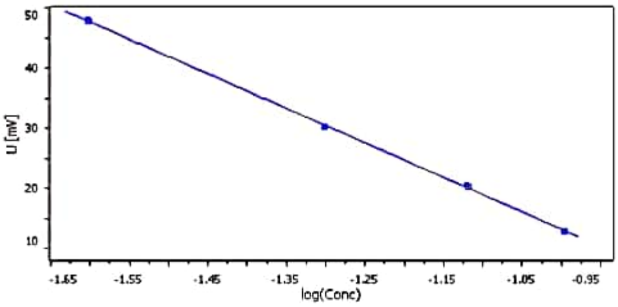
- After completion of the experiment rinse the electrodes with deionised water and keep the reference electrode in the appropriate solution.
- The F-ISE should be stored dry and loosely capped.

**Calculations:**

- Calculate the molarity of NaF accurately.
- Plot a graph of the concentration of NaF Vs potential. Find the best line passing through four standard solution points. Calculate the slope of the calibration curve slope = dE/dlog[NaF]
- By using calibration curve determine the concentration of NaF in your prepared unknown solution. Report this as percent fluoride (% w/v) in the prepared unknown.




## BOILER TROUBLES

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. The steam so generated is used in industries and generation of power. In modern pressure boilers and laboratories, the water required is used pure than the distilled water.

A boiler feed water should correspond with the following composition:

- Its hardness should be below 0.2ppm.
- Its caustic alkalinity (due to $OH^-$) should lie between 0.15ppm to 0.45ppm.
- It's should be free from dissolved gases like $O_2$, $CO_2$, in order to prevent boiler corrosion.

**Excess of impurities in the boiler feed water generally cause the following problems:**

1. Sludge's and Scale formation 2. Caustic embrittlement

Boilers are employed for the steam generation in power plants, where water as continuously heated to produce steam. As more and more water is removed from water in the form of steam, the boiler water gets concentrated with dissolved salts progressively reaches the saturation point. At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate. The precipitation takes place in two ways.

## SLUDGES

Sludge is a soft, loosy and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.

Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$.

**Reasons for formation of sludges:**

The dissolved salts whose solubility is more in hot water and less in cold water produce sludges.

**Disadvantages of sludges:**

1. Sludges are bad conductors of heat and results in the wastage of heat and fuel.
2. Excessive sludge formation leads to the settling of sludge in slow circulation areas such as pipe connections, plug openings, gauge–glass connections leading to the choking of the pipes.

**Prevention of sludge formation:**

a. By using soft water which is free from dissolved salts like $MgCO_3$, $MgCl_2$, $CaCl_2$ and $MgSO_4$ can be prevent sludge formation.

b. By blow down operation carried out frequently can prevent sludge formation.


Sludges and scales in boiler

## SCALES

Scales are hard, adhering precipitates formed on the inner walls of the boilers. Scales are stick very firmly on to the inner walls of the boiler. It is removed with chisel and hammer. Scales are formed by decomposition of calcium bicarbonate in low pressure boilers.

**Reasons for formation of scales:**

a. **Decomposition of calcium bicarbonate:** The calcium bicarbonate at high temperature decomposes to calcium carbonate which is insoluble salt, forms scale in low pressure boilers.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

b. **Hydrolysis of Magnesium salts:** Magnesium salts gets hydrolyzed at high temperature forming $Mg(OH)_2$ precipitation which forms salt type scale.

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

c. **Decomposition of calcium sulphate:** The solubility of $CaSO_4$ in water decreases with the increase in temperature and forms precipitation on the surface of the boiler further which forms hard scale. This type of scales is formed in high-pressure boilers.

d. **Presence of silica:** $Sio_2$ present even in small quantities, deposits as Calcium silicates ($CaSiO_3$) or Magnesium silicates ($MgSiO_3$). The deposits form hard scale and are very difficult to remove.

**Disadvantages of Scales:**

1. **Wastage of heat and fuels**: Scales poor thermal conductivity so that rate of heat transformation is reduced.
2. **Lowering of boiler safety** is due to overheating of the boiler material becomes softer and weaker, which causes distortion of boiler.

