$  and  $\text{Cl}^-$  can pass through i and the water contained in the centre of the electrolytic cell is progressively desalinated obtaining fresh water.

This Method is based on a standard technique of removal of ions from solution which may be applied at room temperatures.

### Advantages

- 1) The cost of installation of plant is economical
- 2) It is compact unit easy to operate when very high purification is not required this method is best suited.
- 3) ~~Diffusion~~ Defluoridation of water

If fluoride is limit amount in body it helps to protect teeth enamel but if it is in excess amount it causes fluorosis which leads to weakening of bones, decay of teeth etc.

Defluoridation → Removal of ~~excess~~ fluoride

Techniques used for defluoridation

- i) Nalgonda Technique (chemical precipitation)
- ii) Adsorption
- iii) Reverse osmosis | electrodialysis

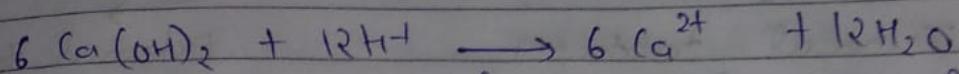
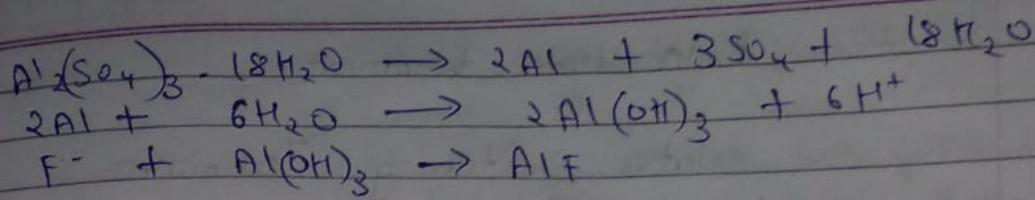
### Nalgonda Technique

It was first developed by NEERI Scientists in India

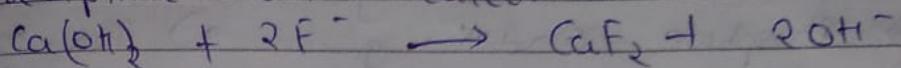
This technique owes its name to the village Nalgonda in Telangana where it was developed.

This Method consists of removal of fluoride from water by adding chemicals like alum and lime followed by flocculation, sedimentation, filtration.

The fluoride ion are precipitated as a calcium and aluminium fluoride.

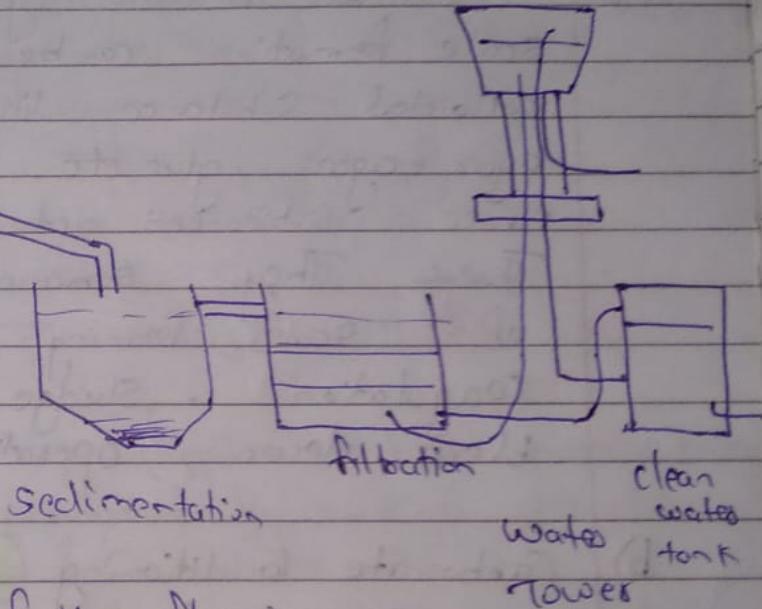
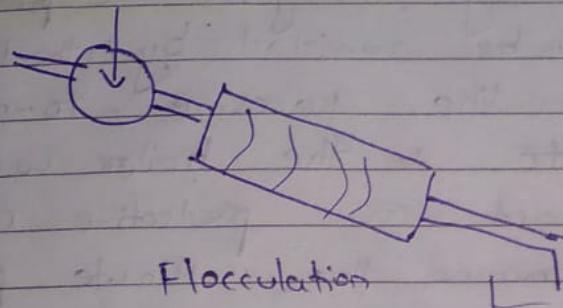


Additionally some fluoride is able to form precipitate with calcium



After ppt flocs are settled down and sedimentation followed by filtration.

lime Alum



### Limitation

- The Method fails if the fluorine content in water is very high
- The quantity of alum and lime has to be carefully controlled for proper results.
- Large quantities of sludge formed.

## Boiler Water treatment

### water softening Techniques

#### Internal treatment

- Colloidal conditioning
- Carbonate conditioning
- Phosphate conditioning
- Calgon conditioning

#### External treatment

- Lime Soda Process
- Zeolite Process
- Ion-Exchange  
or  
Demineralization Process

#### 1) Internal treatment

- a) Colloidal conditioning (Mainly for low pressure boiler)  
 Scale formation can be avoided by introducing colloidal substance like kerosene, tannin, agar-agar, glue etc. to the boiler water.

These substances act as protective coating. They surround the minute particles of scales forming salts and prevent coagulation. Sludge can be removed by blow down operation process.

