WATER TECHNOLOGY

Hard Water:

Definition: It is defined as the presence of certain soluble salts of Ca & Mg in water. Hard water when treated with soap forms a white precipitate because of formation of insoluble salts of calcium & Magnesium.

$$2\text{Na} - \text{stearate} + \text{Ca}^{2+} \rightarrow \text{Ca} - \text{stearate} + 2\text{Na}^{+}$$

Soluble Soluble insoluble ppt (soluble)

Types of hardness of water:

Hard water is classified into two types

i) Temporary Hardness

ii) Permanent Hardness

i) Temporary (or) Carbonate (or) Alkaline Hardness:

It is caused by the presence of dissolved bi-carbonates of Calcium, Magnesium and Other heavy metals. This type of hardness can be removed by simple boiling of water. The bi-carbonates present in water decompose, to form carbonates (or) hydroxides which can be removed by filtration method.

$$\text{Ca}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{CaCO}_3 \downarrow + \text{CO}_2 + \text{H}_2\text{O}$$

$$\text{Mg}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{Mg}(\text{OH})_2 + 2\text{CO}_2$$

ii) Permanent Hardness: It is due to the presence of chlorides and sulphates of Calcium and Magnesium is called permanent hardness. It can't be removed by boiling.

Total Hardness = Temporary Hardness + Permanent Hardness

Degree of hardness of water:

The extent of hardness of water is expressed in terms of degree of hardness of water. The number of parts by weight of salts (or) $CaCO_3$ equivalents present in 1 million parts by weight of water is called degree of hardness of water.

Degree of hardness of water is expressed in terms of $CaCO_3$ equivalents. This is because molecular weight of $CaCO_3$ is 100.

$CaCO_3$ equivalents $= \frac{\text{Weight of Salt}}{\text{GMW of salt}} \times 100$

$= \frac{\text{Wt of Salt}}{\text{GEW of Salt}} \times 50$

Dissolved Salt/ion	**Molar mass**	**Chemical equivalent**	**Multiplication factor for converting into $CaCO_3$ equivalents**
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	100/120
$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Ca(NO_3)_2$	164	82	100/164
$Mg(NO_3)_2$	148	74	100/148
HCO_3^-	61	61	100/122
OH^-	17	17	100/34
CO_3^{2-}	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al_2(SO_4)_3$	342	57	100/114
$FeSO_4.7H_2O$	278	139	100/278
H^+	1	1	100/2
HCl	36.5	1	100/73

Units of Hardness: The degree of hardness is expressed by

i) Parts per million (ppm): It is defined as the number of parts by weight of $CaCO_3$ equivalent present in one million (10^6) parts by weight of water.

1 ppm = 1 Part of $CaCO_3$ in 10^6 parts of water.

ii) Milligrams per litre (mg/l): The number of milligrams of $CaCO_3$ equivalents present in one liter of water.

1 mg/lit = 1 ppm

iii) Clarke's degree of hardness: The number of parts of $CaCO_3$ equivalents present in 70,000 parts of water is called Clarke's degree.

iv) French degree (^{0}Fr): The no. of parts of $CaCO_3$ equivalents present in 10^5 parts of water is called French degree.

1 ppm = 1 mg/litre = 0.1^0Fr = 0.07^0 C l

Boiler Troubles:

Water which is used in boilers for steam generation is known as "Boiler Feed water". Following are the boiler troubles that arise due to the presence of dissolved salts.

1) Scale and Sludge formation
2) Boiler corrosion

1) Scale and Sludge formation**:**

Sludge is soft, loose, slimy, non-sticky precipitates formed within the boiler. These are formed by salts which have greater solubility's in hot water like $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$ etc.

Disadvantages of sludge formation:

a) Sludge is poor conductors of heat and results in wastage of heat and fuel.

b) Decrease the efficiency in boiler.

c) It causes choking of pipes

Prevention of sludge formation:

a) Using soft water

b) By frequent blow down operation

Scale: Scales are hard deposits firmly sticking to the inner surface of the boiler.

Reasons for the formation of scales:

a) Decomposition of $Ca(HCO_3)_2$:

Due to high temperature and pressure in the boilers $Ca(HCO_3)_2$ decomposes to $CaCO_3$ precipitate forms scale in low pressure boilers. In high pressure boilers $CaCO_3$ is soluble.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

Scale

i) Decomposition of $CaSO_4$:

As the temperature of the boilers increases $CaSO_4$ precipitates out to produce hard scale on the surface of boiler.

ii) Hydrolysis of magnesium salts:

Dissolved magnesium salts gets hydrolysed forming $Mg(OH)_2$ precipitate, form a soft scale.

