Unit 2: WATER CHEMISTRY
(E.I.E., BE ¼ Eng Chemistry) October 6, 2015

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1. Hardness of water: Water which does not produce lather with soap solution readily, but forms a white precipitate, is called *hard water*.

$2C_{17}H_{35}COONa$ + $CaCl_2$ → $(C_{17}H_{35}COO)_2Ca$ ↓ + 2NaCl

Sodium stearate Hardness Calcium stearate

Soap (insoluble)

$2C_{17}H_{35}COONa$ + $MgCl_2$ → $(C_{17}H_{35}COO)_2Mg$ ↓ + 2NaCl

1.1 Temporary hardness (Carbonate hardness):

It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and carbonate of iron. Temporary hardness can be removed by boiling of water. Bicarbonates are decomposed into insoluble carbonates or hydroxides.

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

Calcium bicarbonate Calcium carbonate

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

Magnesium bicarbonate Magnesium hydroxide

1.2 Permanent hardness (Non-carbonate hardness):

It is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

2. Equivalents of calcium carbonate:

The concentration of hardness is expressed in terms of equivalent amount of $CaCO_3$, since this mode permits the multiplication and division of concentration, when required. The choice of $CaCO_3$ in particular is due to its molecular weight is 100 (equivalent weight = 50) and moreover, it is the most insoluble salt that can be precipitated in water treatment.

The equivalents of $CaCO_3$ =	*Mass of hardness producing substance*	X 50 / *Equivalent weight of hardness producing substance*

3. Units of Hardness:

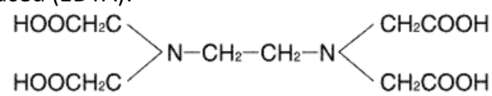
parts per million (ppm): 1 ppm = 1 part of $CaCO_3$ eq. hardness in 10^6 parts of water.

Milligrams per litre (mg/L): 1mg/L = 1 mg of $CaCO_3$ eq. hardness of 1 L of water.

Conversion Factor: 1mg/L = =1ppm = 0.1 ^{o}Fr = 0.07 ^{o}Cl

4. Determination of temporary & permanent hardness of water by EDTA method:

It is a complexometric method. Ethylene diamine tetra acetic aced (EDTA):



In order to determine the equivalence point, indicator erochrome black-T or EBT (an alcoholic solution of blue dye) is employed. However, this indicator is effective at a pH of about 10. When EBT is added to hard water buffered to a pH of about 10 by employing NH_4OH+NH_4Cl buffer, a wine-red unstable complex is formed.

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

So initially a wine-red colored complex is obtained. During the course of titration against EDTA solution, EDTA combines with M^{2+} (Ca^{2+} or Mg^{2+}**)** ions form stable complex M-EDTA and releasing free EBT, and wine-red color changes to blue color (due to EBT).

[M-EBT] complex + EDTA --------→ [M-EDTA] complex + EBT

(*Wine-red)* *(Blue)*

Thus, change of wine-red color to distinct blue marks the end-point of titration.

5. ALKALINITY

Alkalinity of water is measure of acid-neutralizing ability. It is attributed to the presence of the caustic alkalinity (OH^- and CO_3^{2-}) and temporary hardness (HCO_3^-). These can be estimated separately by titration against acid, using phenolphthalein and methyl orange as indicators. The determination is based on following reactions.

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

$[CO_3^{2-}] + [H^+] \rightarrow [HCO_3^-]$

$[HCO_3^-] + [H^+] \rightarrow H_2O + CO_2$

The titration of the water sample against a standard acid upto phenolphthalein indicator end-point marks the completion of reactions i) & ii). This amount of acid used thus corresponds to hydroxide + one half of the normal carbonate present.

On the other hand titration of the water sample against a standard acid to methyl orange indicator endpoint marks the completion of i), ii) & iii).

Hence the amount of acid used after the phenolphthalein end point corresponds to one half of normal carbonate + all the bicarbonates; while the total acid used represents the total alkalinity (due to OH^- , CO_3^{2-} and HCO_3^- ions).

