1. **Hardness of water :-**

Water that does not give immediate lather with soap is called hard water. The hardness is due to dissolving salts like Ca^{+2}, Mg^{+2} and the respective salts like HCO_3^-, Cl^-, SO_4^{-2}, NO_3^- etc.

Soap is a salt of higher fatty acid. These fatty acids are completely soluble in water but these are going to react with hard water form soluble precipitate of Calcium and Magnesium palmitate or stirate or oleate.

$$2C_{17}H_{35}COONa + Ca^{+2} \longrightarrow C_{17}H_{35}(COO)_2Ca + 2Na^+$$

$$2C_{17}H_{35}COONa + Mg^{+2} \longrightarrow C_{17}H_{35}(COO)_2Mg + 2Na^+$$

Hardness of water is of 2 types :-

(i) Permanent hardness

(ii) Temporary hardness

Temporary hardness :-

It is due to presence of 'bicarbonates' of Calcium and Magnesium. It can be removed by boiling.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

Permanent hardness :-

It is due to presence of chlorides, sulphates of Calcium and Magnesium, which cannot be easily removed by boiling process.

Units of hardness of water :-

Hardness of water expressed in terms of Calcium carbonate equivalent.

$$CaCO_3 \text{ equivalent} = \frac{\text{Mass of hardness causing salts}}{\text{Molecular mass of salts}} \times 100$$

(i) ppm (parts per million)

(ii) mg/l (milligram per litre)

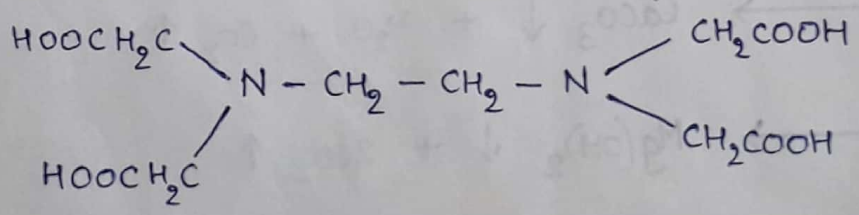
(iii) °Fs (degrees of French)

(iv) °Cl (degrees of Clark)

Estimation of hardness of water by EDTA method (complexometric method :-

The structure of EDTA -

Ethylene diamine tetra acetic acid



Principle :-

$Ca^{+2} + EBT \longrightarrow Ca-EBT$
$Mg^{+2} + EBT \longrightarrow Mg-EBT$
} unstable wine red colour

$Ca-EBT$
$Mg-EBT$
$+ EDTA \longrightarrow$ $Ca-EDTA$ $Mg-EDTA$ $+ EBT$

stable complex — Blue colour

Hardness of water can be estemated by EDTA. In this method hard water mix with buffer of PH = 9-10 and one (or) two drops of EBT indicator, the colour of water changes to wine red due to formation of Calcium, Magnesium EBT complex. Then on titration with EDTA gives blue colour as end point.

Procedure :-

The process is done in three steps :-

(i) Standardization of EDTA.
(ii) Standardization of hard water.
(iii) Standardization of permanent hardwater.

(i) Standardization of EDTA :-

Hardness of water can be estemated by EDTA. In this method the standard hard water of 20ml is taken in a conical flask and mix with the buffer of pH = 9-10 and add one (or) two drops of EBT indicator, the colour of the water changes to wine red due to formation of

end point.

S.No	Volume of water sample in ml	Burette reading		Volume of EDTA

By formula :-

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Here ; $n_1 = n_2 = 1$

$$M_1V_1 = M_2V_2$$

Here ;

M_1 = molarity of standard hard water

V_1 = volume of standard hard water

M_2 = molarity of EDTA solution

V_2 = volume of EDTA solution

$$M_2 = \frac{M_1V_1}{V_2}$$

(ii) Standardization of hard water :-

Hardness of water can be estimated by EDTA. In this method tap water of 20ml is taken into a conical flask and mix with the buffer of pH = 9-10

and add one or two drops of EBT endicator, the colour of the water changes to wine red due to formation of Calcium, Magnesium EBT complex. Then on titration with EDTA gives blue colour as an end point.