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

Scale

iii) Presence of silica: Presence of small amount of silica may deposit as calcium and magnesium silicates [$CaSiO_3$ and $MgSiO_3$] deposit as hard scale.

Disadvantages of scale formation:

a) Scales are poor conductors of heat, excessive heating is required causing wastage of fuel.

b) To maintain constant supply of steam, over heating of boiler lowers boiler safety.

c) Scales deposited in valves cause choking of pipes.

Removal of scales:

a) With the help of scrapper, wire brush remove loose adhering scales

b) By giving thermal shocks, done by heating and sudden cooling of boiler.

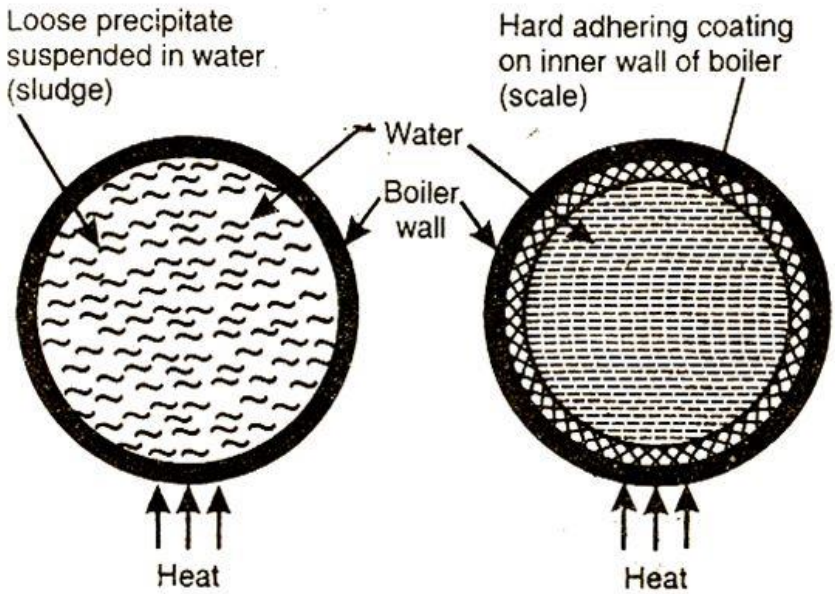
c) If the scale is hard, chemical treatment must be given Eg: $CaCO_3$ scale removed by washing with 5-10% of HCl.

d) Frequent blow down operation.

Prevention: It can be prevented by

a) Softening of water

b) Internal treatment methods



2) **Boiler Corrosion:** Boiler corrosion is decay of boiler body material either due to chemical (or) electrochemical reaction with its environment.

Disadvantages of corrosion:

a) Shortening of boiler life

b) Leakages of the joints & rivets

c) Increased cost of repairs & maintenance

Causes for corrosion:

a) Dissolved Oxygen: Water contains about 8 ppm of dissolved oxygen at room temperature. As the water is heated, dissolved O_2 is set free reacts with iron of boiler in presence of water & under high temperature to form Ferric Oxide (Rust).

$$4Fe + 6H_2O + 3O_2 \xrightarrow{\Delta} 2Fe_2O_3.3H_2O \text{ [Rust]}$$

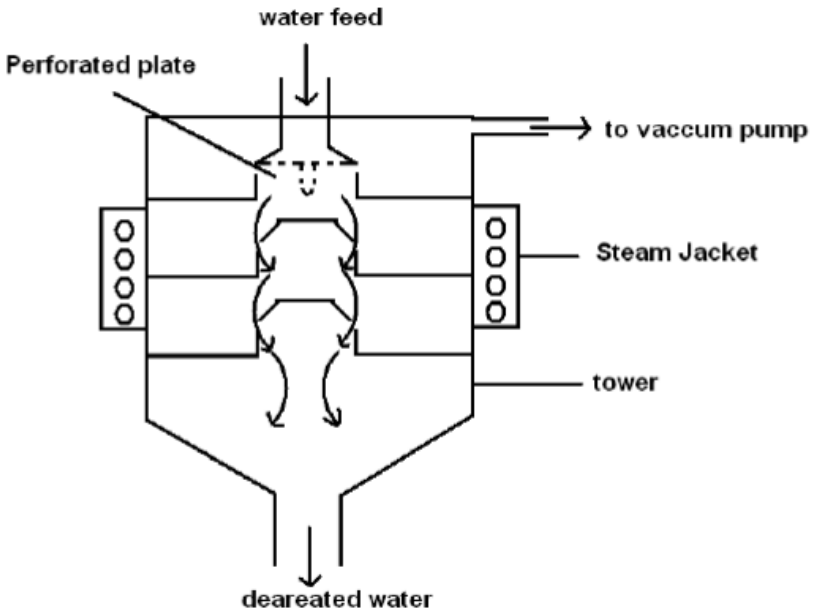
Removal of dissolved oxygen:

a) By adding hydrazine (or) sodium sulphite

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

b) By mechanical deaeration: This process consists of water spraying in a perforated plates fitted in tower, heated from sides and connected to vaccum pump. High temperature, low pressure and large exposed surface reduce the dissolved oxygen in water.



c) Dissolved Carbon dioxide:

There are two sources:

1) Dissolved CO_2 in raw water.

2) CO_2 formed by decomposition of bicarbonates.

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

Carbon dioxide in presence of water from carbonic acid has a corrosive effect on the boiler material.

$$H_2O + CO_2 \rightarrow H_2CO_3 \text{ [Carbonic acid]}$$

Removal of CO_2:

1) By adding calculated quantity of ammonia.

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

2) By mechanical deaeration process along with oxygen.

Acids from dissolved salts:

Water containing dissolved magnesium salts liberate acids on hydrolysis.

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

The liberated acid reacts with iron (of the boiler) producing HCl again causing corrosion of iron.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2\downarrow + 2HCl$$

$$2H_2O + 2Fe(OH)_2 + O_2 \rightarrow Fe_2O_3.3H_2O$$

A small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

Prevention:

1) Softening of boiler water
2) Frequent blow down operation

SOFTENING OR CONDITIONING OF WATER:

Water used for industrial purposes especially for generation of steam should be free from impurities causing hardness. Mostly in water there is formation of scale like impurities in the boiler .This scale formation may be minimized by the following treatments:

i) Internal treatment

ii) External treatment

External Treatment Softening of Water:

Before the water is taken into the boiler the treatment given for the removal of hardness causing salts is called external treatment or softening of water. Softening of boiler feed water includes following methods.

Permutit (or) Zeolite process:

Zeolites are hydrated sodium aluminium silicates represented as $Na_2O.Al_2O_3.xSiO_2.yH_2O$ where x = 2 to10, y = 2 to 6. Zeolites are of two types.

1) Natural zeolites which are natural and non-porous

Eg → Natrolite. $Na_2O.Al_2O_3.4SiO_2.2H_2O$

2) Synthentic Zeolites (permutit) are porous, gel structure synthesized by heating together solutions of sodium silicate, sodium aluminate and aluminium sulphate.

Zeolites are represented as Na_2Ze. These are capable of replacing its sodium ions with cations in water, thereby reducing hardness of water.

Process: Hard water is passed through a zeolite bed fixed in a cylinder at a specific rate. The hardness causing ions Ca^{+2}, Mg^{2+} etc are retained by the zeolites as CaZe and MgZe respectively. The reactions taking place during the softening process are

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow Ca\ Ze + 2NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow Mg\ Ze + 2NaHCO_3$$

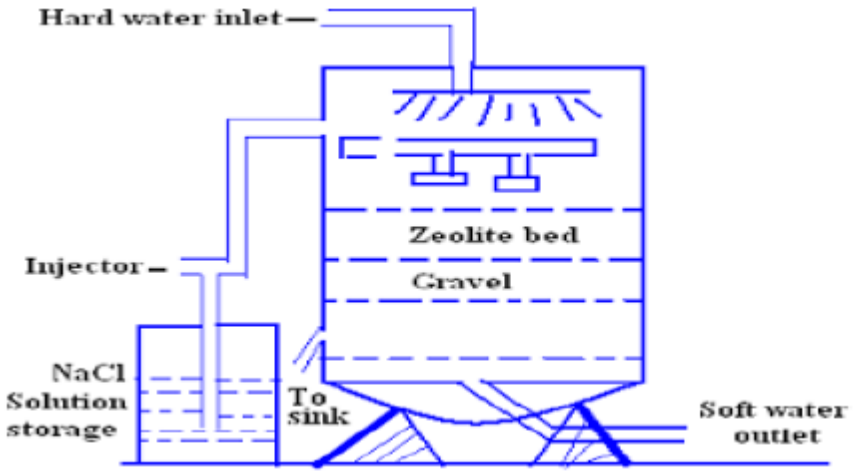
$$Na_2Ze + CaCl_2 \rightarrow Ca\ Ze + 2NaCl$$

