GOKARAJU RANGARAJU INSTITUTE OF ENGINEERING AND TECHNOLOGY

(AUTONOMOUS AND AFFILIATED TO J.N. T. UNIVERSITY , HYDERABAD)

UNIT-II WATER

Q. Explain why hard water does not lather with soap?Or What is the cause of hardness of water?

Or Write short notes on hardness of water Or What is hardness of water due to? (JNTU)

HARDNESS:-

Hardness of water is a characteristic property by which water "*prevents lathering of soap*".

Causes:

- The hardness of water is due to presence of certain salts (mainly bicarbonates, sulphates and Chlorides) of Ca, Mg and few other heavy metal salts dissolved in water.
- A sample of hard water when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) do not produce lather with soap, but on the other hand

  forms a white scum or precipitate.

- The precipitate is formed due to insoluble soaps of Ca and Mg.

Reactions:-

$2\,C_{17}H_{35}COONa + CaCl_2 \rightarrow C_{17}H_{35}COOCa\downarrow + 2NaCl$

Sodium Stearate hardness Calcium Stearate

(Sodium soap) (Insoluble)

$2\,C_{17}H_{35}COONa + MgSO_4 \rightarrow C_{17}H_{35}COOMg\downarrow + Na_2SO_4$

Magnesium Stearate

(Insoluble)

Thus the water which does not produce lather with soap solution readily is called **HARD WATER** and water which lathers easily on shaking with soap solution is called **SOFT WATER**.

Q. **Distinguish between temporary and permanent hardness of water? Or What is meant by carbonate and non-carbonate hardness of water? (JNTU)**

TYPES OF HARDNESS:

1. **TEMPORARY** or **CARBONATE HARDNESS**:-
   - It is caused by the presence of dissolved bicarbonates of Ca, Mg and other heavy metals and carbonate of Iron.
   - Temporary hardness is mostly destroyed by mere boiling of water i.e., when bicarbonates are decomposed, they yield insoluble carbonates or hydroxides, which are deposited as *'crust'* at the bottom of the vessel.

Reactions:-

$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} \underset{\text{(Insoluble)}}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Heat}} \underset{\text{(Insoluble)}}{Mg(OH)_2\downarrow} + 2CO_2\uparrow$$

2. **PERMAMENT** or **NONCARBONATE HARDNESS:-**
   - It is due to presence of chlorides and sulphates of Ca, Mg, Fe and other heavy metals.
   - It is not destroyed upon boiling.
   - It can be eliminated by different techniques like, Lime Soda process, Ion exchange process, Zeolite process,etc.

Total Hardness= Temporary Hardness + Permanent Hardness.

Q. How do you express the hardness? What are the units to express the hardness?Or How is the hardness of water expressed? (JNTU)

EQUIVALENTS OF $CaCO_3$:-

- The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of $CaCO_3$.
- The choice of $CaCO_3$ in particular is due to its molecular weight 100 (equivalent weight=50) and it is the most insoluble salt that can be precipitated in water treatment.
- Hardness of the hardness causing salt in terms of $CaCO_3$ (Or)

The equivalents of $CaCO_3$ =Mass of hardness X chemical <u>or</u> molecular wt

producing substance equivalent of $CaCO_3$ of $CaCO_3$

chemical equivalent of hardness

Producing substance

= Mass of hardness X 50 or 100

producing substance

chemical equivalent of hardness

Producing substance

CALCULATION OF EQUIVALENTS OF $CaCO_3$:

Salt/ion	Molar mass	Chemical Equivalent Or Equivalent Weight	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	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:-

1.Parts Per Million (ppm):- is the parts of $CaCO_3$ equivalent hardness per 10^6 parts of water i.e., 1ppm= 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

2.Milligrams Per Litre (mg/L):- number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.

1mg/L=1mg of $CaCO_3$ equivalent hardness of 1L of water= 1kg=1000g=10^6mg.

$\therefore$ 1mg/L=1mg of $CaCO_3$ eq per 10^6 mg of water=1ppm.

3.Clarke's degree(^{0}Cl):- the no. of grains (1/7000lb) of $CaCO_3$ equivalent hardness per gallon (10lb) of water or it is parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

$\therefore$ 1 ^{0}Cl= 1 grain of $CaCO_3$ eq hardness per gallon of water

= 1 part of $CaCO_3$ hardness eq per 10^5 parts of water.

4.Degree French (^{o}Fr):- parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

$\therefore 1^0$ Fr= 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.

5. Milliequivalent per litre(meq/L):- is the number of milliequivalents of hardness present per litre.

1meq/L= 1meq of $CaCO_3$ per litre of water

= 10^{-3}x 50g of $CaCO_3$ eq per litre

= 50mg of $CaCO_3$ eq per litre.

= 50mg/L of $CaCO_3$ eq = 50ppm.

