

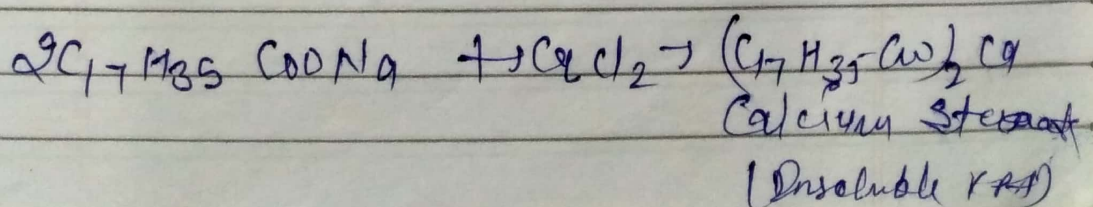
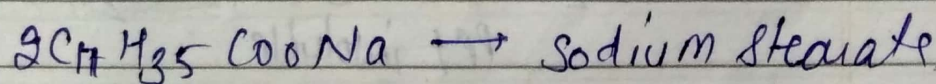
Water chemistry

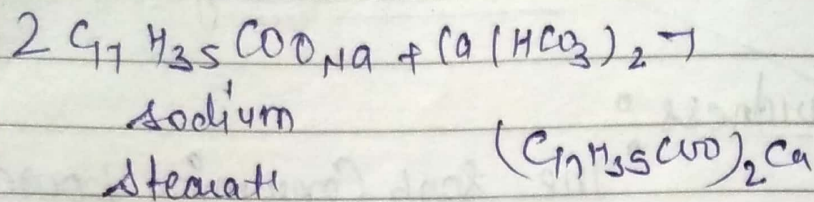
Hardness

The Soap Consuming power of Capacity is known as Hardness of water. This is due to Present in water of certain salt calcium and magnesium and other metal like Al^{3+} , Fe^{3+} , Mn^{3+} dissolve in it.

Generally soap consist of sodium salt of oleic acid palmitic acid and stearic acid. when sodium and potassium salt of oleic acid palmitic acid is dissolve in water then it does not allow leather to be formed due to insolubility.

The Leather does not form due to the reason that CO_2 Present in water break sodium and potassium into three fatty acid. generally the measurement of calcium contains in water is the main reason of hardness the hardness produced insoluble salts of in calcium and magnesium.





* Types of hardness:

(i) Temporary hardness:

due to HCO_3^- of Ca^{++} & Mg^{++}

due to $\text{Ca}(\text{HCO}_3)_2$ & $\text{Mg}(\text{HCO}_3)_2$

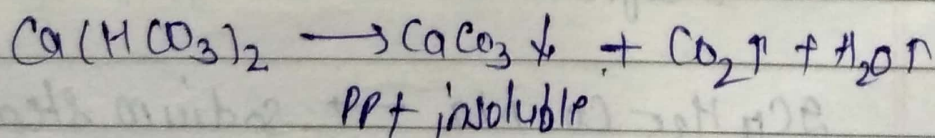
(ii) Permanent hardness:

$\text{Cl}_2, \text{SO}_4, \text{NO}_3$

Chloride
Nitrate
Sulphate

due to the formation of
Calcium chloride, MgCl_2 , CaSO_4 , MgSO_4 ,
 $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$

(i) This is due to the presence of Calcium
and Mg of bicarbonate. This type of
hardness easily be removed by
boiling when bicarbonate
decompose into insoluble carbonate



The insoluble of magnesium carbonate can easily removed by filtration

★ (ii) This type of hardness is present due to the presence of sulphates, chloride and nitrate of calcium and magnesium and other metals.

Permanent can't be removed by boiling of water.

The classification of hardness is based on alkalinity. The alkali hardness is due to the presence of bicarbonate, carbonate & hydroxide of metals, while non-alkali hardness due to the presence of chloride, sulphate, nitrate of metals.

✓ Determination of hardness of water

(i) Soap solution method.

(ii) EDTA method (ethylene diamine tetra acetic acid)

units of

Units of hardness

- (i) Ppm
- (ii) mg/lit
- (iii) Degree of Clarke ($^{\circ}\text{Cl}$)
- (iv) Degree of French ($^{\circ}\text{Fr}$)

Inter relation between various units of hardness :

$$1 \text{ Ppm} = 1 \text{ ml} = 0.1^{\circ}\text{Fr} = 0.07^{\circ}\text{Cl}$$

* Degree of Hardness :

(i) Soap solution method - Soluble soaps consist of sodium or potassium salts of higher fatty acids. When soaps solution is added to hard water, the hardness causing ions first react to form precipitate of calcium and magnesium soap which are insoluble of water.

Thus after all the hardness causing metal ions presents in the hard water sample are precipitated the further addition of soap give lather.

Properties of Hard water and Soft water.

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The total hardness of water sample can be determined by titrating an aliquate of the sample against a standard soap solution in alcohol. The appearance of a stable lather persisting even after shaking for about ~~2 min~~ 2 min marks end point. The water sample is boiled for 30 min to remove temporary hardness and then it is titrated with standard soap solution, the titration value corresponds to permanent hardness of sample.

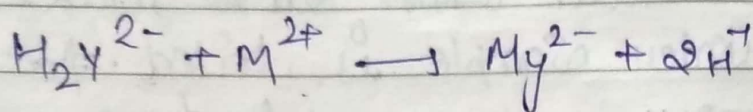
The difference b/w the two measurements corresponds to the temporary hardness.

(ii) EDTA Method:

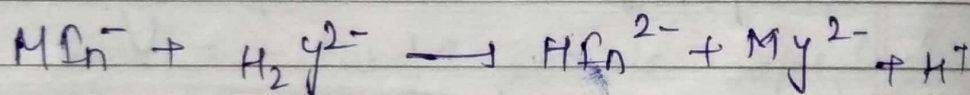
EDTA means (ethylene diamine tetraacetic acid). This EDTA reagent can be forming EDTA-metal complexes by the reaction with metal ions except alkali metals ions. This reagent can form a stable complex with the alkaline earth metal like calcium ion and magnesium in alkaline condition pH above 9.0.

∴ The total hardness of water can be determination by edta titration method.

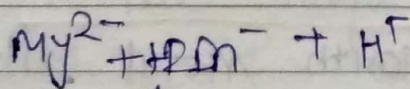
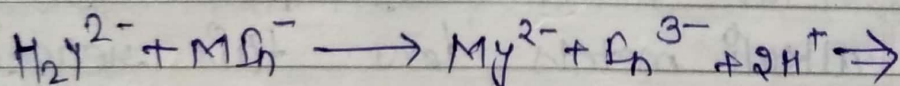
In this method buffer solution is used for attain suitable condition pH level about 9 for the titration. Buffer solution present pH at a balance position.



During titration Eriochrome Black T is used as indicator. The indicator is red in colour while it is forming complexes with metal ions and blue in colour when it is free.



but metal indicator complex is unstable, then EDTA reacts with metal indicator to get blue colour.



↓
Blue M
colour

* Degree of hardness:

Hardness of water generally expressed in terms of equivalent amount of calcium carbonate. The reason for choosing calcium carbonate the standard for reporting hardness in calculation its molecular weight 100 more over, it is the most insoluble salt that can be precipitated in water treatment.

Equivalent of Calcium Carbonate equal to

$$= \frac{\text{Strength of hardness producing substance} \times 50 (\text{eq. wt of } \text{CaCO}_3)}{\text{Eq. wt of hardness producing substance}}$$

Eq. wt of hardness producing substance

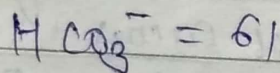
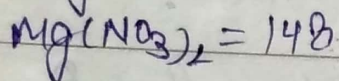
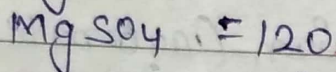
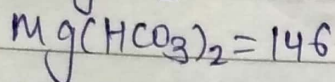
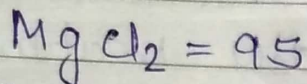
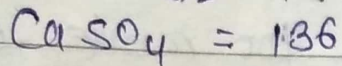
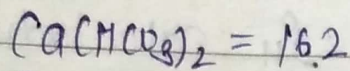
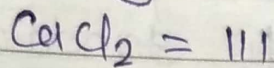
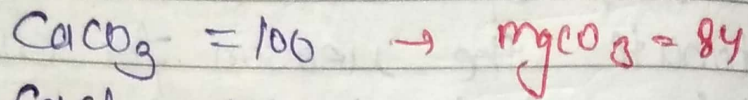
Eq. of $\text{CaCO}_3 \Rightarrow \text{strength of the Hardness producing substance} \times \text{multiplication factor}$

multiplication factor =

$$= \frac{\text{molecular wt of } \text{CaCO}_3}{\text{molecular wt of hardness producing substance}}$$

Note:

Molecular wt of some imp. salt are -



Soap consuming tendency
of water is called hardness

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* Treatment or softening of water:

(1) Zeolite method:

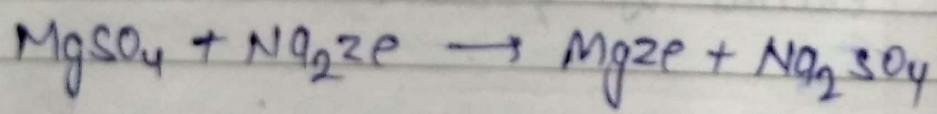
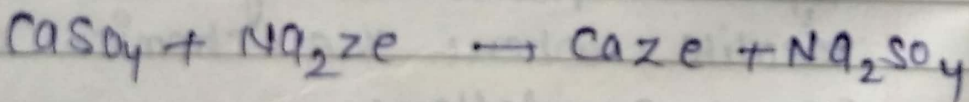
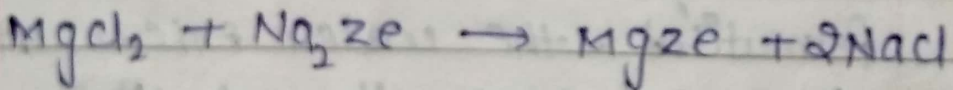
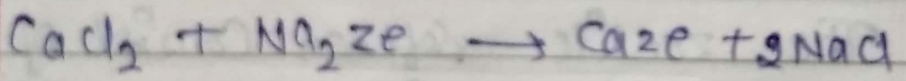
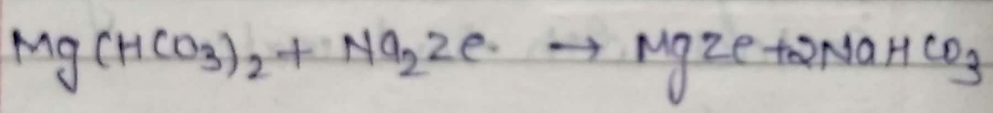
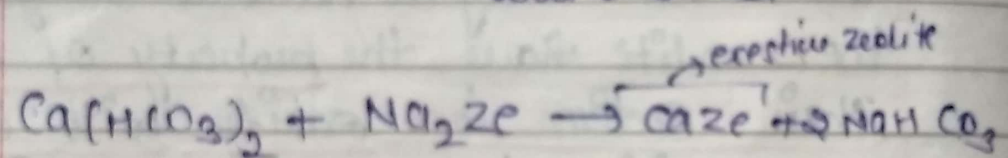
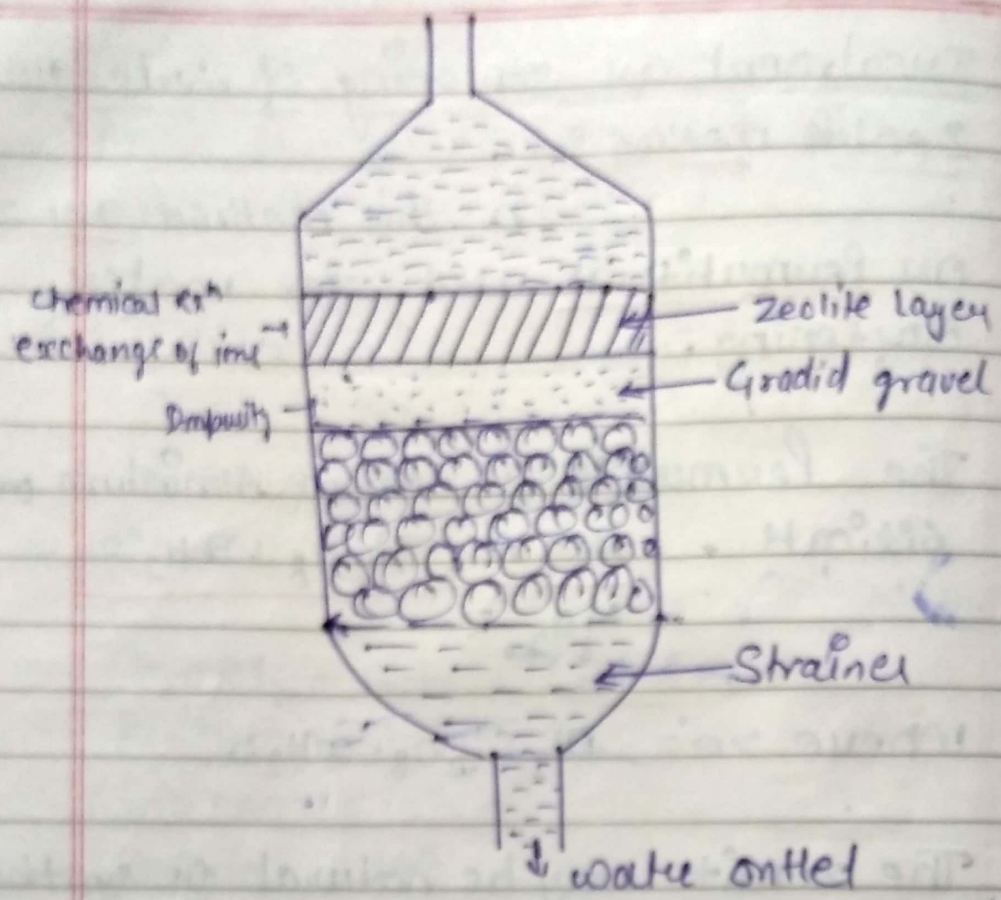
In this method, the zeolite or Permutite is used for water softening.

The Permutite is Sodium Aluminium ortho-silicate. $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$
 $\cdot \text{Na}_2 \text{ ze}$

Where $\text{ze} = \text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$

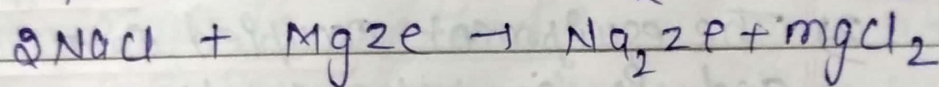
The zeolite may be natural or synthetic. The zeolite have the property of exchanging their sodium ions easily with calcium or magnesium ions. when they come in contact with hard water.

The zeolite softener consist of a steel tank packed with a thick layer of Permutite. the water enters at the top and passes through the bed of zeolite where the chemical rxn occurs as follows.



The Process remove both temp. as well as permanent hardness when the ~~mg~~ zeolite Permutite completely converted into case and mgze then it get exhausted and it ceases to soften water.

The Permutite can be made active by passing 10% solution NaCl and brine solution.



The soluble salt of Calcium and magnesium be removed.

* Limitations of zeolite process:

There are certain limitations for this process.

(i) The water must be free from suspended matter otherwise permutite get clogged.

(ii) If water contains some acids, it must be neutralised with base, because the mineral acids destroy the zeolite.

(iii) This method can not remove lead because it can not be converted into lead of zeolite.

(iv) Coloured ions should be removed by pre treatment because the Ca and Mg zeolite can not be easily converted into zeolite.

* Advantages of zeolite process:

- 1) This method can produce zero hardness
- 2) The equipment occupied small space and is easy to operate.
- 3) No sludge formation occurs during the process.
- 4) This process can automatically adjust itself for different types of hardness of water.
- 5) This method is very cheap because the regenerated permutite can again reuse.

* Disadvantages of zeolite process:

- 1) After treatment water contains more Na salt.

2) This method needs all the acidic ions such as Ca^{2+} and HCO_3^- in the softened water.

3) High turbidity in water can not easily be treated by this method.

4) when such water is boiled in boiler, then CO_2 is liberated. free CO_2 is weakly acidic in nature and highly corrosive to boiler material.

(2*) Lime soda method $\xrightarrow{\text{Ca(OH)}_2 \rightarrow \text{Na}_2\text{CO}_3}$

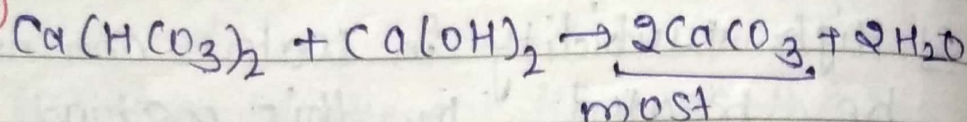
$\text{Na}_2\text{CO}_3 \rightarrow \text{soda}$
 $\text{Ca(OH)}_2 \rightarrow \text{lime}$

The principle of the process is to chemically convert all the soluble hardness causing impurities insoluble ppt which may be removed by settling and filtration. This is done by adding a suspension of milk of lime, Ca(OH)_2 , together with a calculated amount of sodium carbonate Na_2CO_3 (soda), the method is based on following facts.

g) Lime removes the temporary hardness and mg, Al and Iron salts remove permanent hardness.

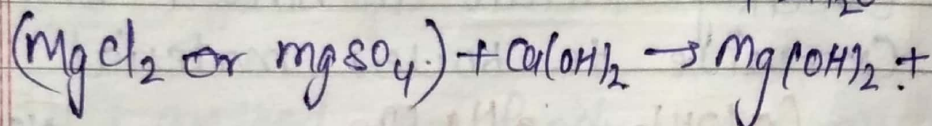
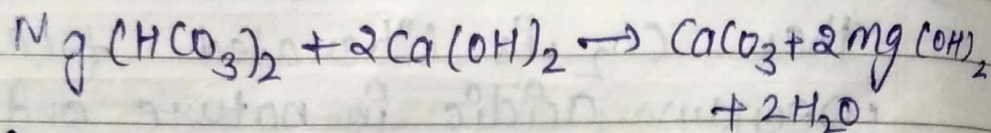
Temp.