Procedure: pipette out 100ml water sample in a clean conical flask. Add to it 2 to 3 drops of a phenolphthalein indicator. Run N/50 HCl from a burette, till the pink colour is disappeared. Then to the same solution, add 2 to 3 drops of methyl orange , continue the titration, till the color changes yellow to orange pink.

i) When P=0, both OH^- & CO_3^{2-} ions are absent, and alkalinity in that case due to HCO_3^- only.

ii) When P=½M, only CO_3^{2-} ion is present, since half of carbonate neutralization reaction i.e. $[CO_3^{2-}] + [H^+] \rightarrow [HCO_3^-]$ takes place with phenolphthalein indicator; while complete carbonate neutralization reaction i.e. $[HCO_3^-] + [H^+] \rightarrow H_2O + CO_2$ occurs when methyl orange indicator used. Thus, alkalinity due to CO_3^{2-} = 2P.

iii) When P=M, only OH^- is present, because neither CO_3^{2-} nor HCO_3^- is present, thus alkalinity due to OH^- = M.

iv) When P > ½M, in this case, besides CO_3^{2-} , OH^- ions are also present. Now half of CO_3^{2-} equal to M-P; so alkalinity due to complete CO_3^{2-} =2(M-P). Therefore alkalinity due to OH^- = M - 2(M-P) = 2P – M.

v) When P < ½ M, ;in this case, besides CO_3^{2-} , HCO_3^- ions are also present now alkalinity due to CO_3^{2-} = 2P. Alkalinity due to HCO_3^- = (M-2P).

Alkalinity	**OH^- ppm**	**CO_3^{-2} ppm**	**HCO_3^- ppm**
P=0	0	0	M
P=½M	0	2P	0
P=M	M	0	0
P > ½M	2P-M	2(M-P)	0
P < ½ M	0	2P	M-2P

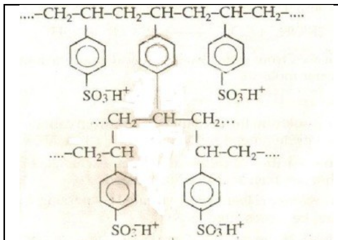
6. WATER SOFTENING METHODS

6.1 Ion exchange method: Removal of all ions present in water is called demineralization. The demineralization of water is done by using Ion exchange resins.

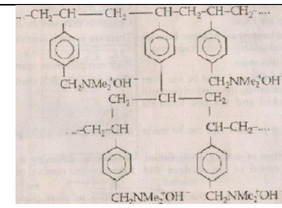
Ion exchange resin: Ion exchange resins are insoluble, cross linked, long chain organic polymers with a microporous structure. The ion exchange property of these polymers is due to mainly the functional groups attached to them. These functional groups may be acidic or basic. Based on functional groups the resins may be classified as: a) Cation exchange resins b) Anion exchange resins.

***Cation exchange resins* (RH^+):** They are mainly *styrene-di vinyl benzene* copolymers, which on sulphonation or corboxylation, $-SO_3H$ or –COOH groups are introduced to polymers. They become capable to exchange their H^+ ions with the cation in water.

***Anion exchange resins* ($R'OH^-$):** They are *styrene-di vinyl benzene* or *amino-formaldehyde* copolymers, which contain *amino* or *quaternary ammonium* or *quaternary phosphonium* or *tertiary sulphonium* groups as an integral part of the resin matrix. These, after treatment with dil.NaOH solution, become capable to exchange their OH^- ion with the anions in water.



Acidic or cation exchange resin (sulphonate form)



Basic or anion exchange resin (hydroxide form)

Process: It consists of two tanks. Cation resins and anion resins are kept in the 1st and 2nd tank respectively. The hard water first is passed first through cation exchange column, which removes all the cations like Ca^{2+}, Mg^{2+} etc. from it, and equivalent amount of H^+ ions are released from this column to water.

$$2\,RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2\,H^+$$
$$2\,RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2\,H^+$$

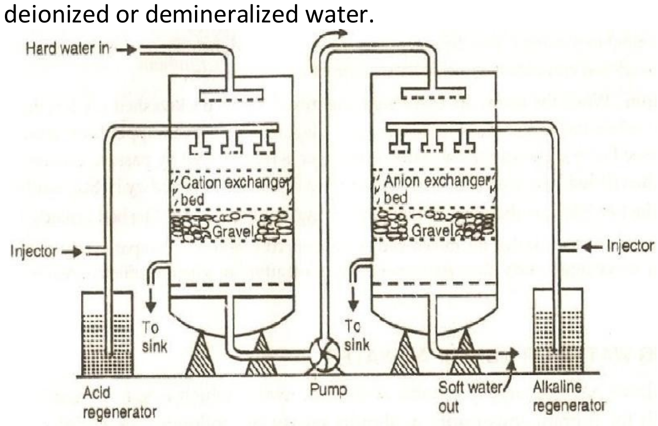
After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-}, Cl^-, etc. present in the water and equivalent amount of OH^- ions are released from this column to water.

$$R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-$$
$$2R'OH^- + SO_4^{2-} \rightarrow R'_2SO_4^{2-} + 2\,OH^-$$
$$2R'OH^- + CO_3^{2-} \rightarrow R'_2CO_3^{2-} + 2\,OH^-$$

The H^+ and OH^- ions released from both the column get combined to produce water molecule.