Relationship between various units of hardness:

1ppm=1mg/L=0.1^o Fr=0.07^{o}Cl=0.02meq/L

1mg/L=1ppm=0.1^{o}Fr=0.07^{o}Cl=0.02meq/L

1^{o}Cl=1.433^{o}Fr=14.3ppm=14.3mg/L=0.0286meq/L

1^{o}Fr=10ppm=10mg/L=0.7^{o}Cl=0.2meq/L

1meq/L=50mg/L=50ppm=5^{o}Fr=0.35^{o}Cl

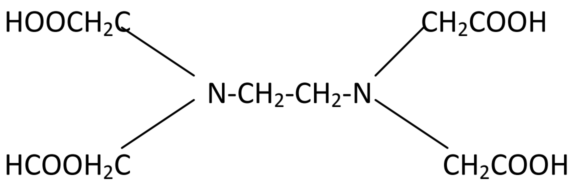
Q. How do you estimate the total hardness of water?(or) Explain any one method for the estimation

of hardness of water. (or) What is the principle of EDTA method? Explain the estimation of

hardness of water by complexometric method. (JNTU)

ESTIMATION OF TEMPORARY AND PERMANENT HARDNESS:-

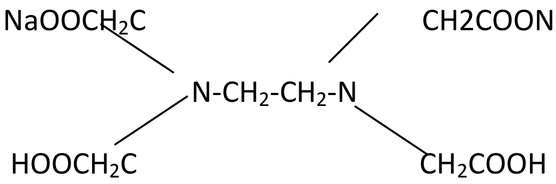
a) ***EDTA(Ethylene Di amine Tetra Acetic acid) Method:***-



Principle:

This is a complexometric method. It is in the form of its sodium salt which yields the anion and this forms complex with Ca^{+2} and Mg^{+2} ions.

(Molecular Wt- 372.24, Equivalent Wt- 186.14 i.e., M=2N)



In order to determine the equivalence point (i.e., just completion of metal-EDTA complex formation) indicator **Eriochrome Black-T** or **EBT** (an alcoholic solution of blue dye) is employed which form unstable *wine red* complex with Ca^{+2} and Mg^{+2} ions. The indicator is effective at about pH 10.

When EBT is added to hard water, buffered to a pH of about 10 (employing NH_4OH-NH_4Cl buffer), a wine red unstable complex is formed. Thus,

$$M^{2+} + EBT \xrightarrow{pH = 10} [M\text{-}EBT] \text{ complex}$$

(M^{+2}= Ca^{+2} or Mg^{+2}) (unstable wine red)

of hard water

During the course of titration against EDTA solution, EDTA combines with M^{+2} (or Ca^{+2} or Mg^{+2}) ions from stable complex M-EDTA and releasing free EBT, which instantaneously combines with M^{+2} ions still present in the solution, thereby wine red colour is retained. Thus, titration

$$[M\text{-}EBT] \text{ complex} + EDTA \longrightarrow [M\text{-}EDTA] \text{ complex} + EBT$$

wine red (stable complex) (blue)

M^{+2} + EBT $\longrightarrow$ [M-EBT]

(Ca^{+2} (blue) wine red complex

or Mg^{+2}

still present)

When nearly all M^{+2} (Ca^{+2} or Mg^{+2}) ions have formed [M-EDTA] complex, then next drop of EDTA added drop wise displace the EBT indicator from [M-EBT] complex and <u>wine red</u> colour changes to <u>blue</u> colour (due to EBT).

Thus at equivalence point,

[M-EBT] complex + EDTA $\longrightarrow$ [M-EDTA] complex + EBT

(blue)

Thus, change of **wine red** to **blue** colour marks the **end point** of titration.

STEPS INVOLVED:

1. *Preparation of Standard Hard Water*: Dissolve 1gm of pure dry $CaCO_3$ in minimum quantity of dil. HCl and then evaporate the solution to dryness on water bath. Dissolve the residue n distilled water to make 1L solution. Each 1ml of this solution contains 1mg of $CaCO_3$ hardness.

2. *Standardization of EDTA solution*: Rinse and fill the burette with EDTA solution. Pipette out 50ml of standard hard water in a conical flask. Add 10-15ml of buffer solution and 4 drops of indicator. Titrate with EDTA solution till wine red colour changes to clear blue. Let the volume used be V_1ml.

3. *Titration of Unknown Hard Water:* Titrate 50ml of water sample just in step5. Let the volume used be V_2ml.

4. *Titration of Permanent Hardness*: Take 250ml of water sample in a large beaker. Boil till the volume is reduced to about 50ml (all the bicarbonates are decomposed into insoluble $CaCO_3$

+$Mg(OH)_2$) filter, wash the precipitate with distilled water collecting filtrate and washings in a 250ml measuring flask. Finally make up the volume to 250ml with distilled water. Then titrate 50ml of boiled water sample just as in step 5. Let the volume used be V_3ml.