Perm. of mg

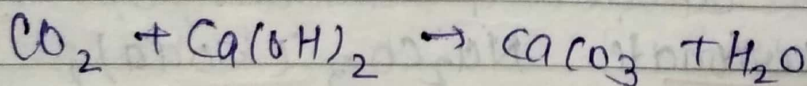
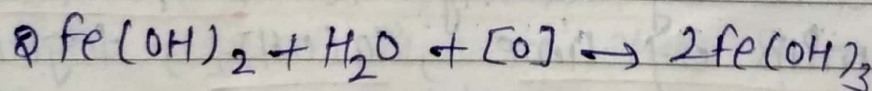
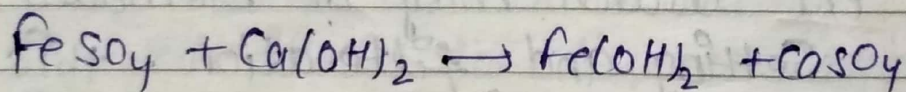
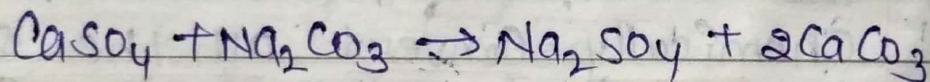


most

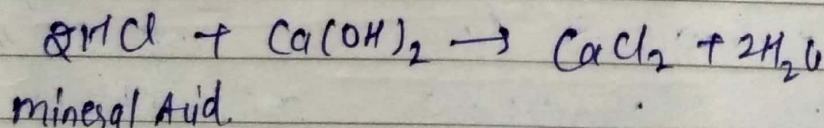
Insoluble salt.



$\text{CaCl}_2 \text{ or } \text{CaSO}_4$



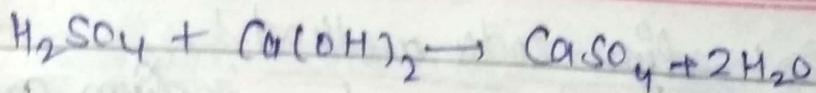
(b) Lime Removes free minerals acids as well as gases like H_2S



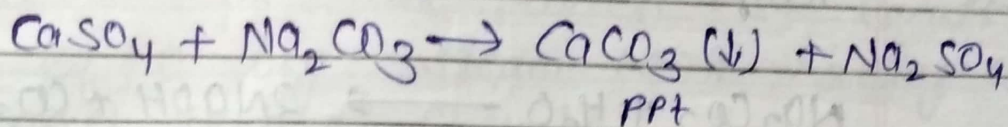
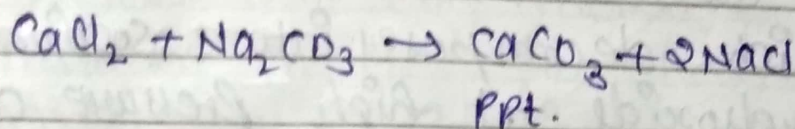
mineral Acid.

Lime $\Rightarrow$ temp. hardness + Perm. of mg, $\text{mgCl}_2 + \text{mgSO}_4$
 Soda $\Rightarrow$ Calcium $\Rightarrow \text{CaSO}_4, \text{CaCl}_2$ Removal of mg

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(c) Soda Removes all the Calcium Permanent hardness which is soluble in water



The lime soda washes may be broadly classified into two categories.

- (1) cold-lime soda method
- (2) hot lime soda method.

(1) Cold lime soda method :

In this process calculated quantities of chemical are mixed with water at room temp. • The ppt formed at room temp. is finely divided and does not settle down easily. These can not be easily filtered. So,

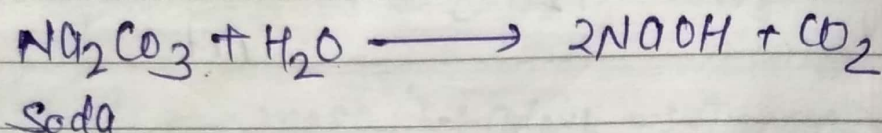
It is essential to add a small quantity of coagulant which hydrolysis to give gelatinous ppt of ~~Al~~ Al-hydroxide and sweep it entraps the fine ppt.

(~~fine ppt~~
 mix coagulant
 for ppt)

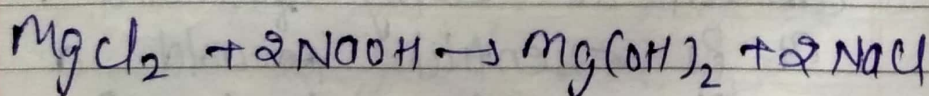
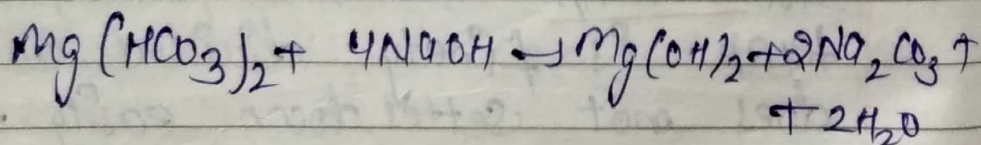
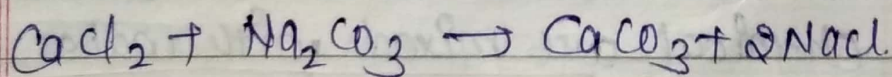
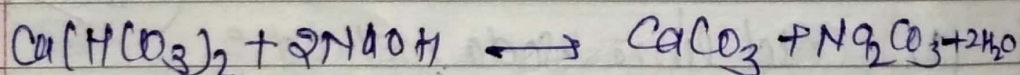
pure soda $\rightarrow$ NaOH $\rightarrow$ age rx

② hot lime soda method!

In this process only sodium carbonate is used for softness. The process of sodium carbonate is carried out into the boiler which decomposes into sodium hydroxide at high pressure and temperature.



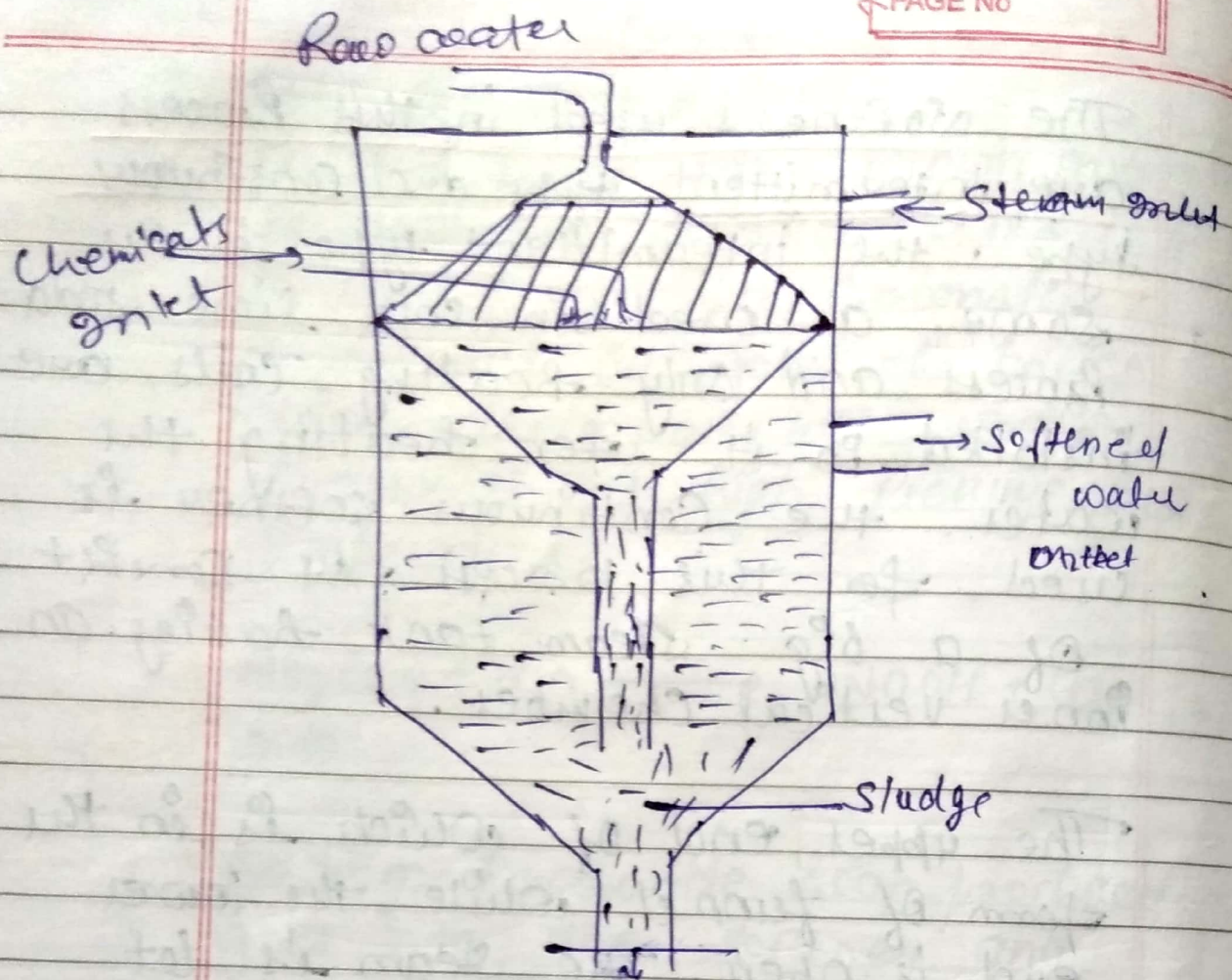
Sodium hydroxide soap produced goes into the softener and reacts with known alkyl hardness of sodium and calcium carbonate



Silicate can also be removed from water by this process.