S.No	Volume of water sample in ml	Burette reading		Volume of EDTA in ml
		Initial	Final	

Formula :-

$$\frac{M_2V_2}{n_2} = \frac{M_3V_3}{n_3} \Rightarrow M_2V_2 = M_3V_3$$

Here $n_2 = n_3$

Here ;

M_2 = Molarity of EDTA solution

V_2 = Volume of EDTA solution

M_3 = Molarity of tap water

V_3 = Volume of tap water

$$\boxed{M_3 = \frac{M_2V_2}{V_3}}$$

(iii) Standardization of permanent Hard water :-

Hard water of water can be estimated EDTA. In this method the hard water is taken and heated at a temperature 50° to 60° and then mix the buffer of pH = 9-10 and add one or two drops of EBT indicator, the colour of the water changes to wine red due to the formation of Calcium, Magnesium EBT complex. Then on titration with EDTA gives blue colour as an end point.

S.No	Volume of water sample in ml	Burette reading		Volume of EDTA in m
		Initial	Final	

Formula :-

$$\frac{M_2V_2}{n_2} = \frac{M_4V_4}{n_4}$$

Here $n_2 = n_4 = 1$

$\therefore M_2V_2 = M_4V_4$

Here;

M_2 = molarity of EDTA solution

V_2 = Volume of EDTA solution

M_4 = Molarity of hot water

V_4 = Volume of hot water

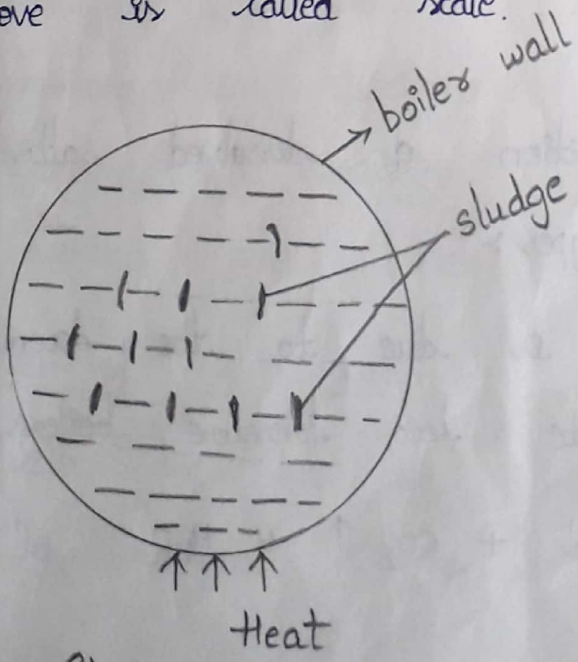
$$M_4 = \frac{M_2 V_2}{V_4}$$

Boilers troubles :-

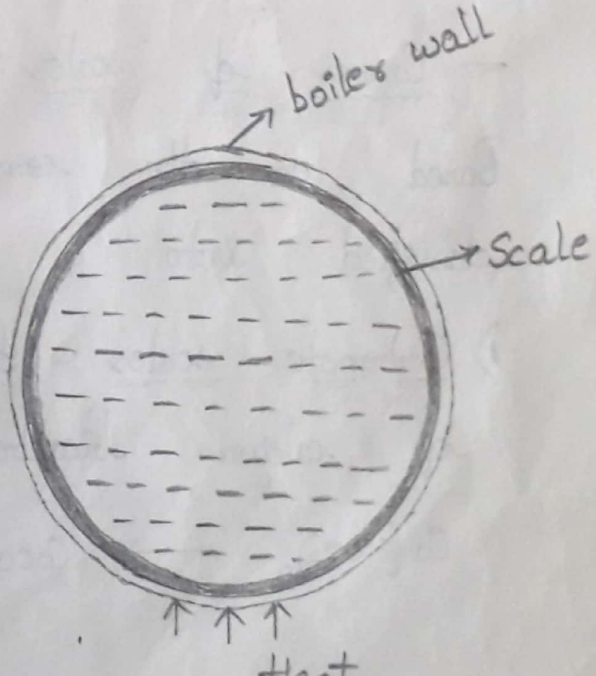
The troubles that are arised on the boiler during steam generation is called boiler troubles. There are different types of boiler troubles, they are :-