Calculations:

50ml of standard hard water = V_1ml of EDTA.

∴ 50x1mg of $CaCO_3$ = V_1ml of EDTA

∴ 1ml of EDTA = $50/V_1$ mg of $CaCO_3$ eq

50ml of given hard water = V_2ml of EDTA.

$$= \frac{V_2 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq}$$

$$\therefore 1L\ (1000ml) \text{ of given hard water } = \frac{V_2 \times 1000}{V_1} \text{ mg of } CaCO_3 \text{ eq}$$

Total Hardness of water = $1000\ V_2/V_1$ mg/l

= $1000\ V_2/V_1$ ppm.

Now 50ml of boiled water = V_3 ml of EDTA.

$$= \frac{V_3 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq}$$

∴1L(1000ml) of boiled water = $1000V_3/V_1$ mg of $CaCO_3$ eq

∴ Permanent hardness = $1000V_3/V_1$ ppm.

Temporary Hardness= total hardness- permanent hardness

$$= 1000 \frac{V_2}{V_1} - \frac{V_3}{V_1} \text{ ppm}$$

$$= \underline{1000(V_2-V_3)} \text{ ppm}$$

V_1

ADVANTAGES OF EDTA METHOD:

This method is preferable because of 1) greater accuracy, 2) convenience, 3) more rapid procedure.

Numerical Problems based on hardness of water:-

1. Calculate the temporary and permanent hardness of water sample containing $Mg(HCO_3)_2$= 7.3mg/L, $Ca(HCO_3)_2$= 16.2mg/L, $MgCl_2$= 9.5mg/L, $CaSO_4$=13.6mg/L)

Solution: conversion into $CaCO_3$ equivalents:

Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 7.3mg/L	100/146	7.3X100/146= 5mg/L
$Ca(HCO_3)_2$= 16.2mg/L	100/162	16.2X100/162=10mg/L
$MgCl_2$= 9.5mg/L	100/95	9.5X100/95= 10mg/L
$CaSO_4$=13.6mg/L	100/136	13.6X100/136= 10mg/L

$\therefore$ Temporary hardness of water due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ =

=5+10=15mg/Lor 15ppm.

Permanent hardness due to $MgCl_2$ and $CaSO_4$ = 10+10=20mg/Lor 20ppm.

2. Calculate the temporary and total hardness of a water sample containing $Mg(HCO_3)_2$= 73mg/L, $Ca(HCO_3)_2$= 162mg/L, $MgCl_2$= 95mg/L, $CaSO_4$=136mg/L.

Solution: calculation of $CaCO_3$ equivalents:

Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 73mg/L	100/146	73X100/146= 50mg/L
$Ca(HCO_3)_2$= 162mg/L	100/162	162X100/162=100mg/L
$MgCl_2$= 95mg/L	100/95	95X100/95= 100mg/L

$CaSO_4$=136mg/L 100/136 136X100/136= 100mg/L

∴ Temporary hardness of water due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ =

=100 + 50=150mg/Lor ppm.

Total hardness of water= 50+100+100+100=350 mg/L or ppm.

3.50ml of a sample water consumed 15ml of 0.01 EDTA before boiling and 5ml of the same EDTA after boiling. Calculate the degree of hardness, permanent hardness and temporary hardness.

Solution: 50ml of water sample = 15ml of 0.01M EDTA

$= \frac{15x100}{50}$ ml of 0.01EDTA=300ml of 0.01M EDTA

= 2x300ml of 0.01N EDTA(Molarity of EDTA=2xNormality of EDTA)

= 600ml or 0.6L of 0.01eq of $CaCO_3$.

= 0.6x0.01x50 g$CaCO_3$ eq

Hence total hardness= 0.30g or 300mg of $CaCO_3$ eq= 300mg/L or ppm.

Now 50ml of boiled water = 5ml of 0.01M EDTA

∴1000ml of boiled water= $\frac{5x1000}{50}$ ml of 0.01M EDTA

= 100mL of 0.01M EDTA

= 200mLor 0.2 L of 0.01N EDTA

= 0.2x0.01x50g of $CaCO_3$ eq

= 0.1g or 100mg of $CaCO_3$ eq

Hence permanent hardness = 100mg/L or ppm

∴Temporary hardness= 300-100=200ppm.

4.0.5g of $CaCO_3$ was dissolved inHCl and the solution made up to 500ml with distilled water. 50ml of the solution required 48ml of EDTA solution for titration. 50ml of hard water sample required 15ml of EDTA and after boiling and filtering required 10ml of EDTA solution. Calculate the hardness.

Solution: 500ml of SHW = 0.5g or 500mg $CaCO_3$ eq

∴1ml SHW= 1mg $CaCO_3$ eq

Now 48ml of EDTA solution = 50/48 mg $CaCO_3$ eq

∴1ml of EDTA solution= 50/48 mg $CaCO_3$ eq

calculation of the total hardness of water:

50ml hard water = 15ml EDTA = 15x50/48 mg of $CaCO_3$ eq

∴1000ml of hard water= $\frac{15.625\text{x}1000}{50}$ = 312.5 mg $CaCO_3$ eq

Hence total hardness= 312.5mg/L or 312.5 ppm.