The softeners used in this process are intermittent type and continuous type. The intermittent type is the same as used in cold lime soda process and only heating coils are installed in it for heating the water. The continuous softener is used for this process. It consists of a big steam tank having an inner vertical chamber.

The upper end of which is in the form of funnel while the lower end is open. The steam is let when the mixture goes down the rxn is completed and water rises up the slag settles down, in this process the residual hardness is far less as compare to lime soda method.



* Advantages:

hot lime soda process have the following advantages,

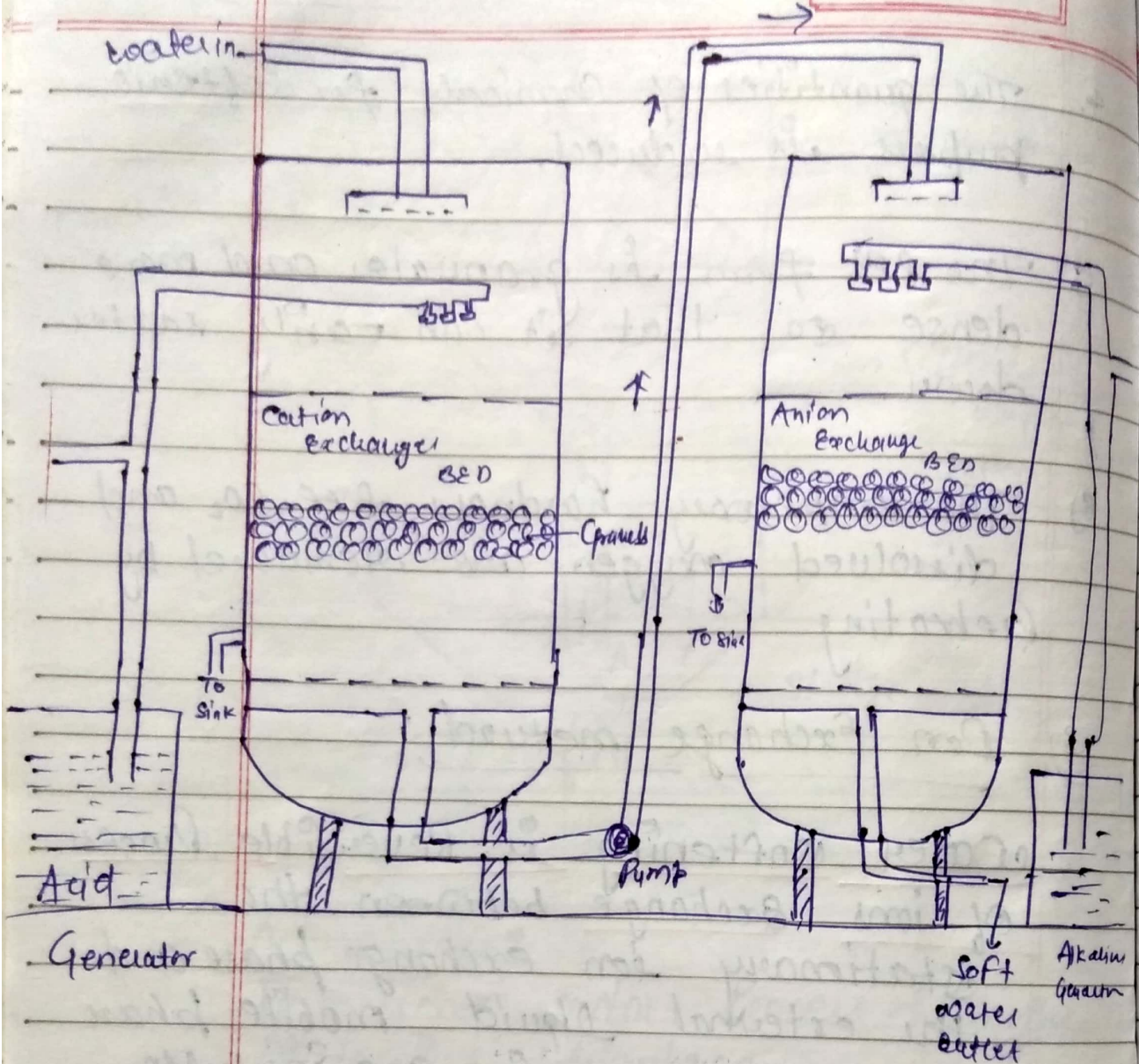
- 1) There is saving of coals as the reheating of water is completed through hot exhaust gases of the boiler.
- 2) The use of lime is avoided.
- 3) The chemical action is accelerated at high temp.

4. The quantities of chemicals for softening purpose is reduced.
5. The PPT form is granular and more dense so, that it can easily settle down.
- 6) The temporary hardness, free CO_2 and dissolved oxygen are removed by heating.

3) Ion Exchange method:

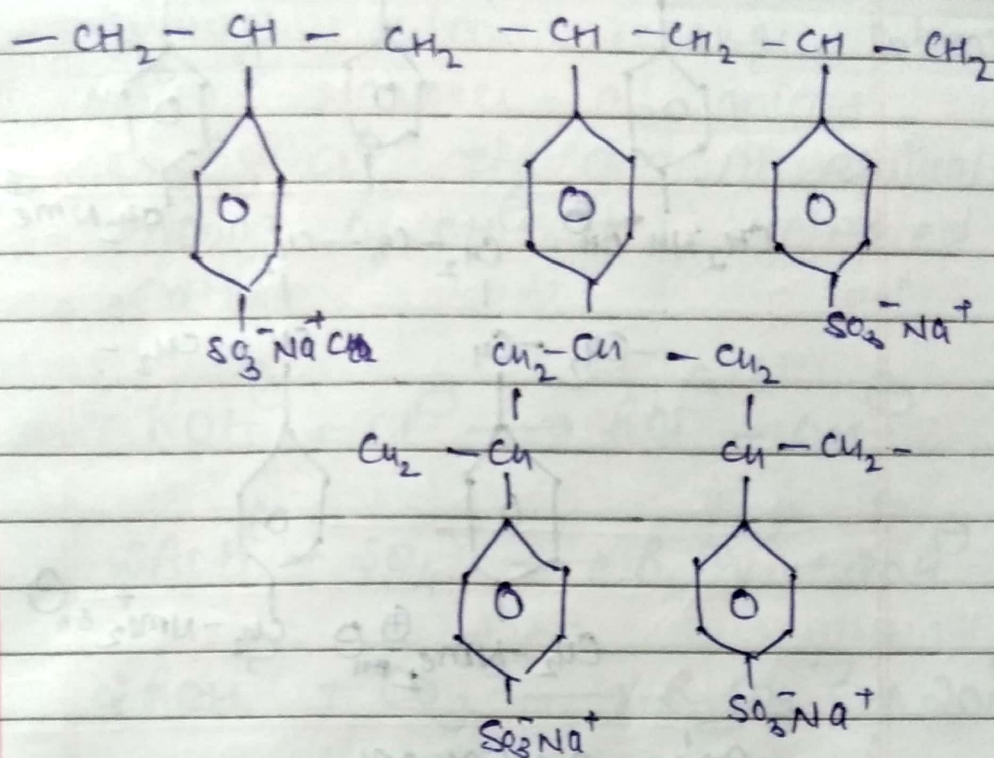
Water softening is Reversible Process of ions Exchange between the stationary ion exchange phase and the external liquid mobile phase. Ion exchange resin are insoluble crossely long chain organic Polymers, these have microporous structure. The function group attached to them are ~~water~~ responsible for ion exchange properties these are classified into two categories.

- i) Cation exchanger resin
- ii) Anion exchanger resin.



* Cation Exchange resin:

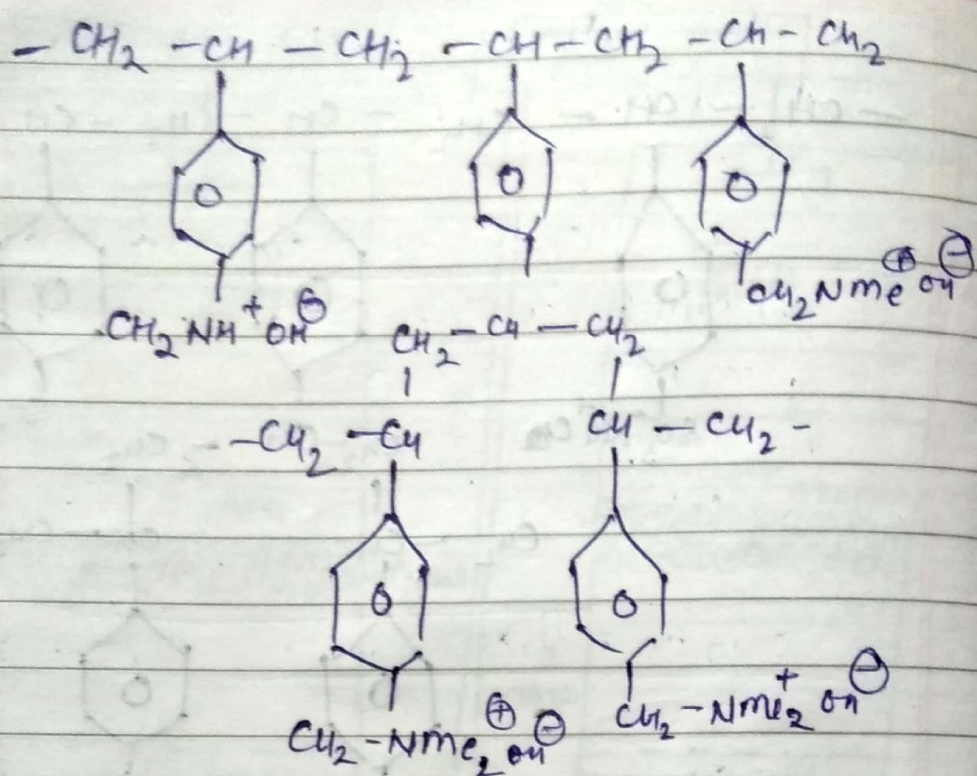
These are Polymer having Sulphate group attached to them and equal no. of replaceable Na^+ ions near them.