3. **Decrease in efficiency** of the boiler due to scales deposited in the values and condensers of the boiler cause choking.

4. **Danger of explosion** which happens the formation of the scales, the boiler plate faces higher temperature outside and lesser temperature inside due to uneven expansion. The water comes suddenly contact with overheated portion and larger amount steam is formed immediately, this results in development of sudden high pressure which may cause explosion of the boiler.

**Prevention of scales:**

a. If the scale formation is soft it can be removed by a scrapper, wire brush.
b. By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing with wire brush.
c. If scale is very hard that is formed by $CaCO_3$ can be removed by washing with 5-10% HCl and $CaSO_4$ can be removed with EDTA solution.

## CAUSTIC EMBRITTLEMENT

The formation of brittle and in crystalline cracks in the boiler shell is called caustic embrittlement.
The main reason for this is the presence of alkali-metal carbonates and bicarbonates in feed water. In lime-soda process, it is likely that, some residual $Na_2CO_3$ is still present in the softened water. This $Na_2CO_3$ decomposes to give NaOH and $CO_2$, due to which the boiler water becomes "Caustic Soda".

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

The $H_2O$ evaporates, the concentration of NaOH increase progressively creating a concentration cell as given below thus dissolving the iron of the boiler as sodium ferrate ($Na_2FeO_2$).

**(-)Anode: 'Fe' at bents | Conc.NaOH ‖ Dil.NaOH | 'Fe' at plane Surface: Cathode (+)**

This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail. The iron at plane surfaces surrounded by dilute NaOH becomes cathodic while the iron at bends and joints surrounded by highly concentrated NaOH becomes anodic which consequently decayed or corroded.

**Caustic embrittlement can be prevented:**

a. By maintaining the pH value of water and neutralization of alkali.
b. By using Sodium Phosphate as softening reagents, in the external treatment of boilers.
c. Caustic embrittlement can also be prevented by adding Tannin or Lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

## INTERNAL TREATMENT OF WATER

Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called **internal treatment** of the boiler feed water. Internal treatment can be done following types.

**1. Calgon conditioning:** Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

Calgon = Sodium hexa meta phosphate = $Na_2[Na_4(PO_3)_6]$

$$Na_2[Na_4(PO_3)_6] \rightarrow 2Na^+ + [Na_4P_6O_{18}]^{-2}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{-2} \rightarrow [Ca_2P_6O_{18}]^{-2} + 2Na_2SO_4$$

**2. Phosphate conditioning:** The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.

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

$$3MgSO_4 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3Na_2SO_4$$

Genarally three types of Phosphates are employed.

i. Tri sodium Phosphate ($Na_3PO_4$): is too alkaline used for treat to too acidic water.

ii. Di sodium Phosphate ($Na_2HPO_4$): is weakly alkaline used for treat to weakly acidic water.

iii. Sodium dihydrogen Phosphate ($NaH_2PO_4$): is too acidic used for treat to too alkaline water.

**3. Colloidal conditioning:** The addition of organic substances such as Kerosene, tannin, Gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

## SOFTENING OF WATER BY ION EXCHANGE PROCESS

Ion exchange process is also known as demineralization process. Ion- Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the "functional Groups" attached to the chains are responsible for the ion-exchanging properties. Resins with acidic functional group are capable of exchanging $H^+$ ions with other cations. Resins with basic functional groups are capable of exchanging $OH^-$ ions with other anions.

Resins are classified as:

i. Cation Exchange Resins ii. Anion Exchange Resins.