(i) Scale and sludge :- The soft, loose and slemy precipitate formed within the boiler is called sludge.

The hard, sticky and firmly attached to the inner side of the boiler and very difficult to remove is called scale.



Sludge



Scale

⇒ Causes of sludge :-

The sludge is formed due to dissolved salts whose solubility is more in hot water than cold water. The sludges were formed comparatively in colder portion of the boilers. The dissolved salts like $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$ are helpful for the formation of sludges.

⇒ Disadvantages :-

1. Sludges are bad conductors of heat.
2. Excessive sludge formation leads to chocking of the pipes.
3. Sludges were interrupted in the scale and deposited as the scale.

⇒ Removal of sludge :-

1. By using soft water instead of hard water.
2. By blow down operation.

⇒ Causes of scales :-

Based on the composition of dissolved salts are classified into 4 types :-

1) Carbonate scales :- It is due to the decomposition of calcium bicarbonate low pressure boilers.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

2) Hydroxide scales :- It is due to the hydrolysis of Magnesium salts.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

3) Sulphate scales :- Sulphate scales formed in the high pressure boilers with increase in temperature.

For example :-

$CaSO_4$ is more soluble in cold water and less soluble in hot water. The solubility of $CaSO_4$ is 3200 ppm at 15°C and it reduces to 27 ppm at 320°C.

4) Silicate scales :- It is formed due to the small amount of silicon dioxide present in water. It is present in the form of Calcium Silicate and Magnesium silicate.

⇒ Disadvantages :-

1. Wastage of fuel.
2. Decrease in efficiency of boiler container.
3. Danger of explosion.
4. Lowering the boiler safety.

⇒ Removal of scales :-

1. With the help of wire brushes.
2. By thermal shocks.

3. Carbonate scales removed by 5-10% of

4. Calcium sulphate scales removed by EDTA

Other than the above, the scales can be removed by internal treatment as well as external treatment.

Internal treatment :- The water which is treated within the boiler is called internal treatment.

Internal treatments are :-

1. Colloidal conditioning :- Organic substances like kerosene, tannin, agar-agar are added in water so that these colloidal substances get themselves coated on the scale forming precipitate. As a result, a loose sludge is formed and that can be easily removed by blow-down operation.

2. Phosphate conditioning :- Phosphate reacts with water and a loose sludge is formed which can be easily removed by blow-down operation. The phosphate selection depends on the pH of the water. Sodium hydrogen phosphate for acidic water and disodium hydrogen phosphate for weakly alkaline water and trisodium phosphate for alkaline water.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$$

3) Calgon conditioning :- Calgon is sodium hexa meta phosphate $(NaPO_3)_6$. It prevents the scale by the formation of soluble complex.

$$Na_2[Na_4(PO_3)_6] + 2CaSO_4 \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

⇒ Caustic embrittlement :-

It is a inter crystalline cracking of boiler metal. It causes due to usage of high alkaline water. During lime soda process small amount of Na_2CO_3 present in the water at high pressure. Na_2CO_3 decomposes to give NaOH and this leads to be caustic embrittlement. or inter metallic corrosion.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2\uparrow$$

$$2NaOH + Fe \longrightarrow Na_2FeO_2 + H_2O$$

By the above reacⁿ this proved that the NaOH dissolves the iron.