Cation exchange resins.

* Anion Exchange resin!

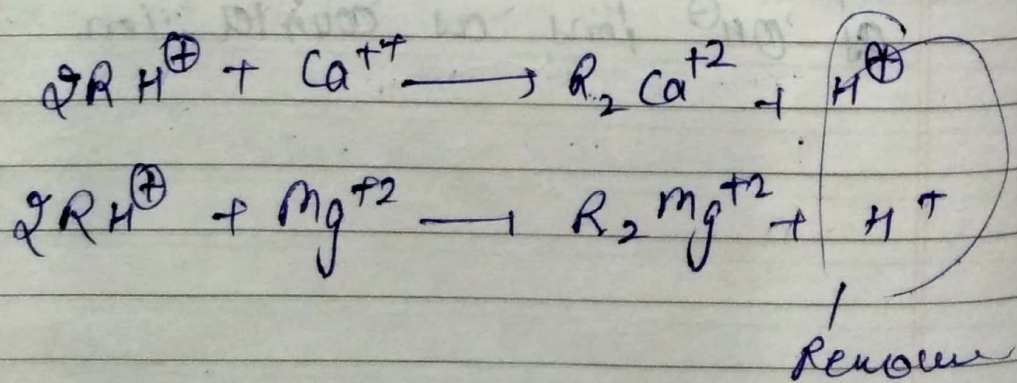
Anion Exchange resins are polymer which ~~contain an~~ contain amine or quaternary ammonia group as integral part of the resins and an equivalent amount of anions, such as OH^- ions as counter ion.



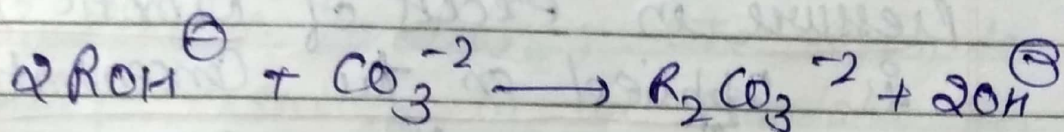
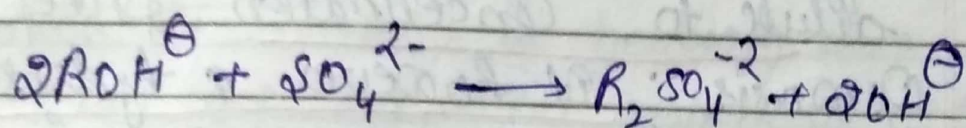
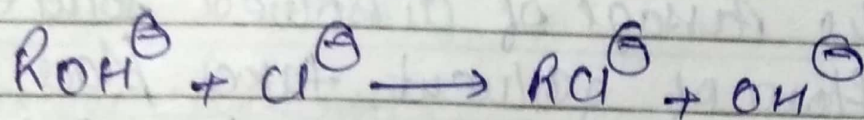
anion exchanger

* Process of softening by exchange Resin:

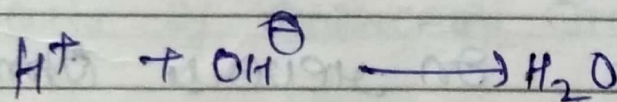
The hard water is first passed through cation exchanger Column which removes all the cation like Ca^{+2} , Mg^{+2} from it and an equivalent amount of H^+ ions are released from this Column to water.



After that water is passed through anion exchange column which removes all anions SO_4^{2-} , Cl^- etc and an equivalent amount of OH^- ions released to water.



H^+ and OH^- ions are released from cation and anion exchange column get combine to produce water molecules.

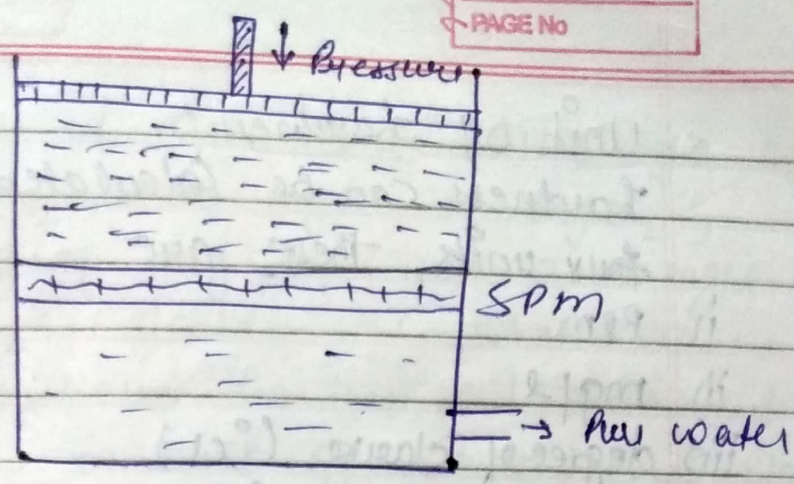


The water coming out from the exchanger is free from cation as well as anion and such water is known as demineralised or deionised water.

* Reverse Osmosis (RO) : Hyperfiltration
or Superfiltration

When two solution of different Conc^n are separated by a semi permeable membrane (SPM) which selectively does not permit the passage of dissolved solute particles, flow of solvent takes place from dilute to concentration sides due to Osmosis. It however a hydrostatic pressure in excess of osmotic pressure is applied on the concentration side the solvent flow reverse i.e. solvent is forced to move from Concⁿ side to dilute side across the membrane. This is the principle of reverse osmosis.

Therefore, in reverse osmosis method, pure solvent, water is separated from its contaminants rather than removing contaminants from the water. This membrane filtration sometimes also called Super Filtration or hyper filtration.



Imp

* Degree of Hardness!

Hardness of water is generally expressed in terms of equivalent amount of CaCO_3 (equivalent of CaCO_3). The reason for choosing CaCO_3 as the standard for reporting the hardness of water is the ease in calculation as its m.wt is 100. Moreover, it is the most insoluble salt that can be ppt in water treatment.

$$\text{Equivalent of } \text{CaCO}_3 = \frac{\text{Strength of hardness} \times 50}{\text{Eq. wt of hardness producing substance}}$$

$$= \frac{\text{Strength of the hardness} \times 50}{\text{Eq. wt of hardness producing substance}}$$

$$\text{Eq. wt of hardness producing substance}$$

$$\text{Eq. CaCO}_3 = \frac{\text{Strength of the hardness} \times \text{multiplication factor}}{\text{producing substance}}$$

$$\text{multiplication factor} = \frac{\text{m.wt of CaCO}_3}{\text{m.wt of hardness producing substance}}$$

Units of hardness:

Hardness can be calculated in terms of four units, these are

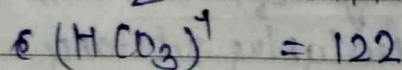
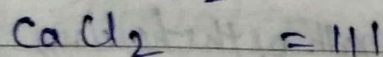
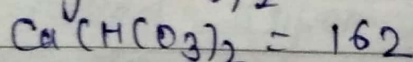
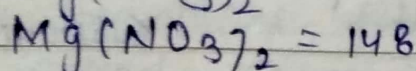
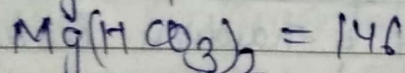
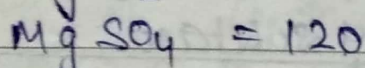
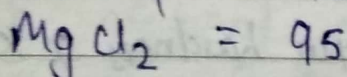
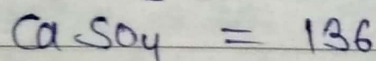
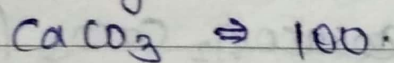
- i) ppm
- ii) mg/l
- iii) degree of Clarke ($^{\circ}\text{Cl}$)
- iv) degree of French ($^{\circ}\text{Fr}$)

Inter relation b/w various units of hardness

$$\begin{aligned}
 1 \text{ ppm} &= 0.07 \text{ Degree of Clarke} \\
 &= 0.1 \text{ Degree of French} \\
 &= 1 \text{ mg/l}
 \end{aligned}$$

Ques) Note:

The m.wt of some compounds are given below



D.O.N
2

Que A sample of water contain 16.8 mg/l of $\text{Mg}(\text{HCO}_3)_2$, 19.0 mg/l of MgCl_2 , 24.0 mg/l of MgSO_4 , and 22.2 mg/l of CaCl_2 . Calculate the total hardness of water, temporary hardness and permanent hardness in terms of CaCO_3 equivalent.