**i. Cation Exchange Resins:** Cation exchange resins are styrene divinyl benzene co-polymers, which on sulphonation (or) carboxylation, which contains –COOH, $-SO_3H$ functional groups which responsible for exchanging their hydrogen ions with cations in water.

$$2RH + Ca(HCO)_2 \rightarrow R_2Ca + H_2CO_3$$

$$2RH + Mg(HCO)_2 \rightarrow R_2Mg + H_2CO_3$$

$$2RH + CaCl_2 \rightarrow R_2Ca + 2HCl$$

$$2RH + MgCl_2 \rightarrow R_2Mg + 2HCl$$

$$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$$

$2RH + CaSO_4 \rightarrow R_2Ca + H_2SO_4$ (RH = Cation exchange resin)

**ii. Anion Exchange Resins:** Anion exchange resins are Phenol formaldehyde (or) amine formaldehyde copolymers, which contains amino or basic functional groups which responsible for exchanging their $OH^-$ ions with anions in water.

$$ROH + HCl \rightarrow RCl + H_2O$$

$$2ROH + H_2SO_4 \rightarrow R_2SO_4 + 2H_2O$$

$$ROH + H_2CO_3 \rightarrow RHCO_3 + H_2O (ROH = \text{anion exchange resin})$$

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove $Ca^{+2}$ and $Mg^{+2}$ ions and exchange equivalent amount of $H^+$ ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of $OH^-$ ions.

Thus by passing hard water through cation hardness is observed by the following reactions. $H^+$ and $OH^-$ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

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

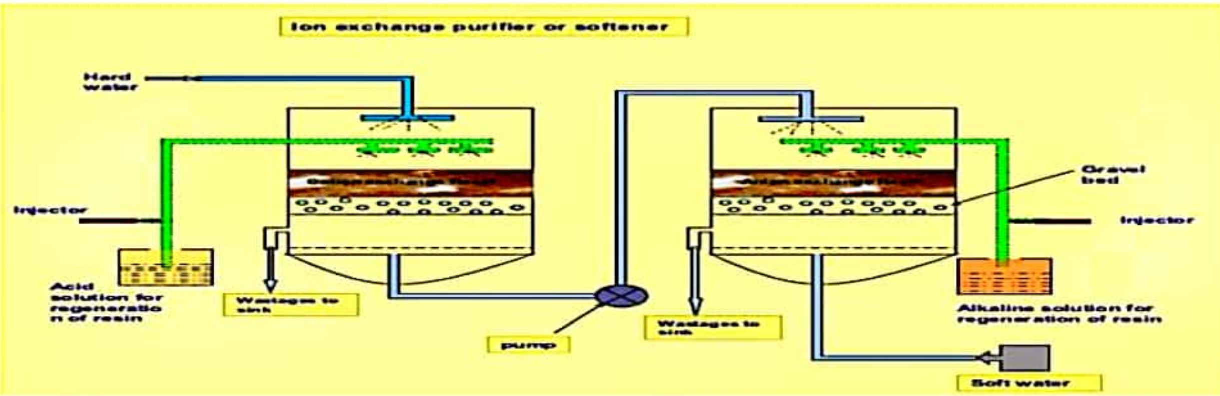
The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

**Regeneration:** When cation exchanger losses capacity of producing $H^+$ ions and exchanger losses capacity of producing $OH^-$ ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.

$$R_2Ca + 2HCl \rightarrow 2RH + CaCl_2$$

$$R_2Mg + 2H_2SO_4 \rightarrow 2RH + MgSO_4$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.




$$R_2SO_4 + NaOH \rightarrow 2ROH + Na_2SO_4$$

$$RCl + NaOH \rightarrow ROH + NaCl$$

$$RHCO_3 + NaOH \rightarrow ROH + NaHCO_3$$

**Merits of Ion-exchange process:**

- The process can be used to soften highly acidic or alkaline water.
- It produces water of very low hardness (2ppm)
- So it is very good for treating water for use in high-pressure boilers.

**Demerits of Ion-exchange process:**

- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, the output of the process is reduced. The turbidity must be below 10ppm; else it has to be removed by coagulation and filtration.