5. In an experiment to determine the hardness of sample of water, 25ml of N/50 Na_2CO_3 solution was added to 100ml of water sample. After completion of precipitation of insoluble carbonate the unreacted Na_2CO_3 was titrated against N/50 H_2SO_4 solution, when 10ml of the acid was required. Calculate the hardness and comment on the nature of hardness so-determined.

Solution: 100ml of water=

25ml of N/50 Na_2CO_3 + 10ml of N/50 H_2SO_4

= (25-10) mL of N/50 Na_2CO_3 = 15/50mL of N- Na_2CO_3

∴1000ml of water= 15/50 x 10mL of N- Na_2CO_3 = 3ml of N- Na_2CO_3

= $\underline{3\text{x}50}$ of $CaCO_3$ eq = 0.150 g of $CaCO_3$ eq

1000

∴ hardness of water = 0.150 g/L or 150mg/L=150ppm.

Since sodium carbonate removes permanent hardness causing ions, so the above result represents permanent hardness.

Q.What are Scales? How are they formed? What are the disadvantages and what are the methods of prevention of scale formation? Or Explain the factors responsible for the corrosion of a boiler.

Discuss the measures for its prevention. (JNTU)

BOILER TROUBLES:-

SCALE AND SLUDGE FORMATION:

- In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively.
- When the dissolved salts concentration increases and reaches saturation point, they are thrown out of water in the form of precipitates on the inner wall of the boiler.
- If the precipitation takes place in the form of loose and slimy precipitate it is called ***sludge***.
- If the precipitated matter forms a hard adhering crust or coating on the inner walls of the boiler, it is called ***scale***.

SLUDGE: It is a soft, loose and slimy precipitate formed within the boiler.

Reasons:

It is formed at comparatively colder portions of the boiler and collects where the flow of rate

is slow or at bends.

Sludges are formed by substances which have greater solubilities in hot water than in cold water.

Eg; $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

Disadvantages:

Sludges are poor conductor of heat which tend to waste a portion of heat generated.

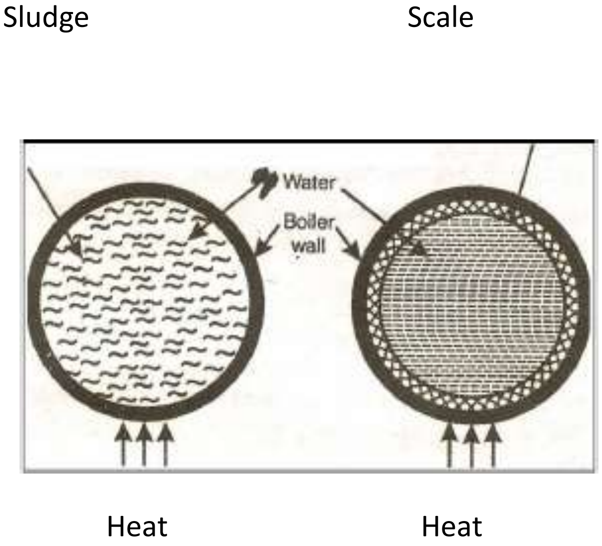
If sludges are formed along with scales, then sludge gets entrapped in the latter and both get deposited as scales.

Sludge formation disturbs the working of the boiler as it settles in the region of poor water circulation such as pipe connection; plug opening, guage-glass connection thereby causing even choking of the pipes.

Prevention:

By using well softened water

By frequent **"Blow Down" operation** i.e., drawing off a portion of the concentrated water.



SCALES: are hard deposits which stick firmly to the inner surfaces of the boiler. These are difficult to remove.

Formation of Scales:

1. Decomposition of $Ca(HCO_3)_2$:-

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

(scale)

The formation of $CaCO_3$ scale is soft and is the main cause of scale formation. In high pressure boilers, $CaCO_3$ is soluble.

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

(soluble)

2. Deposition of $CaSO_4$:-

The solubility of $CaSO_4$ in water decreases with rise in temperature i.e, $CaSO_4$ is soluble in cold water but completely insoluble in super heated water. $CaSO_4$ gets precipitated as hard scale on the heated portions of the boiler. This is the main cause of scales in high pressure boilers.

3. Hydrolysis of Magnesium Salts:-

The Mg salts dissolved undergo hydrolysis at high temperature forming $Mg(OH)_2$ ppt which forms a soft type of scale.

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

(scale)

4. Presence of Silica:-

Silica present in small quantities deposits as calcium silicate ($CaSiO_3$) or $MgSiO_3$. These deposits stick very firmly and are very difficult to remove. Important source of silica in water is the sand filter.