Hardness

Substance	Mass of the Substance (mg/l)	Multiplication Factor	M CaCO ₃ eq.
$\text{Mg}(\text{HCO}_3)_2$	16.8 mg/l	$\frac{100}{146}$	$16.8 \times \frac{100}{146} = 11.51$
MgCl_2	19.0	$\frac{100}{95}$	$19.0 \times \frac{100}{95} = 20$
MgSO_4	24.0	$\frac{100}{120}$	$24.0 \times \frac{100}{120} = 20$
CaCl_2	22.2	$\frac{100}{111}$	$22.2 \times \frac{100}{111} = 20$

Temporary hardness = $\frac{16.8 \times 100}{146} = 11.51$

Permanent hardness = 60

Total hardness = 71.51 mg/l.

Q. Calculate the Alkalinity, non-alkaline and total hardness of water containing the following salts - in mg/l

$$\text{Ca}(\text{HCO}_3)_2 = 16.2$$

$$\text{MgSO}_4 = 15.0$$

$$\text{Mg}(\text{HCO}_3)_2 = 17.3$$

$$\text{CaSO}_4 = 6.8$$

$$\text{MgCl}_2 = 19.0 \text{ and}$$

$$\text{NaCl} = 12.0 \times \text{neglect}$$

Substance	Mass of the Substance	m. f	CaCO_3 eq.
$\text{Ca}(\text{HCO}_3)_2$	16.2	$\frac{100}{162} \times 16.2$	$16.2 \times \frac{100}{162} = 10$
MgSO_4	15.0	$\frac{100}{120} \times 15.0$	$15 \times \frac{100}{120} = 12.5$
$\text{Mg}(\text{HCO}_3)_2$	17.3	$\frac{100}{146} \times 17.3$	$17.3 \times \frac{100}{146} = 11.8$
CaSO_4	6.8	$\frac{100}{136} \times 6.8$	$6.8 \times \frac{100}{136} = 5.0$
MgCl_2	19.0	$\frac{100}{95} \times 19.0$	$19.0 \times \frac{100}{95} = 20.0$
NaCl	NaCl does not cause any hardness		

Alkyl hardness

due to carbonate, bicarbonate
and hydroxides

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$$\text{Total hardness} = 208.59.3$$

$$\text{Alkylne hardness} = (\text{add due to carbonate, bicarbonate and hydroxide}).$$

$$= 21.8$$

$$\text{Non Alkylne} = 87.5$$

Que Calculate the temp. and permanent hardness by using following analysis of water.

Substance	mass of sub.	M.F	Cal $\text{CaCO}_3 \text{ eq.}$
- $\text{Ca}(\text{HCO}_3)_2$	55 ppm	$\frac{100}{182}$	$\frac{55 \times 100}{182} =$
MgCl_2	20 ppm	$\frac{100}{95}$	$\frac{20 \times 100}{95} =$
CaSO_4	32 ppm	$\frac{100}{136}$	$\frac{32 \times 100}{136} =$
$\text{Mg}(\text{NO}_3)_2$	10 ppm	$\frac{100}{148}$	$\frac{10 \times 100}{148} =$
- $\text{Mg}(\text{HCO}_3)_2$	25 ppm	$\frac{100}{146}$	$\frac{25 \times 100}{146} =$

$$\text{temp. hardness} = 51.07$$

$$\text{Permanent hardness} = 51.335$$

$$\text{Total} = 102.405$$

% factor = $\frac{\text{lime 100\% or 56\%}}{\text{purity factor}}$

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* Calculation of amount of soda used Lime Required

Formula

(i) Total Lime Req. = $\frac{74}{100} \left[2 \times \text{temp. of mg} + \text{Temp. of Ca} + \right.$
 $\left. + \text{Perm. of mg} + \text{Salt of Fe \& Al} + \right.$
 $\left. + \text{CO}_2 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- - \text{NaHCO}_3 \right]$
 All in terms of CaCO₃ eq.
 $\times \text{volume of water} \times \% \text{ factor}$

% factor of grain = 74%
 $= \frac{100}{74}$

(ii) Total soda Req. = $\frac{106}{100} \left[\text{Perm. of mg} + \text{Perm. of Ca} + \right.$
 $\left. \text{Perm. of Salt of Fe} + \text{Salt of Al} + \text{HCl} + \text{H}_2\text{SO}_4 - \right.$
 $\left. - \text{HCO}_3^- \right]$ All in terms of CaCO₃ eq.
 $\times \text{volume of water} \times \% \text{ factor}$

Ex

Ques. Calculate the amount of Lime (95% Purity) and soda (98% Purity) required for the treatment of 50,000 liter of water whose analysis as follows

- (i) Ca(HCO₃)₂ = 45.5 ppm,
 Mg(HCO₃)₂ = 38.0 ppm,
 MgSO₄ = 25.0 ppm,
 CaSO₄ = 32.0 ppm,
 CaCl₂ = 28.0 ppm,
 NaCl = 10.0 ppm,

Permanent $\Rightarrow$ mg. both

Lime $\Rightarrow$ temp + Perm (mg)

Soda $\Rightarrow$ Ca, Bau. mg

32
12

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$MgCl_2 = 95.0$ ppm

Substance	mass of the substance	M.F	$CaCO_3$ eq.
$Ca(HCO_3)_2$	48.5 L)	$\frac{100}{162}$	$\frac{48.5 \times 100}{162} = 28.08$
$Mg(HCO_3)_2$	38.0	$\frac{100}{146}$	$\frac{38.0 \times 100}{146} = 26.63$
$MgSO_4$	25.0	$\frac{100}{120}$	$\frac{25.0 \times 100}{120} = 20.83$
$CaSO_4$	32.0	$\frac{100}{136}$	$\frac{32.0 \times 100}{136} = 28.53$
$CaCl_2$	28.0	$\frac{100}{111}$	$\frac{28.0 \times 100}{111} = 25.23$
$MgCl_2$	95.0	$\frac{100}{95}$	$\frac{95.0 \times 100}{95} = 100$
NaCl	does not cause of any hardness		

Req. of

$$\text{Requirement of Lime} = \frac{74}{100} \left[28.08 + (2 \times 26.63) + 20.83 + 100 \right]$$

$$\times \frac{100}{95} \times 50,000 = 7827.2 \text{ gm} = 7.8 \text{ kg}$$

$$\text{Req. of Soda} = \frac{106}{100} \left[20.83 + 28.53 + 25.23 + 100 \right]$$

$$\times \frac{100}{98} \times 25000$$

$$= 9171.70 \text{ gm} = 9.17 \text{ kg}$$

01/4/19

Ques How many gm of $MgCO_3$ dissolved per liter gives 70 ppm hardness

$$70 = x \times 100$$

$$70 = x \times 100$$

$CaCO_3 eq^l$ = strength of the hardness producing substance $\times$ multiplication factor

$$70 = x \times \frac{100}{84} = \frac{560}{10} = 56$$

$$x = \frac{560}{10} = 56.8 \text{ mg}$$

Q. A water sample contains 4.08 gm of $CaSO_4$ per 1000 ml. Calculate the hardness in terms of $CaCO_3 eq^l$.

$$CaCO_3 eq^l = 4.08 \times \frac{100}{136}$$

$$= \frac{408}{136} = 3.0 \text{ gm/l}$$

$$\frac{136}{408}$$

Ques Calculate Amount of lime and soda require for the treatment of 20,000 litres of water whose analysis is as follows

		Mif		
L	$\text{Ca(HCO}_3)_2 = 40.5 \text{ ppm}$	$\frac{100}{162}$	$40.5 \times \frac{100}{162} = 25$	
2L	$\text{Mg(HCO}_3)_2 = 36.5 \text{ ppm}$	$\frac{100}{146}$	$36.5 \times \frac{100}{146} = 25$	
S	$\text{CaSO}_4 = 34.4 \text{ ppm}$	$= \frac{100}{136}$	$34.4 \times \frac{100}{136} = 25$	
1+S	$\text{MgSO}_4 = 30 \text{ ppm}$	$\frac{100}{120}$	$30 \times \frac{100}{120} = 25$	
S	$\text{CaCl}_2 = 27.75 \text{ ppm}$	$= \frac{100}{111}$	$27.75 \times \frac{100}{111} = 25$	

$$\text{Lime Req} = \frac{74}{100} [2 \times 25 + 25 + 25] = 71 \text{ kg} \times 20,000 = 2880000 = 1.48 \text{ kg}$$

$$\text{Soda Req} = \frac{106}{100} \times [25 + 25 + 25] = \frac{106}{100} \times 75 = 1.59 \text{ kg}$$

eq^t wt of $\text{CaCO}_3 = 50$

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Q. The hardness of 1000 L of water sample was completely removed by passing it through a zeolite condenser.

The softener then required 30 L of NaCl solⁿ containing 1.5 g/L of NaCl for regeneration. Calculate the hardness of water sample of water.

Solⁿ: NaCl contained in 30 L of NaCl solution
 $= 1.5 \text{ g/L} \times 30$
 $= 45 \text{ gm}$

11
17
26

$$\text{gm. eq}^t = \frac{45 \times 50}{58.5} = \frac{2250}{58.5} = 38.46 \text{ gm eq}^t \text{ of } \text{CaCO}_3$$

1000 L of water = 38.46 gm eq^t of CaCO_3

$$1 \text{ L of water} = \frac{38.46}{1000} \times 1000 = 38.46 \text{ mg/L}$$

38.46
38.46
9

Drink effect, Rehydration

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* Corrosion:

Certain metals are slowly eaten up on long exposure to atmosphere. Such metals react with the gases or moisture present in environment to form compounds. Generally oxides are formed and depending upon the presence of carbonates, sulphide, sulphates etc may also be formed and this particular process is referred to as corrosion.