- b) Carbonate conditioning (Mainly for low pressure boiler)

$K_{sp} < \text{ionic product}$   
 (Solubility product)

then ppt formed

for precipitation of  $\text{CaCO}_3$  the product of its ions  $\text{Ca}^{+2}$  and  $\text{CO}_3^{-2}$  (ionic product) is greater than solubility product.

Similarly for the precipitation of  $\text{CaSO}_4$  the ionic product of  $\text{Ca}^{+2}$  &  $\text{SO}_4^{-2}$

must exceed the solubility product of  $\text{CaSO}_4$

⇒ The precipitation of  $\text{CaSO}_4$  can be prevented by removing  $\text{Ca}^{+2}$  ion from sol<sup>1</sup>, so that ionic product does not exceed the solubility product.

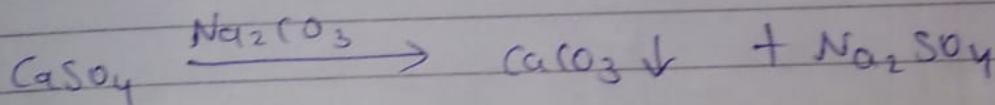
It is done by carbonate conditioning

In which some  $\text{Na}_2\text{CO}_3$  is added

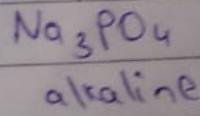
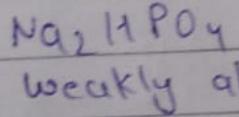
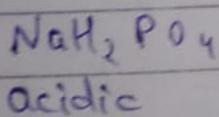
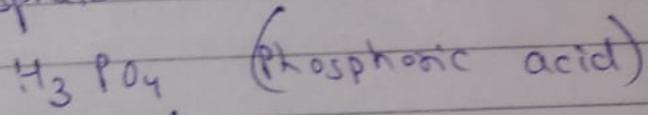
# In order to maintain the solubility product of  $\text{CaCO}_3$  constant some  $\text{Ca}^{+2}$  get precipitated

Reaction

In the carbonate conditioning when  $\text{Na}_2\text{CO}_3$  is added to boiler water the  $[\text{CO}_3^{2-}]$  increases & it becomes greater than  $K'[\text{SO}_4^{2-}]$  &  $\text{CaCO}_3$  get ppted &  $\text{CaSO}_4$  remains in solution



c) Phosphate conditioning (applicable high pressure boilers)  
Scale formation is prevented by adding  $\text{Na}_3\text{PO}_4$  which reacts with Mg & Ca salts forming non-adhesive and easily removable sludge of Ca & Mg phosphate



If  $\text{Na}_3\text{PO}_4$  is most suitable for treatment when the alkalinity of boiler water is low used  $\text{Na}_2\text{HPO}_4$  as it is most alkaline

If the alkalinity of boiler water is sufficient (not low) then used  $\text{Na}_2\text{HPO}_4$   
 If the alkalinity of boiler water is too high & require to be reduced then  $\text{NaH}_2\text{PO}_4$  acidic is used

#### iv) Calgon conditioning

- ⇒ Etag Calgon is the commercial name of Sodium hexameta phosphate
- ⇒ Adding Calgon to boiler water to prevent the scale & sludge formation
- ⇒ Calgon converts the scale forming impurities like  $\text{CaSO}_4$  into soluble complex compound which are harmless to boiled

## External treatment of Boiler Feed water

### D) Lime Soda Process

Principle → To convert all the soluble hardness causing impurities into so insoluble precipitates which may be removed by settling & filtration.

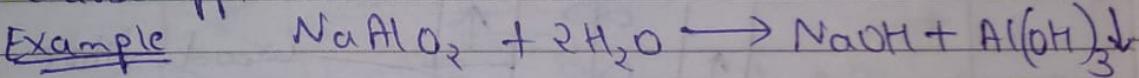
Lime  $\text{Ca(OH)}_2$  and Soda  $\text{Na}_2\text{CO}_3$  are added to raw water which react with calcium and magnesium salts so insoluble precipitate of  $\text{CaCO}_3$ ,  $\text{Mg(OH)}_2$ ,  $\text{Fe(OH)}_3$  and  $\text{Al(OH)}_3$  are filtered off.

Chemical required

Lime $\text{Ca(OH)}_2$	Soda $\text{Na}_2\text{CO}_3$	Coagulants $\text{NaAlO}_2$ , $\text{Al}_2(\text{SO}_4)_3$ or Alum
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Use of coagulants

The precipitation not filtered easily it is very fine so by adding coagulants it become filtered Coagulants helps in the formation of coarse ppt.



