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Department: Engineering Chemistry

Subject: Engineering Chemistry

Unit: II

Topic: Boiler Problems and Softening  
Methods

Water is mainly used in boilers for the generation of steam for industries and power houses. A boiler is an apparatus in which water under pressure is converted into steam by the application of heat and this steam is utilized for various purposes like electricity generation. For boiler feed water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits.

Boiler-feed water should correspond with the following composition:

- Its hardness should be below 0.2 ppm.
- Its caustic alkalinity (due to OH<sup>-</sup>) should be between 0.15 and 0.45 ppm.
- Its soda alkalinity (due to Na<sub>2</sub>CO<sub>3</sub>) should be 0.45 – 1 ppm.

Excess of impurities, if present, in boiler feed water generally cause some boiler-problems like Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.

### I. Sludge and Scale Formation in Boilers:

In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed are soft, loose and slimy, these are known as sludges, while if the precipitate is hard and adhering on the inner wall of boiler, it is called as scale.

**Sludge formation:** Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubility in hot water than in cold water, e.g. MgCO<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub> etc. They are formed at comparatively colder portions of the boiler get collected at places where the flow rate is slow; they can be easily scrapped off with a wire brush. If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.

**Disadvantages of sludge formation:-**

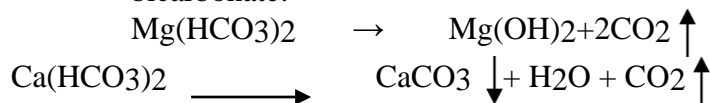
- Sludges are poor conductors of heat, so they tend to waste a portion of heat generated and thus decrease the efficiency of boiler.
- Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

**Prevention of sludge formation:-**

- By using softened water
- By frequent 'blow-down operation' i.e. partial removal of concentrated water through a tap at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high and 'Make-up' water is addition of fresh softened water to boiler after blow down operation.

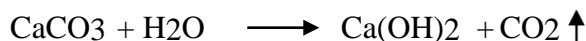
**Scale Formation:** Scales are hard deposits firmly sticking to the inner surfaces of the boiler. They are difficult to remove, even with the help of hammer and chisel, and are the main source of boiler troubles. Scales are mainly formed by;

- Decomposition of Temporary Hardness like magnesium bicarbonate, calcium bicarbonate:-



However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers.

But in high-pressure boilers, CaCO<sub>3</sub> is soluble due to the formation of Ca(OH)<sub>2</sub>



(ii) Deposition of calcium sulphate:- The solubility of  $\text{CaSO}_4$  in water decreases with increase in temperature.  $\text{CaSO}_4$  is soluble in cold water, but almost completely insoluble in super-heated water. It may be due to increase ionization at high temperature so  $k_{sp} < k_{ionic}$  product and less availability of water molecules for solvation at high temperature. Consequently,  $\text{CaSO}_4$  gets precipitated as hard scale on the hotter parts, of the boiler. This type of scale causes troubles mainly in high pressure boilers. Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(iii) Hydrolysis of magnesium salts:- Dissolved magnesium salts get hydrolyzed at prevailing high temperature inside the boiler, forming magnesium hydroxide precipitate, which forms a soft type of scale, e.g.



(iv) Presence of silica:- Even if a small quantity of  $\text{SiO}_2$  is present, it may deposit as calcium silicate ( $\text{CaSiO}_3$ ) and / or magnesium silicate ( $\text{MgSiO}_3$ ). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

Disadvantages of Scale formation;

1. Wastage of fuel. Scales have a poor thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or over- heating is done and these causes increase in fuel consumption.

The wastage of fuel being dependent on the thickness and the nature of scale:

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

2. Lowering of boiler safety. Due to scale formation, over-heating of boiler is done in order to maintain a steady supply of steam. It makes the boiler material softer and weaker. This cause distortion of boiler tube and also makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.
3. Decrease in efficiency. Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of the boiler.
4. Danger of explosion. When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in development of sudden of sudden high-pressure which may cause explosion of the boiler.