## DESALINATION OF WATER -REVERSE OSMOSIS

The process of removing common salt (Sodium Chloride) from the water is known as **desalination.**

The water containing dissolved salts with a salty or brackish taste is called **brackish water**.
Depending upon the quantity of dissolved solids, water is graded as:

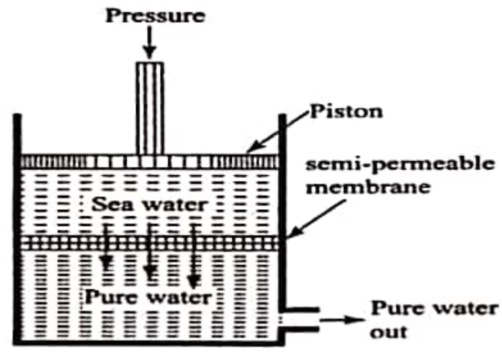
i. Fresh Water: Contains less than 1000 ppm of dissolved solids.
ii. Brackish Water: Contains more than 1000 ppm to less than 35000 ppm of dissolved solids.
iii. Sea Water: Contains more than 35000 ppm of dissolved solids.

Sea water and brackish water can be made available as drinking water through desalination process. Desalination is carried out either by reverse osmosis or electro dialysis.

**Reverse Osmosis:**
Reverse Osmosis is a process in which pressure greater than the osmotic pressure is applied on the high concentration side of the membrane, the flow of solvent move from concentrated side to dilute side across the membrane.

Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane.

In this process pure water is separated from salt water. 15-40 $kg/cm^2$ pressure is applied for separating the water from its contaminants. The membranes used are cellulose acetate, polymethyl acrylate and polyamide polymers. The process is also known as **super or hyper filtration**.



Reverse osmosis cell

**Advantages:**

- It is simple and reliable process & Capital and operating expenses are low.
- The life of the semi-permeable membrane is about two years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.

## SEWAGE WATER –STEPS INVOLVED IN THE TREATMENT

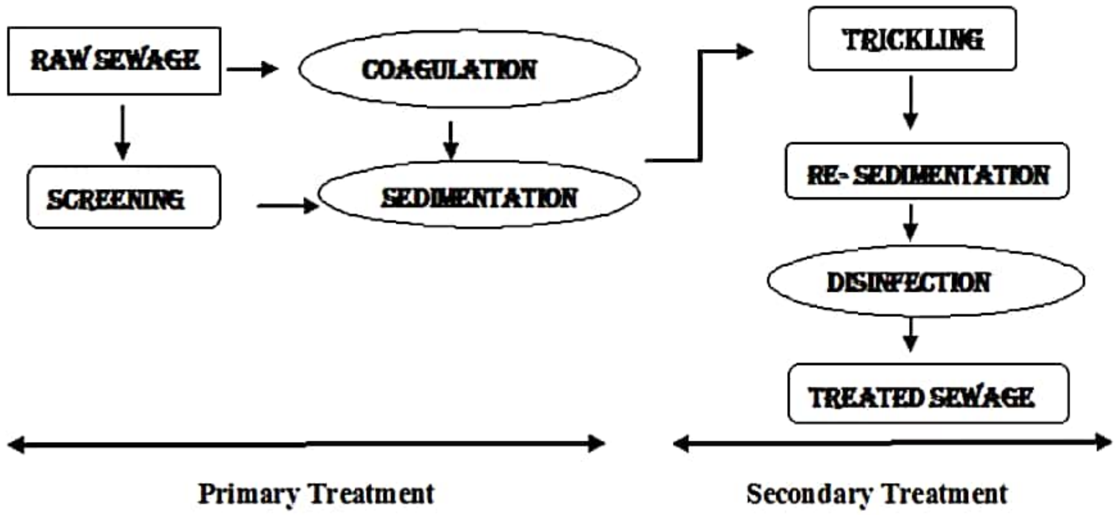
Sewage/Waste water is the water which comes from flushing the toilet, bathing, washing clothes and general cleaning.
Sewage treatment is the process of removing contaminants from waste water. It includes physical, chemical, and biological processes to remove these contaminants and produce environmentally safe treated waste water.

**Steps involved in the treatment of sewage water:** Waste water goes down the drain and into a pipe, which joins a larger drainage pipe under the road; this water can be send to the treatment center. **Five steps** involved in the treatment of sewage water.