Types of lime soda process ~~etc~~

Cold lime soda

Intermittent

Continuous

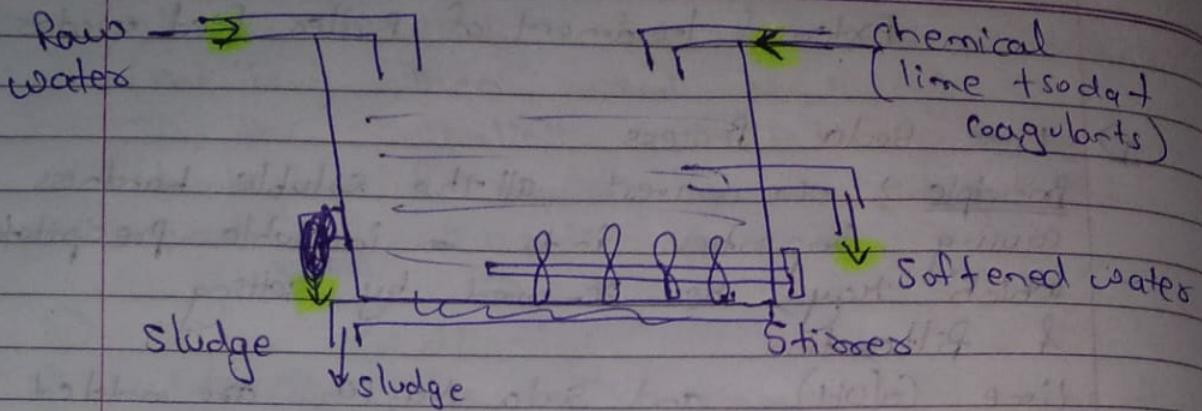
Hot lime soda

Intermittent

Continuous

Cold lime soda → In this Method calculated amount of lime & Soda are mixed with water at room temperature.

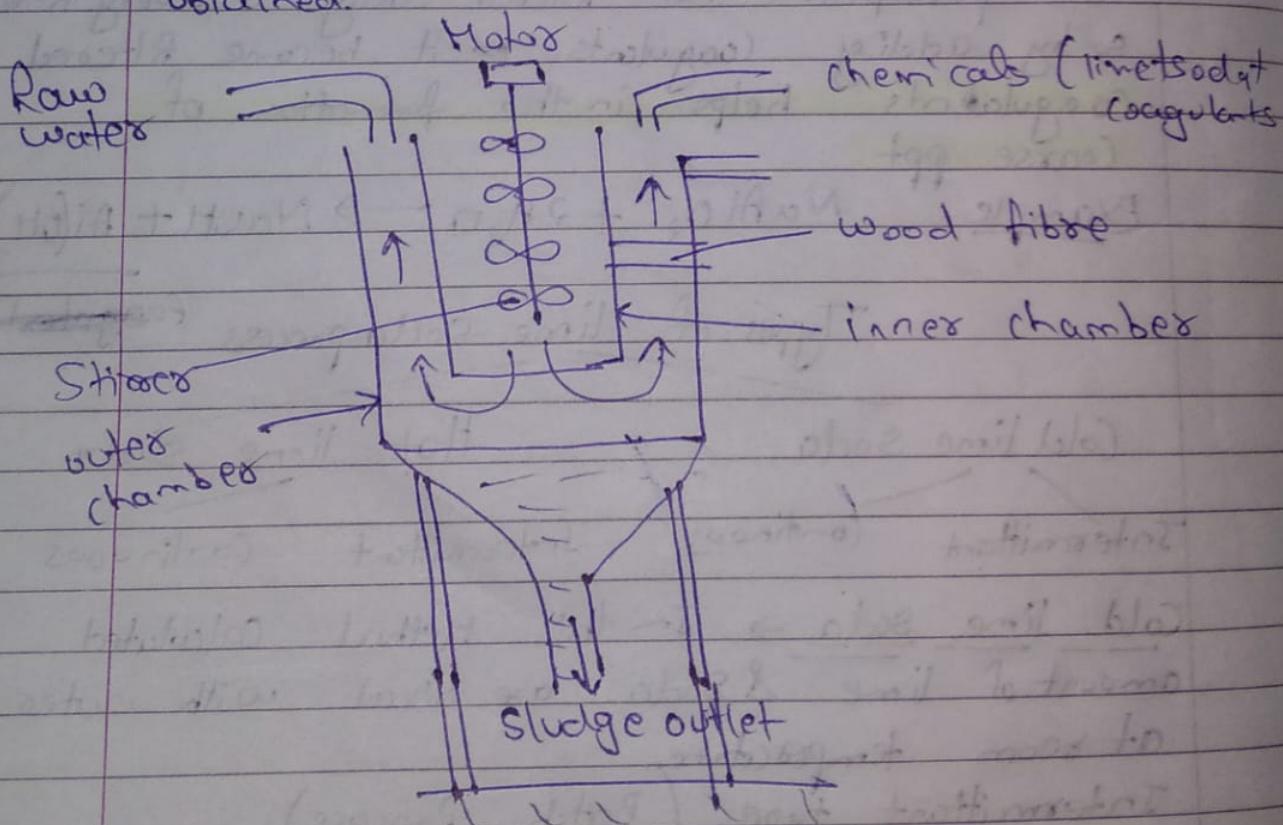
Intermittent type (Batch Process)



It consists of pair of tanks which is used for softening of water. Coagulants  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{NaAlO}_2$  used to settle down the finely ppt.

continuous cold lime Soda process

In continuous softener there is continuous feed of raw water and chemicals & uninterrupted outflow of soft water is obtained.