$$Na_2Ze + CaSO_4 \rightarrow Ca\ Ze + Na_2SO_4$$

$$Na_2Ze + MgCl_2 \rightarrow Mg\ Ze + 2NaCl$$

$$Na_2Ze + MgSO_4 \rightarrow Mg\ Ze + Na_2SO_4$$

Regeneration: After sometimes zeolite bed gets exhausted [as Zeolite bed is completely converted to calcium and mg zeolites]. At this stage, purification is stopped and zeolite bed is regenerated by treating with 10% brine solution.



$$Ca\ Ze + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

$$Mg\ Ze + 2NaCl \rightarrow Na_2Ze + MgCl_2$$

Advantage:

1) Removes hardness of water up to 15ppm
2) Softening time is less
3) Equipment is compact and requires no maintenance
4) No sludge is found as the impurities are not precipitated.

Disadvantages:

1) Treated water contains more sodium salts
2) Only cations are removed.
3) $NaHCO_3$ salt decompose and liberate CO_2 which cause corrosion
4) Na_2CO_3 produced in water is decomposed at high temp to NaOH, which cause Caustic Embrittlement.

Ion-Exchange process: It includes the exchange of cations and anions of the dissolved salt with H^+ and OH^- ions respectively, using ion exchange resins. Ion exchange resins are insoluble, cross-linked long chained organic polymers.

Ion exchange resins are of two types

1) Cation exchangers are capable of exchanging their H^+ ions with cations of dissolved salts.

General formulae is RH containing the Functional groups –COOH, $-SO_3H$ [R is General structures of resin and H is exchangeable with cation].

Ex → Sulphonated Styrene-di-vinyl benzene co-polymer

2) Anion exchange resins are capable of exchange their OH^- ion with anion present in dissolved salts represented by R^1OH. [R^1 is general structure of resin & OH is exchangeable with anion] Eg→ Phenol – formaldehyde (or) Amine – formaldehyde co-polymer.

Process:

Raw water is first passed through cation exchange resin; removal of cations takes place in the following way

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

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

When water is passed through anion exchange resin, OH^- ions are replaced by anions present in hard water

$$2R^1OH + SO^{2-}_4 \rightarrow R^1_2SO_4 + 2OH^-$$

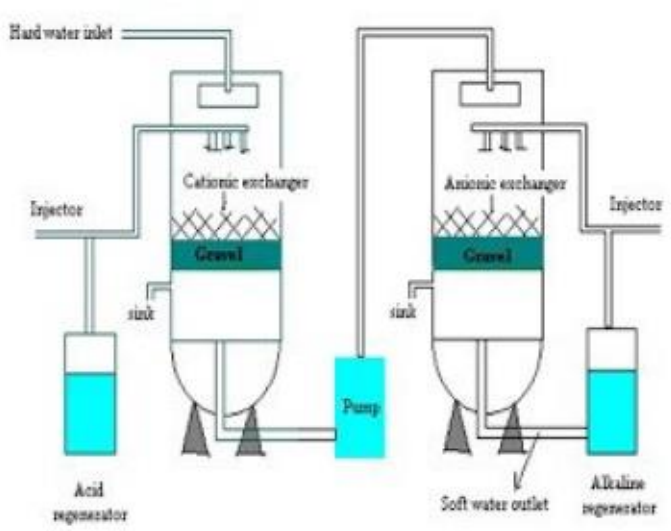
$$R^1OH + Cl^- \rightarrow R^1Cl + OH^-$$

$$R^1OH + HCO_3^- \rightarrow R^1HCO_3 + OH^-$$

H^+ and OH^- ions released will combine to form water when all the H^+ ions of cation exchange resins and OH^- ions of anion exchange resins are replaced, resins are said to be exhausted.