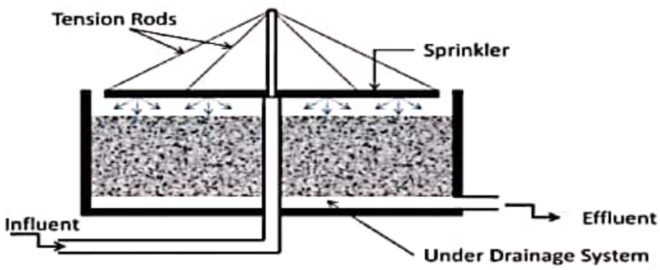
**I. Preliminary treatment (Screening):** Screening is the first stage of the treatment of the sewage water. Screening removes large objects like, plastics, bottles, sanitary items, papers and damaged equipment.

**II. Primary Treatment (or) settling process:** This involves the separation of organic solid matter like human waste. This is done by putting the waste water into large settlement tanks for the solids to sink to the bottom of the tank. The settled solids are called sludge, after removing the sludge the rest water is then send to the secondary treatment.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 6H_2SO_4$$




**III.Secondary Treatment (or) Biological treatment:**




In this stage water is put into larger rectangular tanks, which we called aeration lanes. In this process air is pumped into the water to encourage bacteria to break down biodegradable organic impurities in to the small particles which are separated through scrapping process. This is done by **Trickling filter process.**

**IV. Tertiary Treatment:** After the secondary treatment the treated water send through settlement tank to separate the remaining sludge. The water at this stage is almost free from harmful substances and chemicals. The water is allowed to flow over a wall where it is filtered through a bed of sand to remove additional particles. The filtered water is then released into the river.

**V. Disposal of Sludge:** This is the last stage in the sewage treatment. Sludge formed from different steps can be disposed by dumping into low-lying areas, burning of sludge and using it as low grade fertilizers.

## Important Questions

1. How temporary hardness differs from permanent hardness?

2. Define hardness and estimate hardness of water by using EDTA solution?

3. Explain Caustic embrittlement, Scale & Sludge.

4. Explain determination of fluoride ions ($F^-$) by ion selective electrode method.

5. Explain softening of water using Ion exchange process.

6. What is desalination? Explain reverse osmosis process.

7. Explain Steps involved in treatment of sewage water.

8. What is Potable water and what are its specifications.

9. Explain Steps involved in the treatment of potable water.

10. 0.28 grams of $CaCO_3$ were dissolved in HCl and the solution was made upto one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample consumed 33 ml of same EDTA solution EBT indicator. 100 ml of this water after boiling cooling and filtering required 10 ml of EDTA solution in titration. Calculate the permanent and temporary hardness of water sample in ppm.

11. Explain the following?
    a. Calgon conditioning and Phosphate conditioning of boiler feed water.
    b. What is defluoridation and explain Nalgonda technique.

12. What is Hardness and calculate a sample of water is found to contains following analytical data in milligrams per litre $Mg(HCO_3)_2$ = 14.6, $MgCl_2$ = 9.5, $MgSO_4$ = 6.0 and $Ca(HCO_3)_2$ = 16.2. Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.

## *Objective Questions:*

1. Hard water may be softened by passing it through: [ ]
   (a) Limestone (b) Ion-exchange resins (c) Calgon (d) Rock salt

2. Temporary hardness in water is removed by [ ]
   (a) Filtration (b) Sedimentation (c) Boiling (d) coagulation

3. The colour of EBT indicator is [ ]
   (a) Wine red (b) Blue (c) Colour less (d) Pink

**4.** EDTA method of determining hardness of water can be used to determine: [ ]

(a) All types of hardness (b) Temporary hardness only

(c) Permanent hardness only (d) Alkaline hardness only

**5.** One part of $CaCO_3$ equivalent hardness per $10^6$ parts of water is also called as [ ]

(a) Degree Clarke (b) Degree french (c) ppm (d) mg/L

**6.** The hardness of water is 10ppm it can be expressed in degree clark as: [ ]

(a) 0.07°Cl (b) 0. 7°Cl (c) 7.0°Cl (d) 0.007°Cl

**7.** The process of allowing water to stand and undisturbed in big tank for settling of the suspended Particles due to force of gravity [ ]