Prevention of scale formation:

Scales are removed by mechanical or by chemical methods like if the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush followed by frequent blow-down operation.,

If the scales are brittle, it can be removed by giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water).

If the scales are adherent and hard, they can be removed by dissolving them by adding chemicals e.g.,  $\text{CaCO}_3$  scales can be dissolved by using 5-10%  $\text{HCl}$ . Calcium sulphate scales can be removed by adding EDTA, since the Ca – EDTA complex is highly soluble in water.

## II. Priming, Foaming and Carry over process:

The process of carrying water by steam along with impurities is called "carry over". This is mainly due to priming and foaming. These processes are objectionable

and usually occur together.

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along-with the steam. This process of 'wet-steam' formation is called priming. Due to priming, dissolved salts or suspended solids in boiler water are carried by the wet steam to super heater and turbine blades, where they get deposited as water evaporates. This deposit decreases the efficiency of boiler. Dissolved salts may enter the parts of other machinery, thereby decreasing their life. It is caused by the presence of considerable quantities of dissolved and suspended impurities in water, High steam velocities, sudden boiling, Faulty design of boiler, etc.

Priming can be avoided by controlling rapid change in steaming velocities, the proper design of boilers, maintaining low water levels in boilers, ensuring efficient softening, filtration, by blowing off sludge or scales from time to time.

Foaming is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. Foaming is caused by the presence of oil and alkalis in boiler-feed water. Actually these impurities greatly lower the surface tension of water, and thus increase the foaming tendency of the liquid. Due to foaming the maintenance of the boiler becomes difficult because of improper judgment of actual height of water column.

Foaming can be avoided by: (i) the addition of anti-foaming agents like castor oil which spreads on the surface of water and therefore neutralizes the surface tension reduction (ii) the removal of foaming agent like oil from boiler water by using coagulants which entrap oil drops.

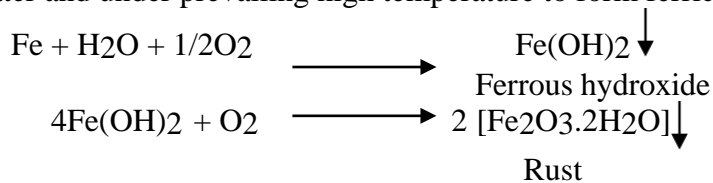
### III. Boiler Corrosion:

Boiler corrosion is "decay" or "disintegration" of boiler material either by chemical or by electrochemical reactions with its environment.

The disadvantages of corrosion are: Shortening of boiler life, Leakages of the joints and rivets, Increased cost of repairs and maintenance, etc.

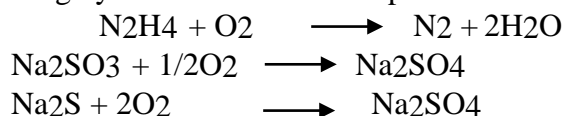
Corrosion in boilers is due to the following reasons:

- a. Dissolved oxygen: This is the most usual corrosion causing factor. In Boilers, oxygen is introduced through the raw water supply. Water usually contains about 8 ppm of dissolved oxygen at room temp. As the water is heated, the dissolved oxygen is set free and the boiler starts corroding. Dissolved oxygen reacts with the iron of boiler in presence of water and under prevailing high temperature to form ferric oxide (rust).



Removal of dissolved oxygen:

1. By adding hydrazine or sodium sulphite or sodium sulphide. Thus:



Hydrazine is an ideal chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Consequently hydrazine removes oxygen without increasing the conc. of dissolved solids/salts.

Pure hydrazine is not used in water treatment because it is an explosive inflammable liquid so

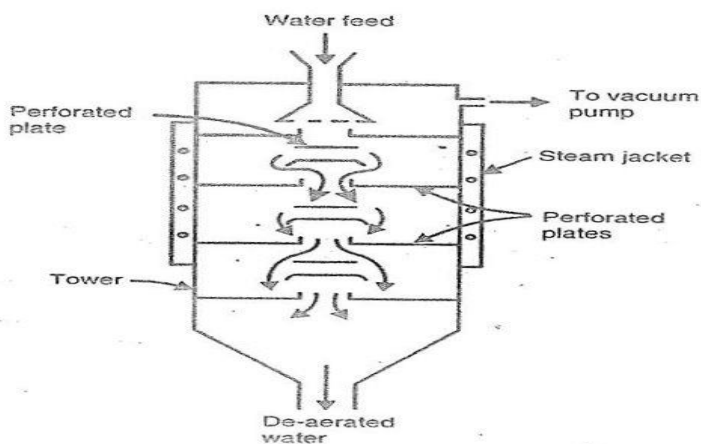
40% aqueous solution of hydrazine is used which is quite safe.