### (old lime soda process)

- 1) It carried out at room temperature
- 2) It is slow process
- 3) Use of coagulants
- 4) Must
- 5) filtration is not easy
- 6) Time taken for softening is longer

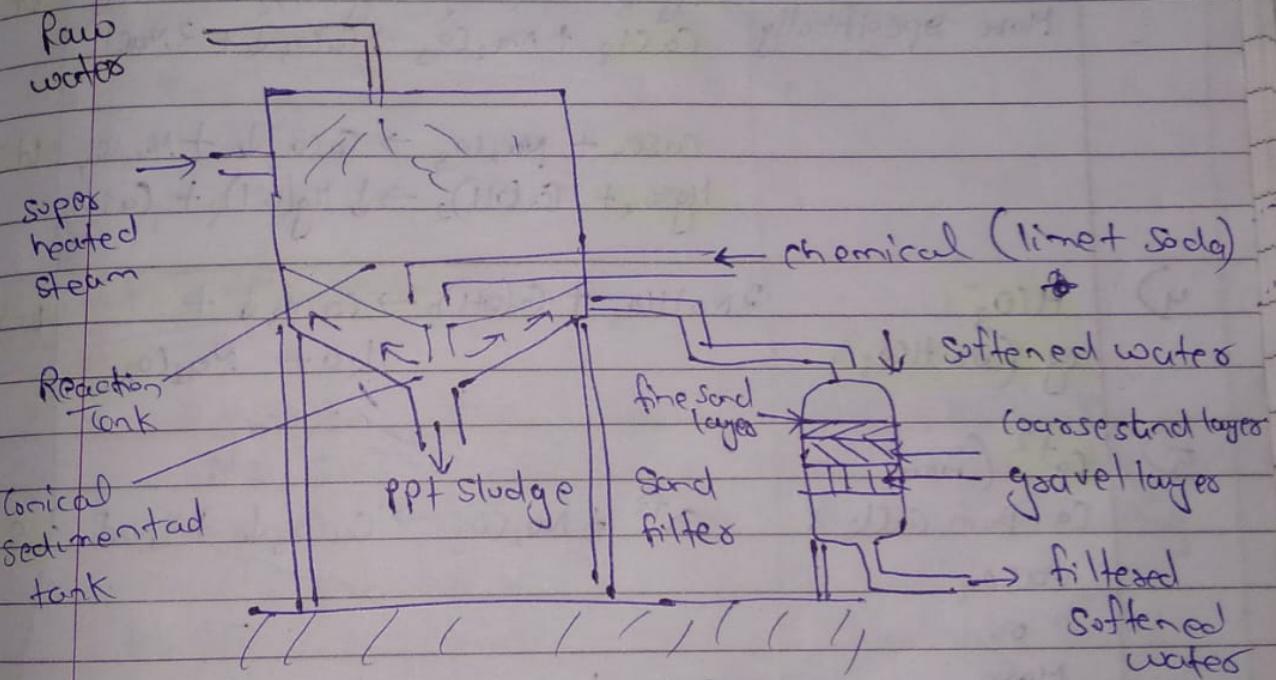
### Hot lime Soda Process

- 1) It carried out at high temperature
- 2) It is fast process
- 3) coagulants are not needed.
- 4) filtration is easy
- 5) time taken for softening is lesser

### Hot lime Soda Process

At high Temperature (it has advantages)

- i) Rate of reaction is increased
- ii) Precipitation rate is increased
- iii) Eliminates the need of adding coagulants



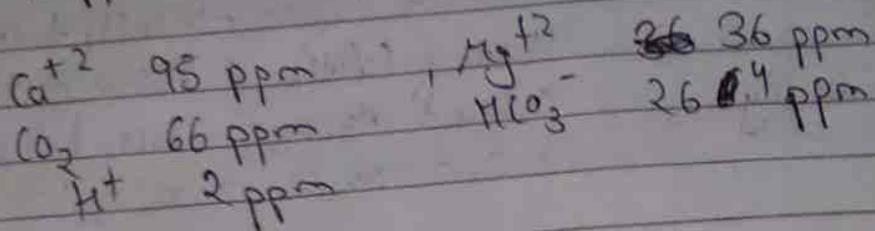
### Continuous Hot lime Soda

~~Wt~~

$$\text{lime or soda Requirement} = \frac{\text{Mg}}{\text{L}} = \frac{2cV}{10^6}$$

Time के लिए L ताल पता है } जल 2 तो तुमने वे  
 Soda के लिए S ताल पता है } तो तुमने जाना

Q) calculate the quantities of lime & Soda required for softening 24000 litres of water with the following analysis using 10 ppm of  $\text{NaAlO}_2$  as coagulant.



Constituent	Amount	Multiplication factor	$\text{CaCO}_3$ equivalent	Need
$\text{Ca}^{+2}$	95	100/40	$\frac{100}{40} \times 95 = 237.5$	S
$\text{Mg}^{+2}$	36	100/24	$\frac{100}{24} \times 36 = 150$	LTS
$\text{CO}_3^{-2}$	66	100/44	$\frac{100}{44} \times 66 = 150$	L
$\text{HCO}_3^-$	26.4	100/12.2	$\frac{100}{12.2} \times 26.4 = 216.39$	LTS
$\text{H}^+$	2	100/2	$2 \times \frac{100}{2} = 100$	LTS
$\text{NaAlO}_2$	10	100/164	$\frac{100}{164} \times 10 = 6.1$	-L

Lime Requirement

$$= \frac{74}{100} [ \text{Mg}^{+2} + \text{CO}_3^{-2} + \text{HCO}_3^- + \text{H}^+ - \text{NaAlO}_2 ] \times \text{Vol in Litre} \times 10^6$$