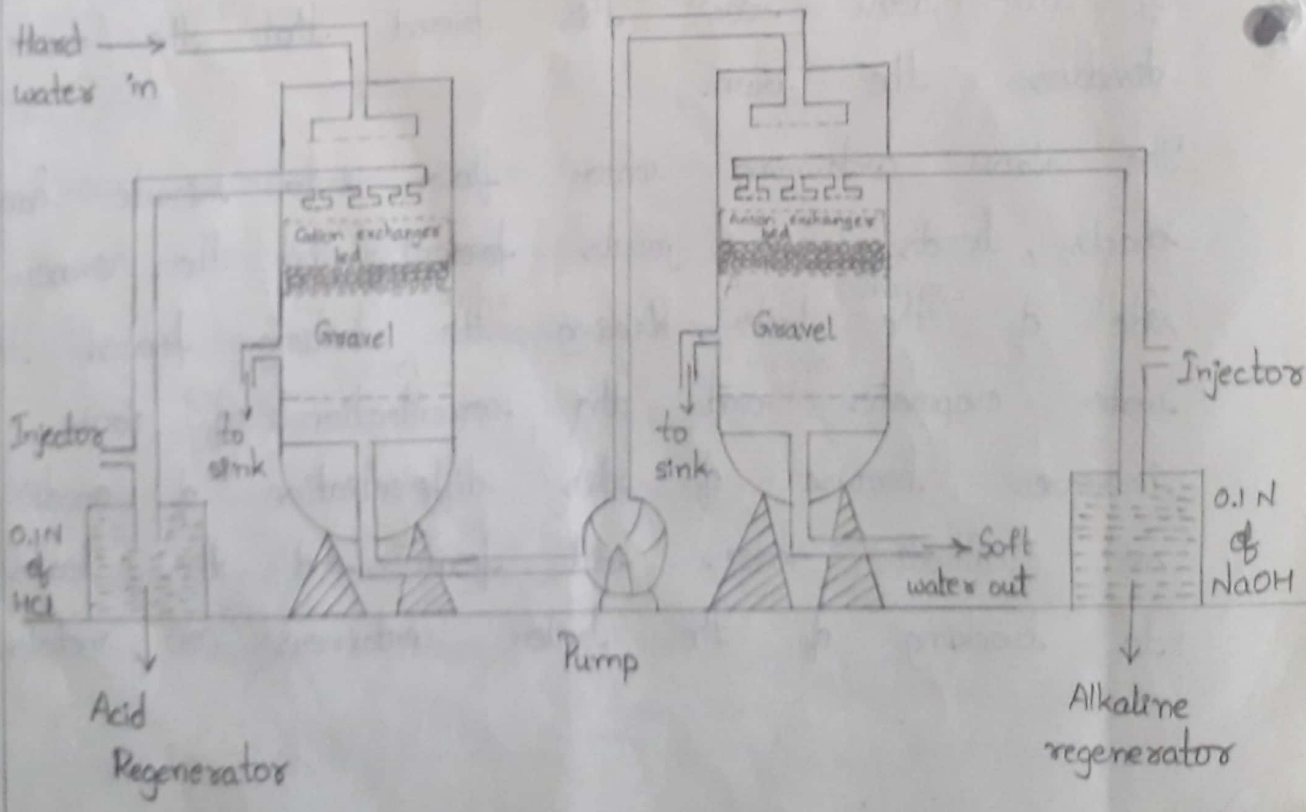
The NaOH containing water flows into minute hair cracks, bends and joints present in the inner side of the boiler. During the boiling process the water evaporates and the concentration of NaOH increases, because of this differentiation of anodic and cathodic areas will form and this leads to cracking of the boiler containers (or) metals.

Anode Iron at rivets, bends, joints	Concentrated NaOH solution	Dilute NaOH solution	Iron surfaces

→ Removal :-

1. By using sodium phosphate as a softening agent instead of Na_2CO_3.
2. By adding sodium sulphate to the boiler, sodium sulphate blocks the hair cracks.
3. By adding tannin or lignin to the boilers, these blocks the hair cracks.