Disadvantages:

1. Wastage of fuel: Scales have a low thermal conductivity so rate of heat transfer from boiler to inside water is greatly decreased. Excessive or over heating is done and this causes increase in fuel consumption.

The wastage of fuel depends upon the thickness and nature of scale as:

Thickness (mm))	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

2. Lowering of boiler safety: The over heating of boiler tube makes boiler softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of steam especially in high pressure boilers.

3. Decrease in Efficiency: Scales may deposit in the valves and condensers of the boilers and choke them partially. This results in decrease in efficiency of the boiler.

4. Danger of explosion: The thick scales formed if cracked due to uneven expansion the water comes suddenly in contact with over heated iron plates. This causes in formation of a large amount of steam suddenly, so sudden high pressure is developed which cause explosion of boiler.

Removal of Scales:-

If scales are loosely adhering they can be removed with the help of scrapper or wire brush or piece of wood.

By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water) they are brittle.

If the scales are hard and adhering, then dissolving them and by adding chemicals. Ex $CaCO_3$ scales are dissolved by using 5-10% of HCl and $CaSO_4$ scales can be dissolved by adding EDTA with which they form soluble complexes.

By frequent blow-down operation if scales are loosely adhering.

Prevention of scales:

1) External Treatment: It includes efficient 'softening of water' (i.e. removing hardness producing constituents of water) which is discussed separately.
2) Internal Treatment: It includes softening of water by adding a proper chemical to the boiler water. It is discussed in softening methods.

Q. Distinguish between scales and sludges. **(JNTU)**

S.No	Sludge	Scale
1.	It is soft, loose and slimy precipitate.	It forms hard deposits.
2.	They form non-adherent deposits and can be easily removed.	They stick firmly to the inner surface of the boiler and are very difficult to remove.
3.	They are formed by substances like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$, etc.	They are formed by substances like $CaSO_4$, $Mg(OH)_2$, etc.

4.	They are formed at comparatively colder portions of the boiler.	They are formed at heated portions of the boiler.
5.	They decrease efficiency of boiler but are less dangerous.	They decrease efficiency of boiler and chances of explosion are also there.
6.	They can be removed by blow down operation.	They can't be removed by blow down operation.

Q. **Write briefly on caustic embrittlement.** **(JNTU)**

CAUSTIC EMBRITTLEMENT:-

- It is a type of boiler corrosion caused by using highly alkaline water in the boiler.
- During softening process by Lime-Soda process, free Na_2CO_3 is usually present in small proportion.
- In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2 and this makes the boiler water '***caustic***'.

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

- The NaOH containing water flows into minute hair cracks always present in inner side of boiler by capillary action.
- Here water evaporates and the dissolved caustic soda concentration increases progressively.
- This caustic soda attacks the surrounding area, thereby dissolving iron of the boiler as sodium ferroate. This causes embrittlement of boiler parts (like bends, joints, etc.,) causing even failure of the boiler.
- Caustic cracking can be explained by considering the following concentration cell:

+

—

Iron at rivets, | concentrated | Dilute | Iron
bends, joints, | NaOH solution | NaOH at plane |
etc. solution surfaces

- The iron surrounded by dil. NaOH becomes the cathodic side; while the iron in contact with con. NaOH becomes anodic part; which is consequently dissolved or corroded.

Prevention of caustic embrittlement:

Caustic embrittlement can be avoided :

i) By using Na_3PO_4 as softening reagent instead of Na_2CO_3.

ii) By adding tannin or lignin to boiler water since these blocks the hair cracks there by preventing infiltration of caustic soda solution in these

iii) By adding Na_2SO_4 to boiler water. If Na_2SO_4 is added to boiler water so that the ratio $\frac{[Na_2SO_4 \text{ concentration}]}{[NaOH \text{ concentration}]}$ is kept

as 1:1:2:1 and 3:1 in boilers working respectively at pressures up to 10, 20 and 30 atmospheres.

Disadvantages of caustic embrittlement:

The cracking or weakening of the boiler metal causes failure of the boiler.

Q. Write a short notes on priming and foaming. (JNTU)

PRIMING AND FOAMING:

PRIMING:

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along with the steam. This process of ***'wet steam'*** formation is known as **'Priming'**.

Causes:

Priming is caused by:

1.The presence of large amount of dissolved salts

2.High steam velocities

3.Sudden boiling

4.Improper boiler design

5.Sudden increase in steam production rate.

Prevention:

1.By fitting mechanical purifiers

2.Avoiding rapid change in steam rate

3.Maintaining low water levels in boilers

4.Effective softening and filtration of boiler fed water

5.Blow down of the boiler.

FOAMING:

The phenomenon of formation of *persistent foam or bubbles* on the surface of water inside the boiler which do not break easily.

Causes:

1.Pure water has very little foaming whereas the water containing dissolved impurities and suspended matter has a greater tendency to produce foam.