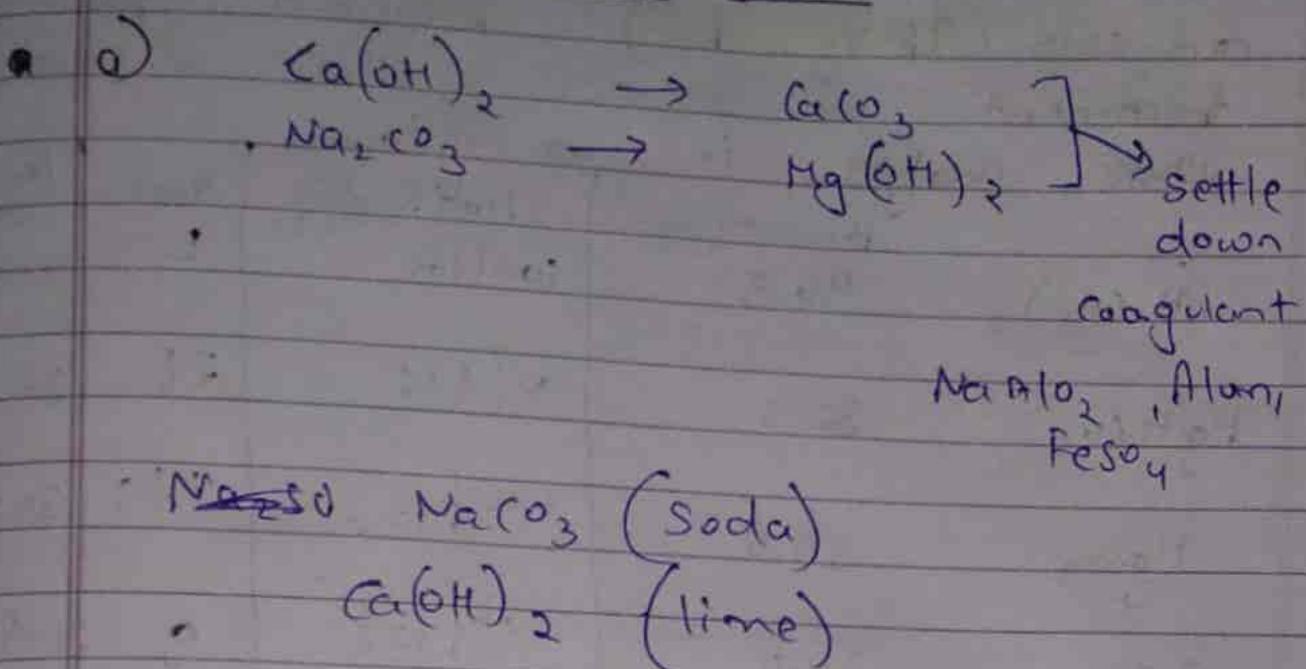
$$= \frac{74}{100} [ 150 + 150 + 216.3 + 100 - 6.1 ] \times 24000 \times 10^6$$

$$= 10.8 \text{ kg} \quad [ 1 \text{ kg} = 10^6 \text{ mg} ]$$

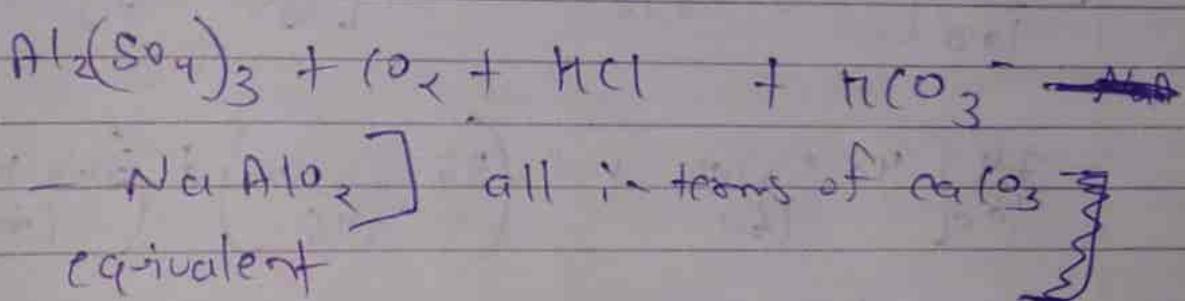
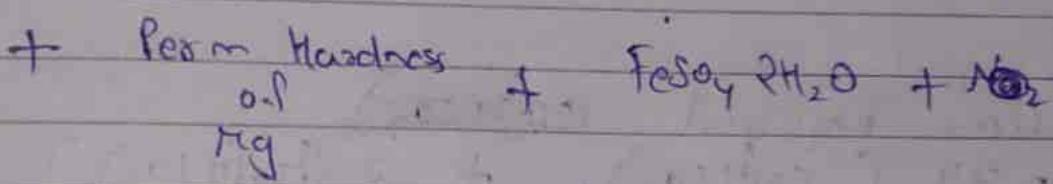
$$\text{Soda} = \frac{106}{100} [ \text{Ca}^{+2} + \text{Mg}^{+2} + \text{H}^+ - \text{HCO}_3^- ] \times \frac{\text{Vol in Litre}}{10^6} \text{ kg}$$

$$= 6.89 \text{ kg}$$

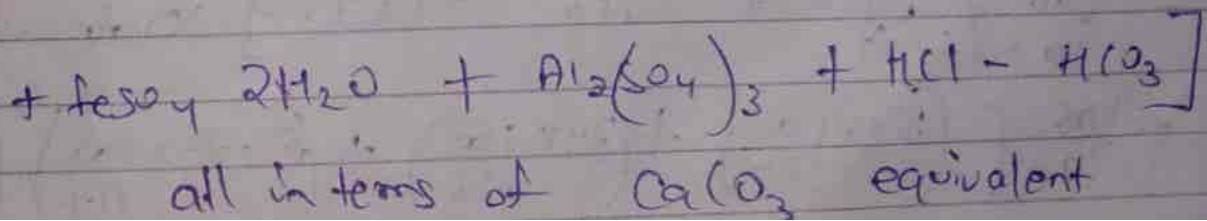
### Lime Soda Process



lime Requirement =  $\frac{24}{100} \left[ \frac{\text{Tern Hard}}{\text{of Ca}} + \left( 2 \times \frac{\text{Tern Hard}}{\text{of Mg}} \right) \right]$