Ion Exchange process (or) Method of De-mineralization process :-



This process is also known as Demineralization process. In this process cation exchangers convey cations as well as anion exchangers convey anions. The cation exchanger as well as anion exchanger are prepared with resins. The resins are highly cross-linked polymer structures having functional groups. The exchangable ions are called counter ions.

Process :-

In this process two long cylindrical columns used, one of the column helpful for cation exchange and another column helpful for exchanging anions and water containing dissolved salts. Calcium and Magnesium ions are passed through cation exchanger that carries exchangable H^+ ions. All the cations like Ca^{+2}, Mg^{+2} are exchanged. After exchanging cation the water is passed through the second column, where the anions are exchangable. The anions exchanger that carries exchangable OH^- ions. Anions like Cl^-, SO_4^{-2}, HCO_3^- are will be exchanged in this column. The H^+ ions released from cation exchanger and OH^- ions exchanged from anion exchanger combined to form water.

Cation Exchange process:-

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

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

Anion Exchange Process:-

$$2R'OH + 2Cl^- \longrightarrow 2R'Cl + 2OH^-$$

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

$$H^+ + OH^- \longrightarrow H_2O$$

When all the H^+ ions and OH^- ions are exchanged with these respective exchangers, then the resin is unable to soften in the hard water, that stage is called 'exhausted'. The resin to be regenerated with proper acids and bases.

Regeneration:-

Cation exchange resin is exchanged with 0.1N HCl and Anion exchange resin is exchanged with 0.1N of NaOH.

Reactions:-

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

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

$$2R'Cl + 2OH^- \longrightarrow 2R'OH + 2Cl^-$$

$$R_2'SO_4 + 2OH^- \longrightarrow 2R'OH + SO_4^-$$

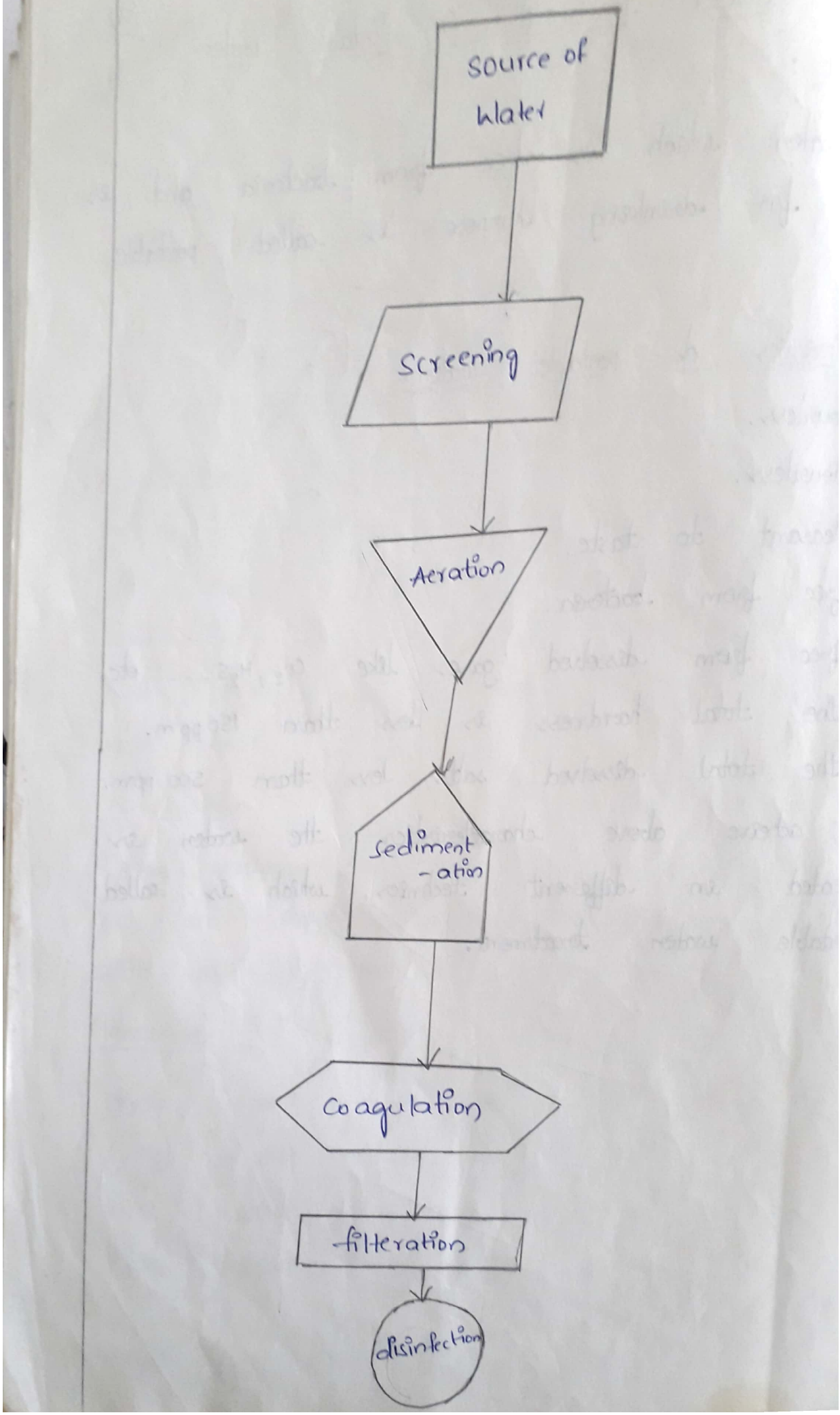
Municipal water treatment (or) Portable water treatment :-