Corrosion can be defined as the degradation of deterioration of the metal by chemical or electrochemical rxn with its environment.
OR

Corrosion is a process of slow conversion of metals into their undesirable compounds by rxn with moisture and other gases present in the environment.

Some examples of corrosion are as follows

1. Rusting of iron

When exposed to the atm. condition a layer of raddish scale and powder of Fe_3O_4 is formed on the surface.

2. Formation of green film on the surface of copper

A green layer of basic carbonate consisting of $\text{CuCO}_3 + \text{Cu(OH)}_2$ is formed on the surface of copper when exposed to moist air.

3. Tarnishing of silver

When silver is exposed to the atmosphere, a black coating is formed.

* Types of Corrosion:

Corrosion is classified as-

- i) dry Corrosion or direct Chemical Cor.
- ii) wet corrosion or immersed Corrosion or electrochemical Corrosion

(i) Dry Corrosion or direct chemical Corrosion

Dry corrosion occurs may be through the direct chemical attack of gases

Such as oxygen, hydrogen, H_2S , SO_2 ,

N_2 or certain anhydrous (not water) in

organic liquid with metal surface in

intermediate contact. Three types of Chemical Corrosions.

- a) ~~Electro~~ Oxidation Corrosion
- b) Corrosion by other gases
- c) Liquid metal corrosion

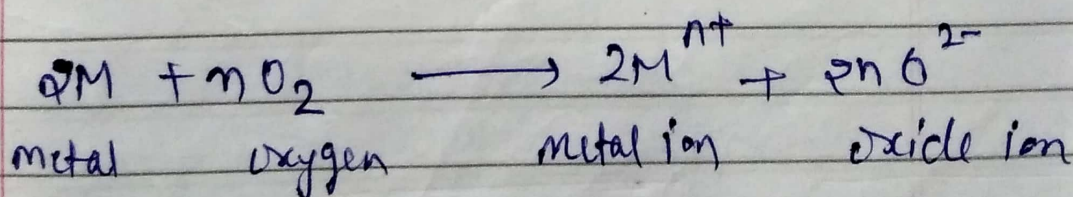
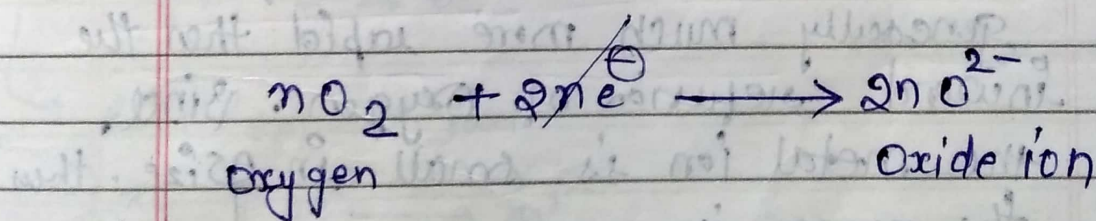
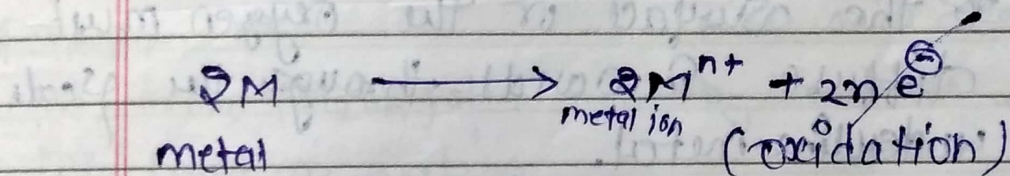
always on pure

↑ (loss of e^-)

c) Oxidation Corrosion:

This type of corrosion brought by the direct attack of oxygen on metal surface at low or high temp, usually in the absence of moisture. Alkali metals (Li, Na, K, Rb, etc) and alkali earth metal (P, Mg, Ca, Sr etc), are highly prone for oxidation even at low temperature, while at high temperature, almost all metals except noble metals (Ag, Au, Pt) are oxidised.

The chemical rxn takes place in the oxidation corrosion are



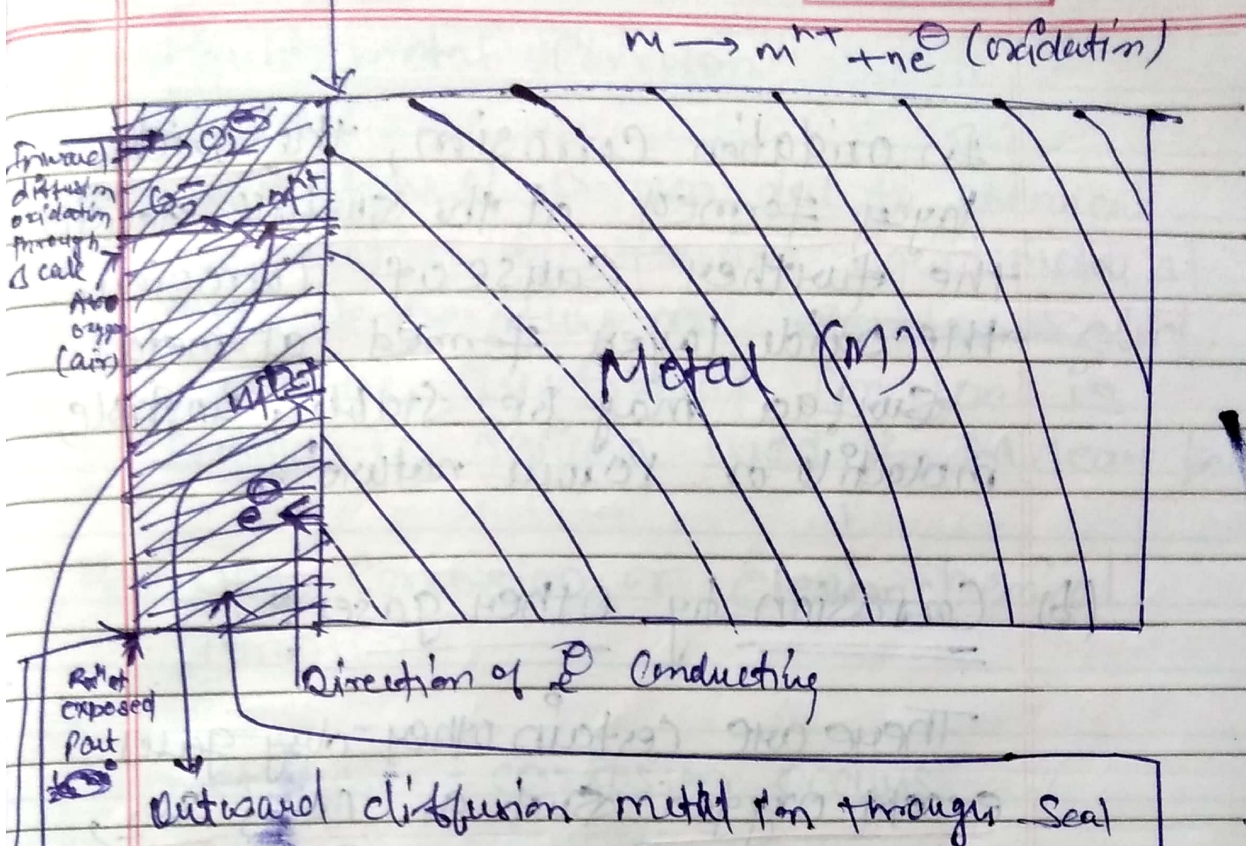
Mechⁿ:

First oxidation occurs at the surface of the metal and the formed metal oxide scale forms a barrier which restricts further oxidation of metal surface. All the gas molecules are adsorbed rapidly by the surface of the metal as atoms, ions or molecules. This is followed by diffusion of gas in metal.

For oxidation to continue, either the metal must diffuse outwards to the scale or the oxygen must diffuse inwards through the scale under the metal.

The outward diffusion of metal is generally much more rapid than the inward diffusion of oxygen. Since the metal ion is small in size than the oxygen ion.

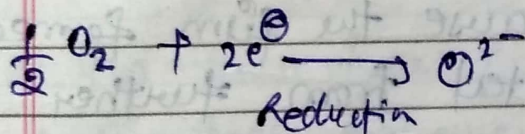
Reaction at metal - metal oxide interface



Formation of metal oxide (M_2O_n) at the point of meeting of M^{n+} & $2O^{2-}$

metal oxide seal formed by direct reaction of metal & O_2 ions

Reaction at exposed part



In oxidation corrosion, the oxide layer formed at the surface decides the further cause of corrosion. The oxide layer formed at metal surface may be stable, unstable, molative or porous nature

(b) Corrosion by other gases:

There are certain other dry gases except oxygen such as CO_2 , SO_2 , Cl_2 , H_2S , F_2 etc. which also cause corrosion. The extent of corrosion depends mainly on the chemical affinity of metal and the gas involved

If the film formed is protective or non porous, the extent of attack decreases because the film formed protects the metal from further attack

If film formed is not protective or porous, the surface of the metal is gradually destroyed

g) Liquid metal Corrosion:

Such type of corrosion due to chemical ~~act~~ action of flowing liquid metal at high temperature on ~~solid~~ solid metal. This type of corrosion is common in devices used for nuclear power.