Regeneration:

Regeneration of exhausted cation exchange resin and anion exchange resin are carried out by passing dil.HCl and dil.NaOH solution into the bed and washing with distilled water.



Advantages:

1) A highly acidic (or) alkaline water sample can be purified by this process
2) Residual hardness of treated water is 2ppm
3) De-ionized water is most suitable for high pressure boilers.

Disadvantages:

1) Cost of purification is high, ion exchange resins are expensive.
2) Turbidity of water should be below 10ppm. Otherwise pores in resin will be blocked.

Comparison of Permutit and Ion exchange process:

S.No	Permutit	Ion exchange

1	Zeolites are used.	Cation and anion exchange resins are used.
2	Only Ca^{+2} & Mg^{+2} ions are exchanged as CaZe and MgZe.	All cations and anions were exchanged by cation and anion exchangers.
3	Only Ca^{+2} and Mg^{2+} ions are removed from water.	All cations and anions are removed from water.
4	Water contains hardness of 10-15 ppm and alkalinity.	Water contains hardness upto 2ppm

The essential qualities of drinking water/potable water:

Water free from contaminants (or) water that is safe for drinking purpose is called potable water.

i) It should be i) sparkling clear and odourless

ii) Pleasant in taste

iii) Free from suspended impurities like mud-particles

iv) Free from dissolved salts like nitrates, phosphates, sulphates etc of Calcium and Magnesium dissolved poisonous metals like Hg, As, Cd etc.

v) Free from dissolved gases like H_2S, CO_2, SO_2, etc.

vi) Free from disease causing micro-organisms like bacteria, fungi, virus, etc.

vii) Turbidity of water should not exceed 10ppm & hardness should be less than 200ppm.

viii) pH of water lies in between 7 and 8

ix) Fluorides should be less than 3ppm.

Water Quality Standards: Water quality standards are important because they help to identify the water quality .The parameters for water quality by BIS and WHO Standards are

Column1	Column2	Column3	Column4	Column5	Column6
	PARAMETER			W.H.O STANDARDS	
		DESIRABLE	MAX.PERMISSIBLE		
	COLOR	5	25		
	ODUR	UNOBJECTIOPNABLE	UNOBJECTIOPNABLE		
	TASTE	AGREEABLE	AGREEABLE		
	PH	6.5-8.5	6.5-8.5	6.5-9.2	
	TH	300	600	300	
	TASTE	200	600	500	
	TDS	300	1500	250	
	Cl-	250	1000	200	
	(SO4)2-	250	400	50	
	(NO3)-	45	45	50	
	F^-	1	1.5	0.5	
	CA+2	75	200	100	
	Mg+2	30	100	150	
	K+			200	
	Na+			200	
	(NH4)+			1.5	
	PHENOL			0	
	B			0.3	
	Fe			0.3	
		EXCEPT PH AND COLOR (HAZEN UNIT) ALL UNITS ARE IN Mg/l			

Desalination of brakish water:

Water containing high concentration of dissolved salts about 3.5% with a salty or brackish taste is called Brackish Water.

The process of removal of dissolved salts like NaCl from saline water is known as desalination of water.

The methods used for desalination of brackish water are

a) Reverse Osmosis

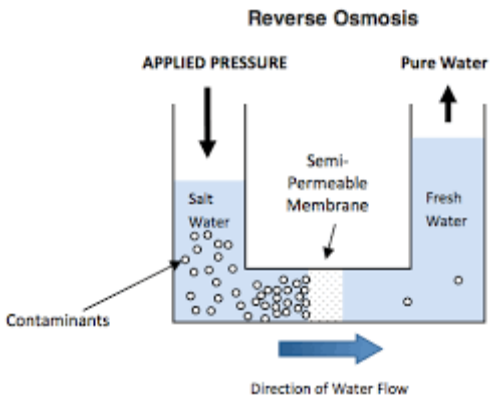
b) Electro dialysis

Reverse Osmosis: [Hyper filtration] or [super filtration]

Osmosis may be defined as a phenomenon in which pure solvent molecules pass through semi permeable membrane from solution of low concentration to a solution of high concentration.

Osmotic pressure is defined as the excess pressure which must be applied to the solution in order to prevent flow of solvent into solution through semi permeable membrane. If a pressure higher than the osmotic pressure is applied on the concentrated side of the solvent, then flow of solvent takes place from higher concentration to lower concentration.