The water which is free from bacteria and is useful for drinking purpose is called portable water.

Characteristics of portable water:-

1. colourless.
2. odourless.
3. pleasant to taste.
4. free from bacteria.
5. free from dissolved gases like CO_2, H_2S ---- etc.
6. The total hardness is less than 150 ppm.
7. The total dissolved salts less than 500 ppm.

To acheive above characteristics the water is treated in different technics which is called portable water treatment.



Screening :-

The raw water is passed through the screens have large number of holes. In this method the following "Floating objective or matter" is seperated out

Aeration

It is nothing but passage of air through the water for the removal of dissolved gases.

Sedimentation :-

It is nothing but simple setteling. After the removal of floating matter, the heavier particles present in the water are remored by this technique, By which force of gravity acts for this purpose the water is kept in a bigger tankers and the particles will settle down. The time required for the sedimentation is depend on weight, size and shape of the particles. Water kept in sedimentation takes for 4 to 12 hrs.

usually 70% of particles are settledown by plane sedimentation. finally divided matter and colloidal matter is not settled by this process. for this coagulation technique is used.

Coagulation

It is the process of removing the Suspended and colloidal matter by adding coagulants. There are different types of coagulants are used. They are alum aluminium, sulphate, sodium aluminate, ferrous sulphate, etc.

These Coagulants on reaction with water form a h... precipitate of respective hydroxides. these are call... flocculent precipitate. which are having gelatinus ... due to this property, these can interupt suspended ma... and the colloidal matter effectively removed.