Soda Requirement =  $\frac{106}{100} \left[ \frac{\text{Post Hardness}}{\text{of Ca}} + \frac{\text{Post Hardness}}{\text{of Mg}} \right]$



Q) Calculate the amount of lime (92% pure) and soda (98% pure) required for the treatment of 30000 litre of water whose analysis is as follows

	Amount (mg/L)	Multiplication factor	Need	Amount of reagent
$\text{Ca}(\text{HCO}_3)_2$	40.5	100/162	L	$40.5 \times \frac{100}{162}$
$\text{Mg}(\text{HCO}_3)_2$	36.5	100/146	2L	$36.5 \times \frac{100}{146}$
$\text{MgSO}_4$	30.0	100/120	1.75L	$30 \times \frac{100}{120}$
$\text{CaSO}_4$	34.0	100/136	S	$34 \times \frac{100}{136}$
$\text{CaCl}_2$	27.75	100/111	S	$27.75 \times \frac{100}{111}$
$\text{NaCl}$				

$$\text{lime Required } \leftarrow \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2[\text{Mg}(\text{HCO}_3)_2] + \text{MgSO}_4]$$

$$= \frac{74}{100} \left[ \frac{40.5 \times 100}{162} + 2 \left( \frac{36.5 \times 100}{146} \right) + \left( \frac{30 \times 100}{120} \right) \right] \times$$

$$\text{volume of water} \times \frac{100}{92}$$

soda Required

$$= \frac{106}{100} [\text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2] \times \text{volume of water} \times \frac{100}{92}$$

$$= \frac{106}{100} \left[ \left( \frac{30 \times 100}{120} \right) + \left( \frac{34 \times 100}{136} \right) + \left( \frac{27.75 \times 100}{111} \right) \right] \times 30000 \times \frac{100}{92}$$

If the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  permanent hardness  
 consider  $\text{HCO}_3^-$

$\text{CaCO}_3$  temporary hardness  
 $\text{MgCO}_3$

c) Same as previous one

Constituent	Amount (mg/l)	Multiplication Factor	$\text{CaCO}_3$	Need
$\text{MgCO}_3$	84	100/84	$\frac{100}{84} \times 84$	RL
$\text{CaCO}_3$	40	100/100	$\frac{100}{100} \times 40$	L
$\text{CaCl}_2$	55	100/111.0	$\frac{100}{111.0} \times 55$	S
$\text{Mg}(\text{NO}_3)_2$	37	100/148	$\frac{100}{148} \times 37$	LTS

Q

100 ml of a water sample contain hardness equivalent to 25 ml of 0.08 N Mg

i) What is the hardness of water sample

in ppm

ii) What is the amount of lime and soda required as the treatment of the water sample.

Sol) i)

$$\text{Water} \quad \text{MgSO}_4$$

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = 0.08 \times 25$$

$$N_1 = 0.02$$

$$\boxed{\text{MgSO}_4 = \text{LTS}}$$

Hardness of water sample in terms  
of  $\text{CaCO}_3$  =  $N \times 50 \times 1000$   
 $= 0.62 \times 50 \times 1000$   
 $= 1000 \text{ ppm}$

ii) Amount of lime Required

$$\begin{aligned} &= 74 \left[ \frac{\text{MgSO}_4 \text{ as } (\text{CaCO}_3 \text{ equivalent})}{100} \right] \text{ ppm} \\ &= \frac{74}{100} \times 1000 = 740 \text{ ppm} \end{aligned}$$

Amount of lime required for 100 ml = 0.1 lit

$$\begin{aligned} &= \cancel{740} \quad \cancel{740 \times 0.1} = \cancel{74} \\ &= 740 \text{ mg} \times 0.1 \text{ L} \\ &= 74 \text{ mg} \end{aligned}$$