Method: It consists of a chamber fitted with a semi-permeable membrane, above which impure water is taken & a pressure of (15kg – 40kg)/cm^2 is applied on the impure water. The pure water is forced through the semi-permeable membrane. Mostly the membranes are made of cellulose acetate, poly methacrylate and polyamide polymer.

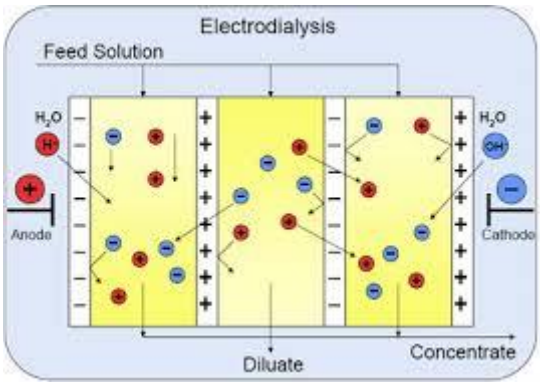


Advantages of Reverse Osmosis:

1) It removes colloidal silica.
2) Low capital cost, simplicity & high reliability of water
3) Life time of membrane is high

Electro dialysis: It is a method in which the charged ions (salts) are removed from water by passing direct current, using electrodes and thin rigid ion selective semipermeable membranes.

Principle: It is based on the principle that the ions present in saline water migrate towards their respective electrodes through ion selective membranes, under the influence of applied EMF.



Process: It consists of a chamber with two electrodes (i.e.) the cathode & anode. The chamber is divided into three compartments with the help of ion selective membranes which are permeable to either cation (or) anion.

The anode is placed near anion selective membrane while cathode is placed near cation selective membrane. Under the influence of applied EMF across the electrodes, cations move towards cathode through the membrane and anions move towards anode through the membrane. The net result is depleted ions in the central compartment while it increases in the cathodic and anodic compartments.

Desalinated water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.

Advantages: 1) The unit is compact

2) Low capital cost and operational expenses.

THEORETICAL QUESTIONS

1. Explain R.O process of purifying brakish water.

2. Explain electro dialysis with advantages and disadvantages.

3. What is scale? Write the cause, disadvantages and prevention of it.

4. What is sludge? Write the cause, disadvantages and prevention of it.

5. What are the cause of boiler trouble and prevention of it.

6. Explain zeolite with disadvantages and advantages.

7. Explain ion exchange processes with advantages and disadvantages

8. What is hardness of water ? How is it determined by E.D.T.A method?

9. What are the requirements of water for domestic use. Summarise water quality standards.

10. Differentiate between Scale and Sludge.

11. What is meant by temporary and permanent hardness of water. Give the list of salts causing hardness.

12.Differentiate Zeolite and ion-exchange process.

MULTIPLE CHOICE QUESTIONS

1.The temporary hardness in water is due to [d]

a) OH^- b) CO_3^{2-}

c) H^+ d) HCO_3^-

2. Hardness of water is due to the presence of salts of [c]

a) Potassium b) Chlorine

c) Magnesium d) Boron

3. Select the incorrect statement from the following option.[d]

a) The taste of hard water is better than soft water

b) The dissolved calcium in hard water can help to produce strong teeth

c) Hard water coats the lead piping with a layer of insoluble calcium carbonate which prevents poisonous lead dissolving in water

d) Boiler feed water should also be hard in nature

4. Hardness of water is conventionally expressed in terms of equivalent amount of [c]

a) H_2CO_3 b) $MgCO_3$

c) $CaCO_3$ d) $Na_2 CO_3$

5. The chemical equivalent of $MgSO_4$ salt is [a]

a) 60 b) 47.5

c) 82 d) 68

6.Which of the following is not a unit of hardness? [b]

a) Parts per million b) Degree centigrade

c) Degree Clarke d) Degree French

7.1 degree Clarke = 1 part of $CaCO_3$ per _____ parts of water. [d]

a) 10,000 b) 30,000

c) 50,000 d) 70,000.