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

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



Demineralization of water.

Regeneration: When capacities of cation and anion exchangers lost to exchange H+ and OH- ions, they are then said to be exhausted.

The exhausted cation exchange is regenerated by passing a solution of dil.HCl or dil.H_2SO_4.

$$R_2Ca^{2+} + 2\,H^+ \rightarrow 2\,RH^+ + Ca^{2+}\text{(washings)}$$
$$R_2Mg^{2+} + 2\,H^+ \rightarrow 2\,RH^+ + Mg^{2+}\text{(washings)}$$

The column is washed with deionized water and washings which contain Ca^{2+}, Mg^{2+} , SO_4^{2-} , Cl^- ions is passed to sink or drain.

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

$$R'_2SO_4^{2-} + 2\,OH^- \rightarrow 2R'OH^- + SO_4^{2-} \text{ (washings)}$$
$$R'_2CO_3^{2-} + 2\,OH^- \rightarrow 2R'OH^- + CO_3^{2-} \text{ (washings)}$$
$$R'Cl^- + OH^- \rightarrow R'OH^- - + Cl^- \text{ (washings)}$$

Advantages:

The process can be used to soften highly acidic or basic waters.

It produces water of very low hardness (2ppm), so it is very good for treating water for use in high pressure boilers.

Disadvantages:

The equipment is costly and more expensive chemicals are needed.

If water contains turbidity, then the out put of the process is reduced. The turbidity must be below 10ppm. If it is more it has to be removed first by coagulation and filtration.

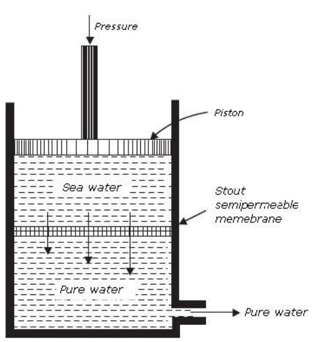
6.2 Reverse osmosis: When two solutions of unequal concentrations are separated by a semi permeable membrane (does not permit the ions, atoms, molecules etc.), flow of solvent takes place from dilute to concentrated sides.

If, however, 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 side across the membrane. This is the principle of reverse osmosis.

Thus, in reverse osmosis process methods pure water is separated from its contaminants, rather than removing contaminants from the water.

This membrane filtration is some times also called “super-filtration” or “Hyper filtration”.

Method **:** In this process, pressure of the order 15 to 40 kg cm^{2-} is applied to the sea water/ impure water to force its pure water out through the semi permeable membranes; leaving behind the dissolved solids.



The membrane consists of very thin film of *cellulose acetate*, affixed to either side of a perforated tube. However, more recently superior membranes made of *polymethacrylate* and *polyamide* polymers have come into use.

Advantages:

Reverse osmosis process is a distinct advantage of removing ionic as well as non ionic, colloidal and high molecular weight organic matter.

It removes colloidal silica, which is not removed by demineralization.

The maintenance cost is almost entirely on the replacement of the semi permeable membrane.

The life time of membrane is quite high, about 2years.

The membrane can be replaced within a few minutes, there providing uninterrupted water supply.

Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

7. Specifications of potable water:

How much water is required per person per day?

As per universal standards (Average)

For drinking 5 litres
Sanitation 20 litres
Bathing 15
Food preparation 10

S.No.	Characteristic	Acceptable Limit
1	Color	5 Hazen Units
2	Odour	Agreeable
3	pH	6.5 – 8.5
4	Taste	Agreeable
5	TDS	500 ppm
6	Ca	150 ppm
7	Mg	100 ppm
8	Alkalinity	300 ppm
9	Total Hardness	350ppm

8. DISINFECTION OF WATER

8.1 CHLORINATION: chlorination is the most commonly used disinfectant in water treatment throughout world. It can be employed directly as gas or in the form of concentrated solution in water. It produces hypochlorous acid, which is a powerful germicide.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$
$$\text{Bacteria} + HOCl \rightarrow \text{Bacteria are killed}$$

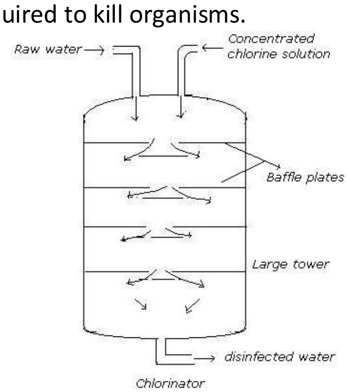
Death of micro-organism, bacteria etc. results from chemical reaction of hypochlorous acid with the enzymes in the cells of organism etc. Since enzyme is essential for the metabolic processes of the micro-organism, so death of micro-organism results due to inactivation of enzyme by hypochlorous acid.