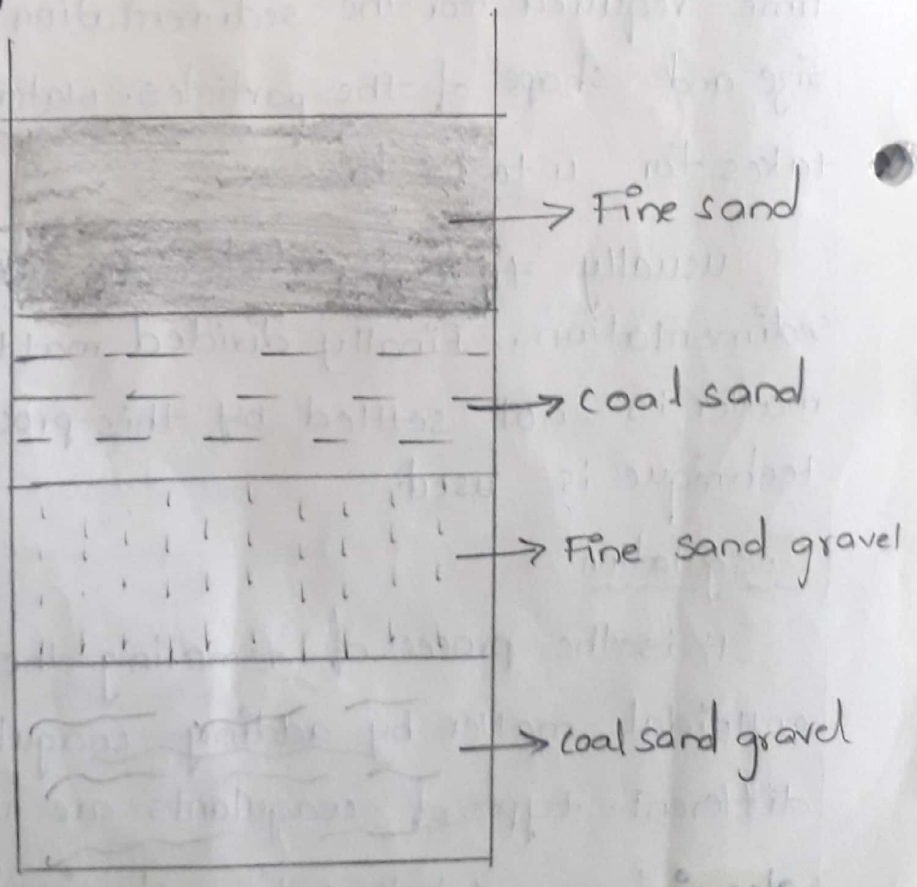
$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH.$$

Filteration :-

Filteration may be defined as the process of passing a liquid containing suspended matter, through a suitable porous material in such a manner, so as to effectively remove the suspended matter from liquids

Ex :- Sand Filter.

Filteration using Sand paper :-



Filters are like large shallow tanks made of concrete. At the bottom there is an under drain system through which the filterd water goes to the storage tank. Gravel is placed in the tank above the underdrain system; on the gravel bed of coarse sand and above it a larger of fine sand are placed.

As water percolates through the filter the suspended particles are retained on the top 5 to 10cm layer of the fine sand. In fact the layers of coarse sand and gravel do not filter at all. They support the fine sand top layer.

Suspended matter has been deposited to such an extent that the rate of filteration becomes very slow. Then a portion of the top layer is scrapped, it becomes necessary to replace the top layer completely.

Disinfection :-

It is the process of killing pathogenic bacteria and microorganisms from the water and making it safe for drinking. The chemicals used for killing pathogenic bacteria are called disinfectants.

i) Boiling :-

By boiling water for 15-20 min, harmful bacteria are killed. This is not possible for muncipal supply of water. This method of disinfection is adopted for domestic process.

ii) passing ozone :-

ozone when passed into water acts as disinfectant. It is an unstable isotope of oxygen produces nascent oxygen which is a powerful disinfectant.

$$O_3 \rightarrow O_2 + [O]$$

nascent oxygen.

this treatment is costly and ozone is unstable and cannot be stored for a long time.

iii) Bleaching powder :-

It is a method of disinfection in which water is mixed with a required amount of bleaching powder and the mixture is allowed to stand for several hrs for the completion of disinfection. freshly prepared Sample of bleaching powder contain N 36% available chlorine.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