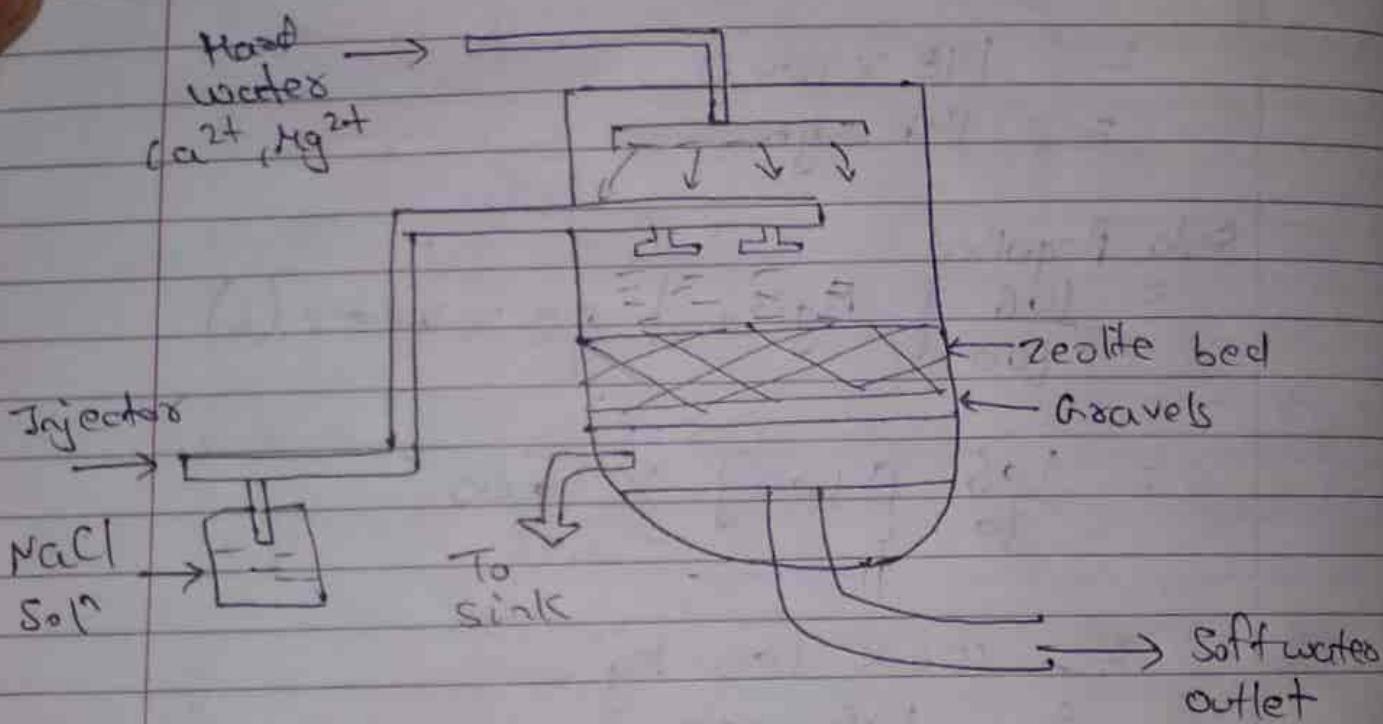
\* Amount of soda required

$$\begin{aligned} &= \frac{106}{100} \left[ \frac{\text{MgSO}_4 \text{ as } (\text{CaCO}_3 \text{ equivalent})}{100} \right] \text{ ppm} \\ &= \frac{106}{100} \times 1000 = 1060 \text{ ppm} \end{aligned}$$

$$= 1060 \times 0.1 = 106 \text{ mg } \cancel{\text{mg}}$$

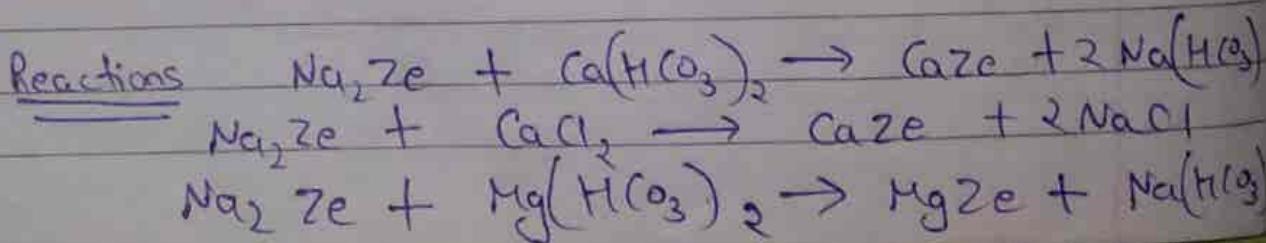
## Zeolite process (Base exchange process)

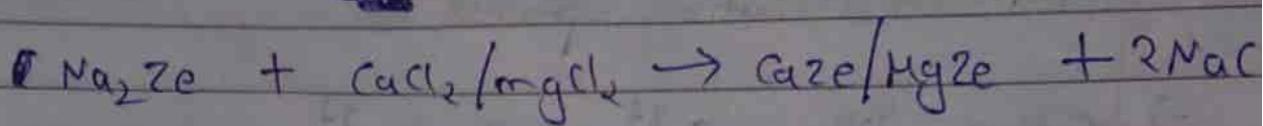
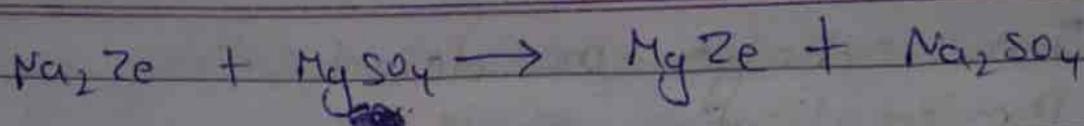
- ① Zeolite is hydrated Sodium alumino Silicate Also known as Pernovits
- ② Represented as Ze
- ③ Zeolite is capable of exchanging hardness causing ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$
- ④ Chemical formula  
 $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$
- ⑤ Zeolite are of two types Natural and Synthetic



### Process

- 1) Hard water is passes through the bed of zeolite
- 2) The hardness causing ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  etc) are captured by the zeolite



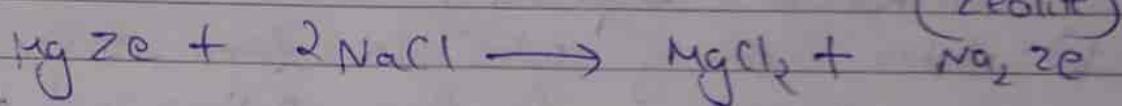
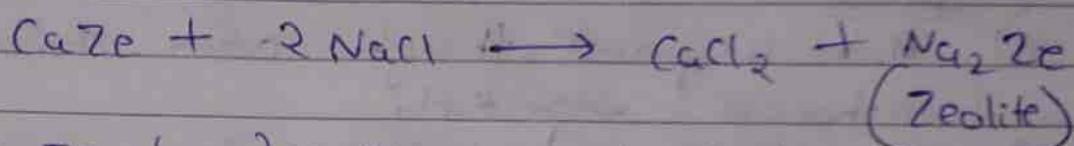