Apparatus used for disinfection by chlorine is known as ***chlorinator*.** It is a large tower which contains number of baffle plates. From its top, raw water and proper quantity chlorine solution are introduced. These get thoroughly mixed during their passage through the water. For filtered water, about 0.3 to 0.5ppm of Cl_2 is sufficient. Disinfected water is taken out from the out let at the bottom of chlorinator.

Factors affecting efficiency of chlorine:

Time of contact: death rate of micro-organisms by chlorine is proportional to the number of micro-organisms remaining alive. Initially, the death rate is maximum and with time, it goes on decrease.

pH of water: at lower pH values (between 5 – 6.5), a small contact is required to kill organisms.



Advantages of chlorination:

it is effective and economical.

It is stable, require small space for storage, and does not deteriorate on keeping.

It can be used at high as well as low temperatures.

It does not introduce any impurity in water.

It is most ideal disinfectant.

Disadvantages:

excess of chlorine, produces bad taste and disagreeable odor.

Excess chlorine produces irritation on muscus membrane. The quantity of free chlorine in treated water should not exceed 0.1 to 0.2ppm.

It is more effective below pH 6.5 and less effective at higher pH vales.

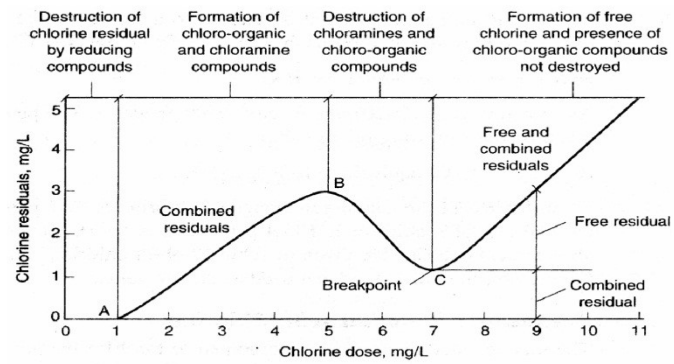
8.2 Break-Point chlorination: It means that chlorination of water to such an extent that living organisms as well as other organic impurities in water are destroyed. It involves in addition of sufficient amount of chlorine to oxidize organic matter, reducing substances and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfecting action against pathogenic bacteria's. It is also known as free-residual chlorination.

Initially for lower doses of Cl_2 , there is no free residual chlorine since all the added chlorine gets consumed for doing complete oxidation of reducing substances present in water.

As the amount of chlorine dosage is increased, amount of residual chlorine also show steady increase. This stage corresponds to the formation of chloro-organic compounds without oxidizing them.

At still higher dose of applied chlorine, oxidation of organic and micro-organisms gets in consequently the amount of free residual chlorine also decrease. When the oxidative destruction is completed it reaches minima.

After minima, the added chlorine is not used in any reaction. Thus, the residual chlorine keeps increasing in proportion to added chlorine. Hence, for effectively killing micro organisms, sufficient chlorine has to be added. Addition of chlorine in such dosages is known as *break-point* or *free residual chlorination*.



Advantages: it ensures complete destruction of organic compound which impart color, bad odor and unpleasant taste to water. It completely destroys all the disease causing bacteria. It prevents the growth of any weeds in water.

8.3 OZONATION: Ozone is a excellent disinfectant. It is produced by passing silent electric discharge through cold and dry oxygen.

$$3O_2 \xrightarrow{\text{Silent electric current}} 2O_3$$

Ozone is highly unstable and breaks down, liberating nascent oxygen.

$$O_3 \rightarrow O_2 + \underset{\text{nascent}}{[O]}$$

The nascent oxygen is very powerful oxidizing agent and kills all the bacteria as well as oxidizes the organic matter present in water.

For carrying out the disinfection by ozone, ozone is injected into the water and the two are allowed to come in contact in a sterilizing tank. The disinfected water is removed from the top. The contact period is about 10-15 minutes and the usual dose strength 2-3ppm.

Advantages: removes colour, odour and taste without giving residue, not harmful, since it is unstable an decompose into oxygen.

Disadvantage: quit expensive.

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