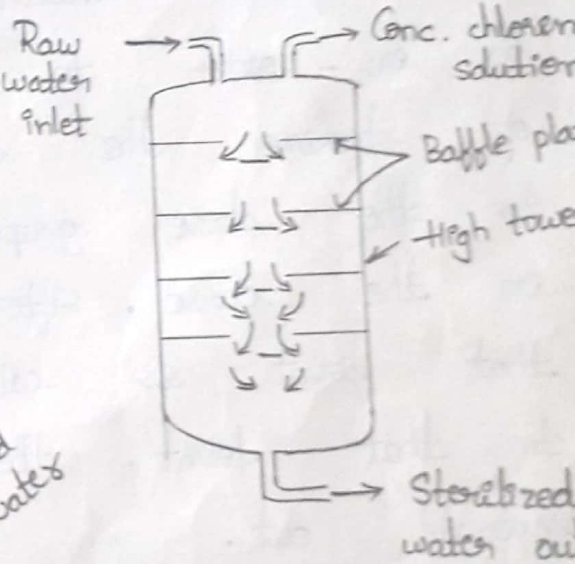
$$Cl_2 + H_2O \rightarrow HCl + HOCl \text{ (hypochlorous acid)}$$

This disinfection action of bleaching power is due to available chlorine released from the bleaching powder on reaction with water. chlorine reacts with water to form hypo chlorous acid and hydro chloric acid. HOCl reacts with pathogenic bacteria paralyses the enzyme present in bacteria and kills the bacteria. This method is suitable for towns that required bleaching powder not more than 10 kg per day

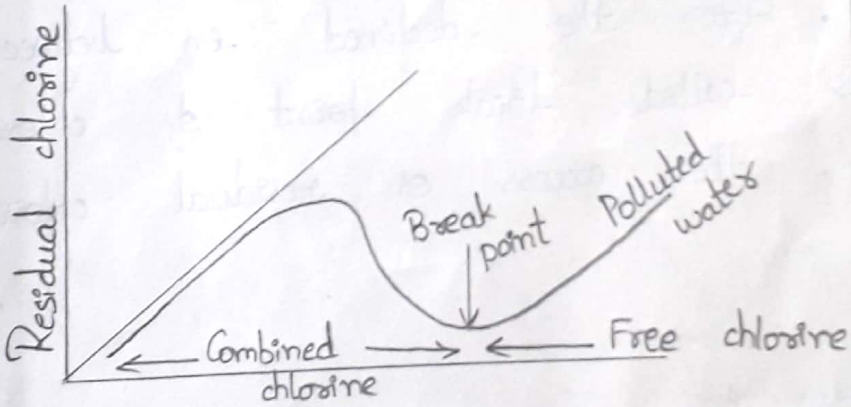
Chlorination:-

It is mainly used for killing the disease causing bacteria. This method is suitable for cosmopolitan waters. In this process the chlorine is mixed with water and it is passed through a height tower having a number of baffle plates, then the water thoroughly mixed. and the process of killing of pathogenic bacteria will takes place as follows.

$$Cl_2 + H_2O \longrightarrow \underset{\text{Hypo chlorous acid}}{HOCl} + HCl$$



Break point of chlorination:-



$$NH_3 + Cl_2 \longrightarrow NH_2Cl + HCl$$

$$NH_2Cl + Cl_2 \longrightarrow NHCl_2 + HCl$$

$$NHCl_2 + Cl_2 \longrightarrow NCl_3 + HCl$$

$$2NCl_3 \longrightarrow N_2 + 3Cl_2$$

It is a specialized process applied for the treatment of highly polluted water.

Different pollutants like ammonia, organic compounds weeds causes color changes and smell to water.

To resolve this problem we are going to add calculated amount of chlorine.

If the chlorine ratio is got excess then it leads to pollution of the water. So we have to add the required amount.

So in - order to calculate the required amount of chlorine the above graph is shown.

In the above graph where the sudden raise in the curve, After the declined in between that point is called break point of chlorination In that point the excess or residual chlorine seperate out.

Advantages :-

It removes colour in smell and water.

It destroys all desease producing bacteria.

It prevents the growth of weeds.