- 3) After some time the zeolite is completely converted into calcium and magnesium zeolite

### Regeneration Process

The zeolite minerals get exhausted when all the  $\text{Na}^+$  are replaced by  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions

Zeolite can be regenerated by passing  $\text{NaCl}$  solution



### Advantages

- In this process water about less than 10-15 ppm obtained
- It requires less time for softening
- Process automatically adjusts depending on hardness of water
- Equipment required less space
- It requires skill operations

### Disadvantages

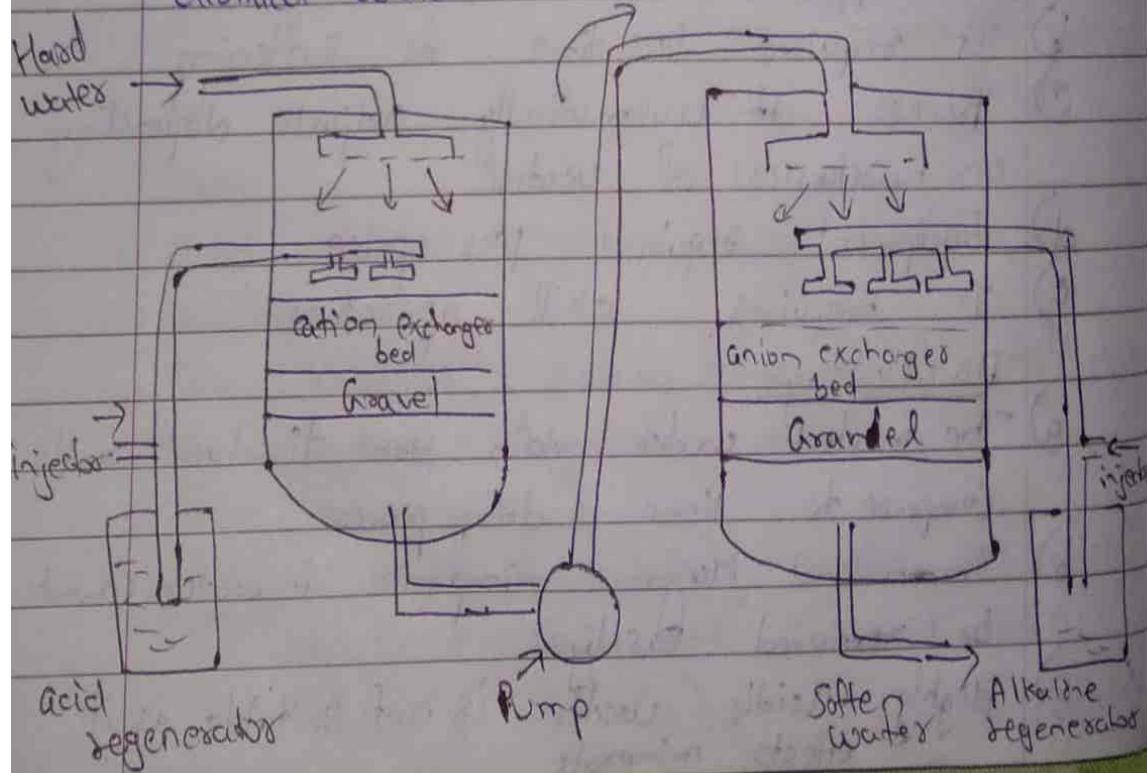
- The treated water contains more dissolved salts compare to lime soda process
- Zinc and Manganese impurities in water cannot be removed easily
- Highly acidic water is not suitable as it effects minerals

### 3) Ion exchange or deionization Demineratilization process

- ⇒ Cation like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and anions like  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  can be removed by cation and anion exchange resins.
- ⇒ Resins containing  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  are capable for exchanging their  $\text{H}^+$  ions to cationic position of Minerals. It is called cation exchanger.
- ⇒ Resins containing  $-\text{NH}_2$ ,  $\text{NH}(\text{H})$  are capable for exchanging the anionic position of the Minerals. It is called anionic exchanger.

#### Process

- Water is passed through cation and anion exchangers respectively.
- Water coming out side from anion exchanger is completely free from cations and anions.
- It is known as deionised water or demineralised water and it is pure as distilled water.

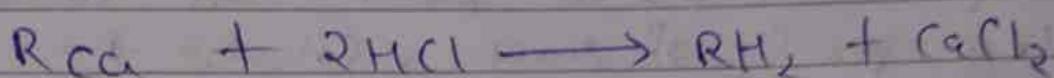


Acid generator  $\rightarrow$  To generate cation exchanger bed  
 Alkaline generator  $\rightarrow$  To generate anion exchange resin

In cation exchanged bed the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  are removed then in anion exchanged bed the  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  sulphate are removed

### Regeneration

Cation Exchange resins are regenerated by passing a dilute solution of  $\text{HCl}$  through them



Anion exchange resin are generated by passing a dilute solution of  $\text{NaOH}$



### Advantage

- Highly acidic, alkaline wastes can be treated
- water of nearly zero hardness can be obtained.

### Disadvantage

- Equipment is costly and expensive chemicals are needed
- If water contain turbidity then the output of process is reduced.
- Turbid water decreases the efficiency of the process.