2.The presence of large quantity of suspended impurities and oils lowers the surface tension producing foam.

Prevention:

1. Adding antifoaming chemicals like castor oil. The amount of castor oil to be added varies with the boiler because excess of castor oil can cause foaming.

2. Besides castor oil, gallic acid and tannic acids, corn oil, cotton seed oil, sperm oil, bees wax, etc., are also used as antifoaming agents.

3. Blow down operation of the boiler can prevent foaming.

4. Removing oil form boiler water by adding compounds like sodium aluminate.

Disadvantages of Priming and Foaming:

Priming and Foaming usually occur together. They are objectionable because:-

1. The dissolved salts in boiler water are carried by the wet steam to super heater and turbine blades where they get deposited and reduce the efficiency.

2. The dissolved salts enter the parts of other machinery where steam is used thereby decreasing the life of machinery.

3. The actual height of the water column cannot be judged thereby making the maintenance of boiler pressure becomes difficult.

Q. What are external and internal treatment of water? Or Write short notes on phosphate conditioning. Or Write short notes on the following: (JNTU)

(a) Colloidal conditioning (b) Sodium aluminate condition (c) Calgon conditioning

(d) Carbonate conditioning Or Compare Phosphate conditioning with calgon conditioning.

SOFTENINIG METHODS:-

1) **INTERNAL TREATMENT**
2) **EXTERNAL TREATMENT**

Water used for industrial purposes should be sufficiently pure. It should therefore be free from hardness producing salts before use.

The process of removing hardness producing salts from water is known as ***'Softening'*** of water.

1) INTERNAL TREATMENT: (SEQUESTERATION)

- In this process, an ion is prohibited to exhibit its original character by *complexing* or converting into other more soluble salt by adding appropriate agent.
- An internal treatment is accomplished by adding a proper chemical to the boiler water either:
- i) To precipitate the scale forming impurities in the form of sludges which can be removed by blow-down operation or

- ii) To convert them into compounds which will stay in the dissolved form in water and thus do not cause harm.
- The important internal conditioning /treatment methods are:

a) Colloidal Conditioniong:

In low pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar etc., which get coated over the scale forming precipitates, thereby yielding non-sticky and loose deposits which can be removed by blow-down operation.

b)Phosphate Conditioning:

In high pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming non-adherent and easily removable, soft sludge of Ca and Mg phosphates which can be removed by blow-down operation.

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

The main phosphates employed are

1.NaH_2PO_4: sodium dihydrogen phosphate(acidic)

2.Na_2HPO_4: disodium hydrogen phosphate(weakly alkaline)

3.Na_3PO_4: trisodium phosphate(alkaline)

The choice of salt depends upon the alkalinity of boiler feed water.

c)Carbonate Conditioning:

In low pressure boilers, scale formation can be avoided by adding Sodium carbonate to boiler water, when $CaSO_4$ is converted to $CaCO_3$ in equilibrium.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

d)Calgon Conditioning:

Involves adding calgon(sodium hexa meta phosphate $(NaPO_3)_6$) to boiler water.

It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

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

(sodium meta aluminate)

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

(soluble complex ion)

e)**Treatment with sodium aluminate($NaAlO_2$):**

Sodium aluminate gets hydrolysed yielding NaOH and a gelatinous precipitate of aluminium hydroxide. Thus:

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

(sodium aluminate)

The NaOH formed precipitates some of Mg as $Mg(OH)_2$ i.e.,

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2\downarrow + 2NaCl$$

The flocculent precipitate of $Mg(OH)_2$ and $Al(OH)_3$ produced inside the boiler, entraps finely suspended and colloidal impurities including oil drops and silica.

f) **Electrical Conditioning:**

Sealed glass bulbs containing mercury connected to a battery are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges which prevents scale forming particles to stick together to form a scale.

g) **Radioactive Conditioning:**

Tablets containing radioactive salts are placed inside the boiler water at few points. The energy radiations emitted by these salts prevent scale formation.

h) **Complexometric Method:**

It involves adding 1.5% alkaline (pH=8.5) solution of EDTA to feed water.

EDTA binds the scale forming cations to form stable and soluble complex.

It also prevents the deposition of iron oxides in the boiler.

It reduces the carry over of oxides with steam.

It protects the boiler units from corrosion by wet steam (steam containing liquid water).

EXTERNAL TREATMENT

Q. Write short notes on Ion-exchange process. Or What are ion-exchange resins? How will you purify water by using them? Or What are the advantages of this method over other methods?

ION EXCHANGE/DEIONISATION/DEMINERALISATION:-

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure and the functional groups are attached to the chains are responsible for ion exchanging properties.

Resins containing acidic functional groups (-COOH, $-SO_3H$) are capable of exchanging their contact; those containing basic functional groups ($-NH_2=NH-$) as HCl are capable of exchanging their anions with other anions, which comes in their contact.