* Wet Corrosion or Electrochemical Corrosion:

Wet type of corrosion occurs.

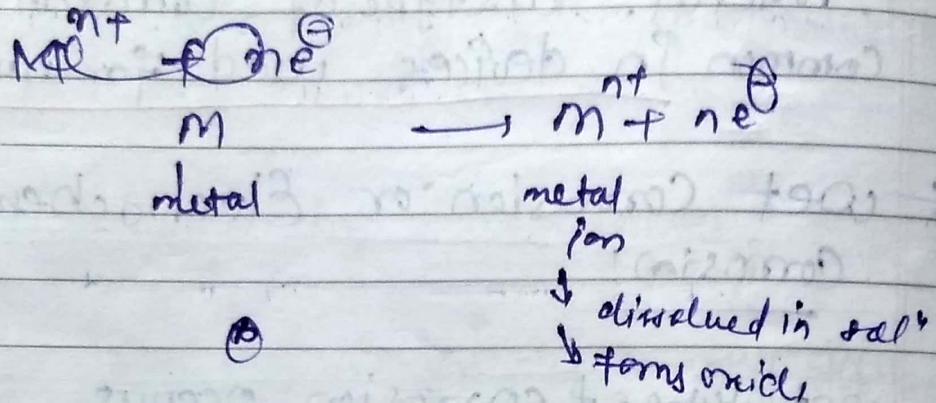
1) When a conducting liquid is in contact with metal

2) When two different metals or alloys are either dipped or immersed partially in a solution

In this type of corrosion impure metal surface behaves like a small electrochemical cell and called as corrosion cell. In these miniature cells, pure metal acts as anode and impure surface acts as cathode.

at anode oxidation of metal takes place. metal atom pass into solution as metal ions, leaving behind electrons in the metal which are pushed into cathodic area.

Reduct



at cathode, reduction R^{n+} takes place. usually, at cathode, dissolved constituent in the conducting medium ~~accept~~ e^- to form R^{n-} ions.

The metallic ion at anode and some other ions formed at cathode diffused towards each other through conducting medium and formed a corrosion b/w anode and cathode.

Dmk:

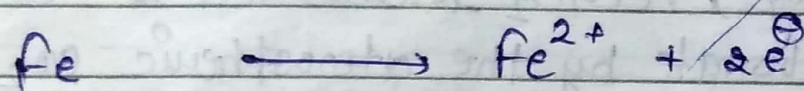
Dmk

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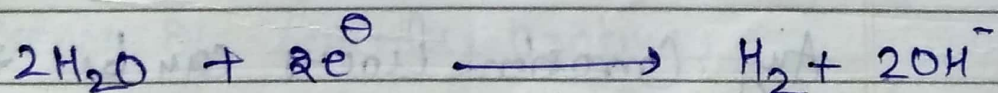
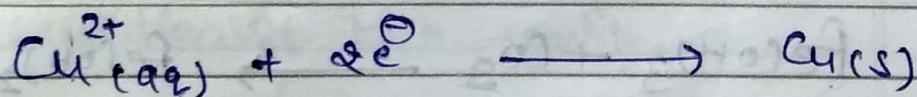
* Electrochemical theory of corrosion:

According to this theory the chemical unevenness of metals behave like small electric cells in presence of water containing dissolved O_2 and CO_2 . therefore, corrosion takes place as a result of local action, the main features are

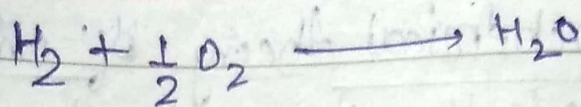
- a) the covered part of the metal surface act as the anode where iron changes to Fe^{2+} ions by giving electrons.



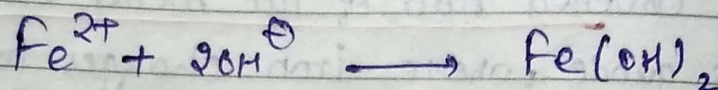
- b) A less electropositive metal like copper which is present as impurity takes away the electrons and develops the cathode where OH^- ions are formed.



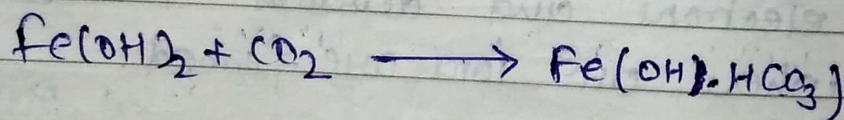
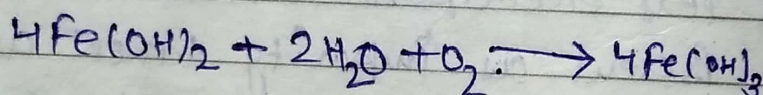
The evolved hydrogen make as accumulate at the cathode and cause Polarisation, but it is depolarised by atmospheric O_2 .



c) Due to the presence of two oppositely charged ions at the surface of metal, a galvanic flow of ions may take place and then these two ions combine to form a compound.



Finally, $\text{Fe}(\text{OH})_2$ is converted to basic carbonate by the atmospheric CO_2 and O_2



Any Corrosion process can be termed as an electrochemical process in which cathode and anode are formed on the metal surface and an electrolyte (water or salt) must be present to permit ionic flow to form corrosion products.

* Factors which affect the Corrosion:

1) Position of metal in electrochemical series:
the reactivity of metal depends upon the position in the electrochemical series. more the reactive, the more will be the possibility of getting corroded.

2) Presence of impurities in metal:

The impurities help in increasing speed of corrosion.
Boltic cell, which

3) Presence of electrolyte:

Presence of water, increasing the rusting of iron.

4) Presence of CO_2 in water:

increase the dissociation of H_2O reactivity.

5) Presence of protective coating:

When the iron surface is coated with layer more active than iron then the rate of corrosion decrease.

* Prevention of Corrosion!

the corrosion can be prevented by method given below

1) Barrier Protection

In this method a barrier is placed b/w metal and environment. The Barrier Protection can be achieved by the following methods

- a) the surface is coated with paint
- b) " " " protected by applying a thin layer of oil or grease
- c) The metal is electroplated with metal like tin, Zn, Ni etc

2) Sacrificial Protection:

In this method the metal is protected by corrosion by covering it with a layer of other metal which is more reactive than the parent metal.

This is due to loss of electrons from the parent metal. The active metal loses electrons in reference to parent metal and goes into ionic state.

Therefore the covering metal consume with time as long as it is present on the surface of parent metal, the parent metal is protected and this is known as Sacrificial Protection.

For ex. Zn is commonly used for covering iron surfaces. Thus the process of covering iron with Zn is called Galvanisation.

2] Electrical Protection:

This method is used for protecting iron articles which are in contact with water such as underground pipe. The article of iron are connected more active metals like Mg or Zn.

The active metal has lower reduction potential than iron and will lose electrons in presence of iron.

For ex- Mg has lower reduction potential than iron. Then Mg will be oxidised in presence of iron and it will protect iron being rusted.

4) Using Anticorrosion Solution:

To retard the Corrosion of metal, certain anticorrosion solution are used. For ex- alkylene solution of phosphate and chromates are used as anticorrosion solution.

Ques! A sample of water on analysis was found to contain following in mg/l

$\text{CaSO}_4 = 0.4$	82.0
$\text{MgCO}_3 = 0.44$	80.
$\text{CaCO}_3 = 2.00$	100
$\text{MgSO}_4 = 0.80$	120
$\text{MgCl}_2 = 0.78$	84
$\text{SiO}_2 = 2.40$	
$\text{NaCl} = 2.50$	

Calculate the amount of Lime required to Soften the 20,000 litres water per day of a year, if purity of lime and soda is 90%.

<chem>CaSO4</chem>	0.4	100/32	0.29	S
<chem>MgCO3</chem>	0.44	100/80	0.52	2L
<chem>CaCO3</chem>	2.00	100/100	2	L
<chem>MgSO4</chem>	0.80	100/120	0.66	L+S
<chem>MgCl2</chem>	0.78	100/95	0.82	
<chem>SiO2</chem>	2.40			
<chem>NaCl</chem>	2.50			

$$\text{Lime Req.} = \frac{74}{100} (2 \times 0.52 + 2 + 0.66 + 0.82) \times \frac{100}{90}$$

$\times 20000$

$$= \frac{74}{100} [1.04 + 2 + 0.66 + 0.82] \times \frac{100}{90} \times$$

$\times 20000$

$$= 7422.2 \text{ mg} = 74.22 \text{ g} = 0.0742 \text{ kg/day}$$

$$\text{Req. of Soda} = \frac{106}{100} [0.29 + 0.66 + 0.82] \times$$

$$\times \frac{100}{90} \times 20000$$

$$= \frac{106}{100} [1.77] \times \frac{100}{90} \times 20000 = 4169 \text{ mg}$$

$$= 41.69 \text{ g} = 0.0415 \text{ kg/day}$$

$$\text{Lime Req. for 1 yr} = 0.0742 \times 365 = 27.08 \text{ kg}$$

$$\text{Soda Req. for 1 yr} = 0.0415 \times 365 = 15.14 \text{ kg}$$