8. How many grams of $MgCO_3$ dissolved per litre gives 84 ppm hardness? [a]

a) 70.56 mg/L b) 48.23 mg/L

c) 81.49mg/L d) 66.12 mg/L

9. State true or false. EDTA method for hardness determination is less accurate and inconvenient procedure.

a) True b) False c) to high d) to low

10. Water is mainly used in boilers for the generation of [c]

a) Power b) Electricity

c) Steam d) Current

11. Which of the following is not a result of excess of impurity in boiler-feed? [b]

a) Scale and sludge formation b) Decomposition

c) Corrosion, priming and foaming d) Caustic embrittlement

12. If the precipitate formed is soft, loose and slimy, these are _____ and if the precipitate is hard and adhering on the inner wall, it is called _____. [a]

a) Sludges, scale b) Scale, sludges

c) Sludges, rodent d) Scale, roden

13. Which of the following option is incorrect about the sludges? [c]

a) Sludges are soft, loose and slimy precipitate

b) They are non-adherent deposits and can be easily removed

c) Formed generally at heated portions of the boiler

d) Can be removed by blow down operation

19.Electrodialysis is based on the fact that the ions present in saline water migrate towards their respective electrodes under the influence of applied [d]

a) Current b) Resistance

c) Conductance d) EMF

1.The demineralisation of water is called

A. zeolite C. lime-soda process

[C]

B. ion-exchange process D. none

2.Blow down operation causes the removal of

[A]

A. sludges C. Nacl

B. scales D. acidity

6.The water which is fit for drinking is called _____ [c]

A. hard water C. potable water

B . brakish water D. mineral water

7.Loose and sludge precipitate formed within the boiler is called [B]

A. scale C. priming

B. sludge D. corrosion

8. The hydrolysis product of the following salt in water and form scale in boilers

A. $Na_2 co_3$ C.$NaHCo_3$

[B]

B. $Mgcl_2$ D.K_2Co_3

9. Distilled water can be obtained by

A. boiling C. lime-soda process

[ ]

B.zeolite process D. ion-exchange process

11. The exhausted anion exchange resin can be regenerated by treating it with

A. dil NaoH C. distilled water

[A]

B. dil HCl D. dil Nacl

14.Mechanical deaeration of water can decrease

A. boiler corrosion C. caustic embrittlement [A]

B.foaming D. sludges

15.Hydrazine is used to remove

A. oxygen from boiler water C. scales from boiler

B.nitrogen from hard water D. co_2 from water [ ]

16. A sample of water contains 11.1 mg/l of each .its hardness is $caco_3$ equivalents is

A. 111 Mg/L C. 10 Mg/L [C]

B. 100 Mg/L D. 1 Mg/L

17.The hardness of water is 10 ppm. it can be expressed in degree clark as

A. 0.07^0cl C. 7.0^0cl [B]

B. 0.7^0cl D. 0.0007^0cl

19.The process of removing common salt from water is called

A. hardening C. scaling [ ]

B. filiration D. softening

20.The maximum number of binding sites in EDTA

A. 6 C. 2 [ ]

B. 4 D. 8

21.In electrodialysis,the species transported through membrane are _____

A. atoms C. ions [C]

B. molecules D. complexes

22.Permanent hardness is due to

A. carbonate of Ca C. Chloride and sulphates of Ca and Mg [C]

B.Bicarbonate of Mg D. none

23.Scales in boilers are formed due to

A . deposition of $CaCo_3$ C. hydrolysis of magnesium salts [d]

B. deposition of $CaSo_4$ D. All the above

24. The maximum premissible limit of fluoride in drinking water

A. 1.5 ppm B. 5 ppm C. 3 ppm D. 8 ppm [A]

26.Residual hardness in ion-exchange process is

A.10-15ppm B.30-60ppm C.0-2ppm D.15-30ppm [ ]

27.Alkalinity in water is due to

A. OH^- B.CO_3^{-2} C. HCO_3^- D. All the above [D]

28. The maximum permissible limit of fluoride in drinking water is

A. 1.5ppm B.5ppm C.3ppm D.8ppm [B]

32.The ion-exchange resins used for softening of water are (a

a) cross-linked polymers with microporous structure

b Branched polymers with porous structure

c Cross-linked polymers with non-porous structure

d) Branched polymers with non-porous structure

33. The method of disinfection by bleaching powder is also called hypo-chlorination method because the disinfection is due to [a]

a hypo chlorous acid b) hypochloric acid c) hypochloride d) hypochloramine

Answers:

1. d 2. c 3.d 4. c 5. a 6. b 7. d 8. a 9. a 10. c

11. b 12. a 13. c 14. b 15. d 16. c 17. d 18. a 19. d