The ion exchange resins may be classified as :-

1) **Cation Exchange Resins (RH^+):-** are mainly styrene-divinyl benzene co-polymers which on sulphonation or carboxylation become capable to exchange their H_2 ions with cations in the water.
2) **Anion Exchange Resins ($R'OH^-$):-** are styrene-divinyl benzene or amine formaldehyde copolymers which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of resin matrix. These, after treatment with dil NaOH solution, become capable to exchange their OH^- anions with anions in water.

Process:-

Raw water is first passed through cation exchanger and the removal of cations take place like Ca^{+2}, Mg^{+2} etc and equivalent amount of H^+ ions are released from this column to water. Thus,

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

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

After cation exchange column the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-}, Cl^- etc present in the water and equivalent amount of OH^- ions are released from this column to water.

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

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

$2\ R'OH^- + CO_3^{2-} \rightarrow R'CO_3^{2-} + 2OH^-$

H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combinedto produce water molecule.

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

Thus, water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as **deionized or demineralized water.**

Regeneration:

The deionization of certain amount of raw water the cation and anion exchangers will be exhausted.

Regeneration of cation exchanger is carried out by passing dil. HCl or H_2SO_4 solution into the bed.

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

The column is washed with deionized water and the washing (Ca^{+2}, Mg^{+2} etc and Cl^- or SO_4^{2-}) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH.

$R_2\ SO_4^{2-} + 2\ OH^- \rightarrow 2R'OH^- + SO_4^{2-}$ (washing)

The column is washed with deionized water and washing containing Na^+ and SO_4^{2-} or Cl^- ions is passed to sink or drain.

The regenerated ion exchange resins are then used again.

Advantages:

1) Highly acidic or alkaline water samples can be purified by this process.
2) The hardness possessed by the deionised water is 2ppm.
3) The deionised water is the most suitable for high pressure boilers.

Disadvantages:

1) The ion exchanging resins are expensive hence the cost of purification is high.
2) Raw water should contain turbidity below 10ppm. Otherwise pores in the resin will be blocked and output of the process is reduced.

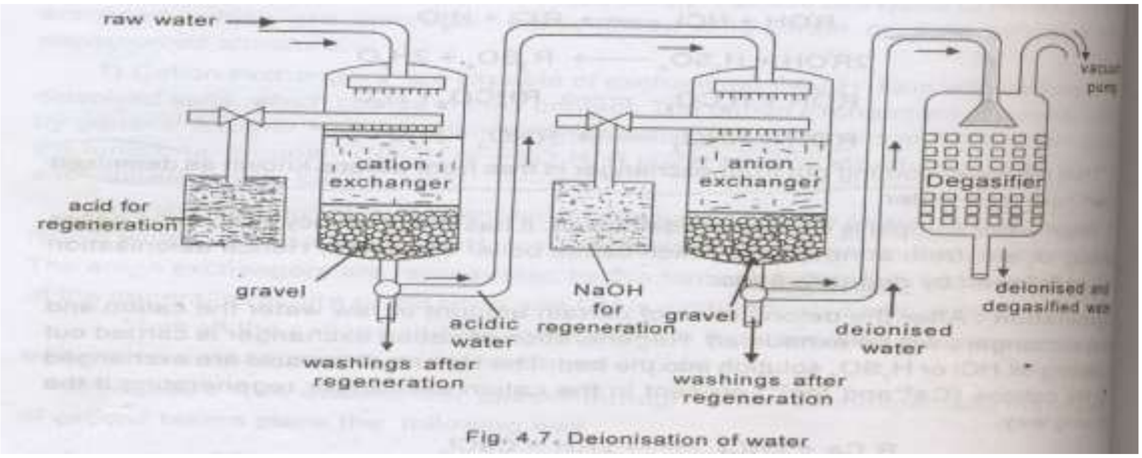


Fig. 4.7. Deionisation of water

Q. What is meant by desalination? Explain the different methods used for the desalination of brackish water. Or Explain the desalination of water by electro dialysis. (JNTU)

DESALINATION OF BRACKISH WATER:-

The process of removing common salt (sodium chloride) from the water is known as **"Desalination".**

The water containing dissolved salts with a peculiar salty or brackish taste is called **"Brackish water".**

Ex. Sea water (contains an average of about 3.5% salts) is an example of brackish water.

It is totally unfit for drinking purpose.