(a) Coagulation (b) Sedimentation (c) Conditioning (d) Screening

**8.** The Soft, loose and slimy precipitate formed within the boiler is called [ ]

(a) Scale (b) sludge (c) embrittlement (d) Coagulation

**9.** The Hard and adherent precipitate formed on the inner walls of the boiler is called [ ]

(a) Scale (b) sludge (c) embrittlement (d) Coagulation

**10.** Potable water treatment does not involve [ ]

(a) Demineralization (b) sedimentation (c) filtration (d) disinfectation

**11.** Caustic embrittlement is due to the [ ]

(a) NaOH (b) $Na_2CO_3$ (c) Mg $(OH)_2$ (d) $H_2SO_4$

**12.** Caustic embrittlement can be avoided by using [ ]

(a) Sodium phosphate (b) hydrogen (c) ammonium hydroxide (d) sodium sulphate

**13.** The exhausted anion exchange resin can be regenerated by the addition of [ ]

(a) dil. HCl (b) dil. NaOH (c) dil. $H_2SO_4$ (d) dil. Mg $(OH)_2$

**14.** Brackish water mostly contains dissolved [ ]

(a) Calcium salts (b) Magnesium salts (c) Turbidity (d) Sodium Chloride

**15.** The purification of brackish water by reverse osmosis is also … called [ ]

(a) Super-Filtration (b) Supra-Filtration (c) hypo-Filtration (d) Filtration

**16.** Which of the fallowing methods separating both ionic and non ionic impurities from water [ ]

(a) electrodialasis (b) Demineralization (c) reverse osmosis (d) ion exchange process

***Fill in the blanks:***

1. Hardness of water is expressed in terms of _______ equivalents.
2. Temporary hardness of water can be removed by _______________.
3. $MgCl_2$ and $MgSO_4$ present in water produces _________________ hardness.
4. In the estimation of hardness of water by EDTA method, the wine red colour is due to __________.
5. The process of killing germs in potable water is called _______.
6. ______________ is the main advantage of usage of chlorine gas than the Chloramine as a disinfectant.
7. Chlorine, when treated with water produce _____________ acid, which act as a powerful germicide.
8. The pH of the potable water should be __________.
9. Sodium aluminate is used as _________________ during purification of water.
10. _______, __________ &___________Chemicals are required in Nalgonda de-fluoridation technique.
11. The chemical name of the calgon is __________.
12. In phosphate conditioning if boiler feed water is too alkaline _________________ is used for internal conditioning.
13. Cation and Anion exchange resins are regenerated by using ___________& ______.
14. Best method of removing hardness of water is _______________________ process.
15. ___________ is a measure of oxidizable impurities present in the sewage.

## Two Marks and Three Marks Questions

1. Write two balanced equations to describe when hard water is heated.

2. What are the constituents that cause hardness in water? Explain the terms Carbonate hardness and Non-Carbonate hardness.

3. What is the inter relation of units of hardness?

4. Write the principle involved in complexometric method for the determination of hardness of water.

5. What is the need for an alkaline buffer in the determination of hardness of water by EDTA titration?

6. Write the specifications of potable water.

7. Explain disinfection by chlorination.

8. What is Break-point of chlorination?

9. What is meant by deflouridation.

10. How is Nalgonda technique carried out?

11. Write differences between scales and sludges.

12. What is Caustic embrittlement? Explain and also write its prevention.

(or)

Explain the cause of caustic embrittlement in boilers and suggest a remedy.

13. Calgon treatment prevents scale formation in boilers. Give reasons.

14. What is Phosphate conditioning?

15. Write the principle of Ion exchange process of softening water.

16. What are advantages of Ion exchange process?

17. What is ment by Reverse osmosis? How is it applied in the desalination of water?

18. What are advantages of Reverse osmosis?

19. What is sewage water?

## Draw the neat diagrams of the following

1. **Ion – exchange process:**

**2. Reverse Osmosis:**

**Draw the flow charts of the following:**

1. **Steps involved in the treatment of the "POTABLE WATER":**

2. Steps involved in the treatment of the "**Defluoridation – NALGONDA TECHNIQUE**":

3. **Steps involved in the treatment of the "SEWAGE WATER":**