Commonly used methods for desalination of brackish water are:-

1) Electro dialysis
2) Reverse Osmosis

ELECTRODIALYSIS:-

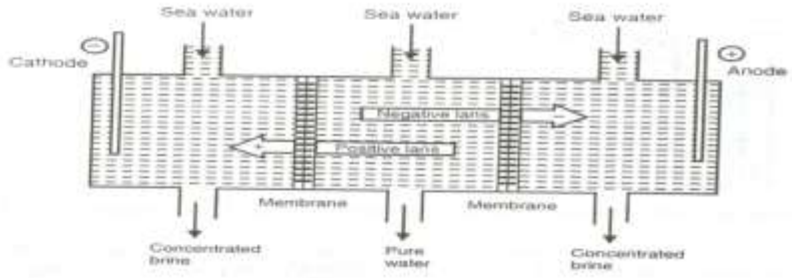
It is a method in which the ions (of the salt) are pulled out of the sea water by passing direct current using electrodes and thin rigid plastic membrane pair.

Process:

When direct current is passed through saline water, the sodium ions (Na^+) start moving towards negative pole (cathode); while the chloride ions (Cl^-) start moving towards the positive pole (anode) through the membrane.

As a result, the concentration of brine decreases in the central compartment; while it increases in two side compartments.

Desalinated brine (or pure water) is removed from the central compartment from time to time; while con. Brine (in the side compartment) is replaced by fresh brine or sea water.



For more efficient separation, usually, ion selective membranes are employed. Ion selective membrane has permeability for only one kind of ions with specific charge.

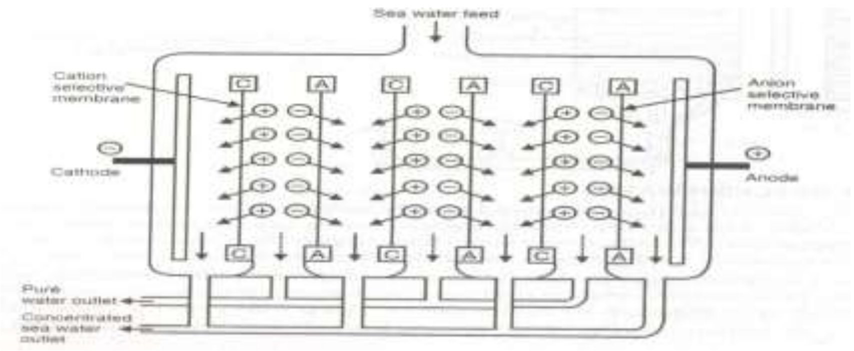
An electrodialysis cell consists of a large no. of paired sets of rigid plastic membranes.

Process:

Saline water is passed under a pressure (5-6 kg/m^2) between membrane pairs and an electric field is applied perpendicular to the direction of water flow.

Just as magnets of like charges, repel each other, the fixed positive charged ions inside the membrane repel positively charged ions (Na^+) permit negatively charged ions (Cl^-) to pass through. Similarly, the fixed negative charges inside the other type of membrane repel negatively charged ions (Cl^-) and permit positively charged ions (Na^+) to pass through.

Therefore, water in one compartment of the cell is deprived of its salts; while the salt concentration in adjacent compartments is increased. Thus we get alternate streams of pure water and con. brine.



Advantages:

It is most compact unit.

The cost of installation of the plant and its operation is economical.

If electricity is available, it is a best process.

REVERSE OSMOSIS:-

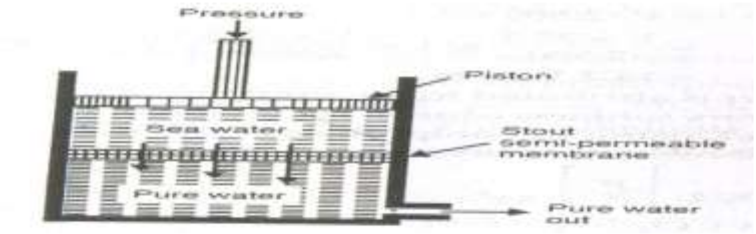
When two solutions of unequal concentrations are separated by a semipermeable membrane (which does not permit selectively the passage of dissolved solute particles i.e., molecules, ions etc) flow of solvent takes place from dilute to concentrated sides, due to Osmosis.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses i.e., solvent is forced to move from concentrated side to dilute across the membrane. This is the principle of reverse osmosis.

Thus, in reverse osmosis, pure solvent (water) is separated from its contaminates, rather than removing contaminants from water. This membrane filtration is also called **"Super/ Hyper filtration".**

Method:

In this process, pressure (15-40 kg/cm^2) is applied to sea water/impure water (to be treated) to force its pure water through the semi-permeable; leaving behind the dissolved solids (both ionic and non-ionic).



The principle of reverse osmosis as applied for treating saline/sea water is as follows: given in fig above.

The membrane consists of very thin film of cellulose acetate, affixed to either side of a perforated tube. Superior membranes recently developed are made of polymethacrylate and polyamide polymers has come into use.

Advantages:

1) Reverse osmosis process has distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.

2) It removes colloidal silica, which is not removed by demineralization.
3) The life time of membrane is quite high, about 2 years.
4) The membrane can be replaced within a few minutes thereby providing nearly uninterrupted water supply.

5) Low capital cost, simplicity, low operating cost and high reliability.
6) The reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.