Excess hydrazine must not be used because excess of it decomposes to give NH<sub>3</sub>, which causes corrosion of some alloys like brass etc. used in condenser tubes.



On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate is formed. Under high pressure it decomposes giving SO<sub>2</sub>. The SO<sub>2</sub> enters the steam pipes and appears as corrosive sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) in steam condensate. So as a rule a very low concentration of 5-10 ppm of Na<sub>2</sub>SO<sub>3</sub> in the boiler is maintained, rather adding it intermittently.

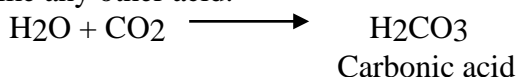
- By mechanical de-aeration. This process consists of spraying water over preheated perforated plates stacked in a degasifier. Removal of dissolved O<sub>2</sub> is ensured by applying high temperature and vacuum.



- Carbon dioxide: There are two sources of CO<sub>2</sub> in boiler water, viz. dissolved CO<sub>2</sub> in raw water and CO<sub>2</sub> formed by decomposition of bicarbonates in H<sub>2</sub>O according to the equation:



Carbon dioxide in presence of water forms carbonic acid which has a corrosive effect on the boiler material like any other acid.



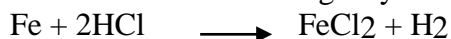
CO<sub>2</sub> can be removed by mechanical de-aeration along with O<sub>2</sub> or Addition of appropriate quantity of ammonium hydroxide



- Mineral acids: Magnesium chloride, if present in boiler feed water, can undergo hydrolysis producing HCl



The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust in the following way:



Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Consequently presence of even a small amount of MgCl<sub>2</sub> causes corrosion of iron to a large extent.

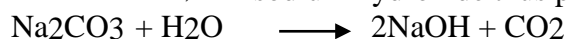
As the boiler water is generally alkaline and hence the acid is usually neutralized. In case the amount of acid is more, calculated quantity of alkali is added from outside to neutralize the

acid for preventing this corrosion.

#### IV. Caustic Embrittlement

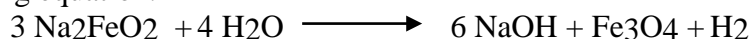
Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by lime-soda process, it is likely that some residual Na<sub>2</sub>CO<sub>3</sub> is still present in the softened water. In high pressure boilers Na<sub>2</sub>CO<sub>3</sub> decomposes to give sodium hydroxide and CO<sub>2</sub>, and sodium hydroxide thus produced makes the boiler water "caustic".



This caustic water flows into the minute hair-cracks, present in the inner side of boiler, by capillary action. On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, thereby dissolving iron of boiler as Sodium ferrous (Na<sub>2</sub>FeO<sub>2</sub>).

From its place of formation, sodium ferrous decomposes a short distance away as per the following equation.



Further dissolution of iron takes place because of the precipitation of Fe<sub>3</sub>O<sub>4</sub>, and the regeneration of NaOH. This causes embrittlement of boiler walls more particularly at stressed parts like bends, joints, rivets, etc., causing even failure of the boiler.

Mechanically embrittlement arises due to the setting up of a concentration cell with the iron surrounded by dil. NaOH acting as the Cathode, while the iron surrounded by conc. NaOH acting as the anode. The iron in the anodic part gets dissolved or corroded.

Caustic embrittlement can be prevented: by using sodium phosphate as softening reagent instead of sodium carbonate in external treatment of boiler water.

by adding tannin or lignin to boiler water which blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution into these areas.

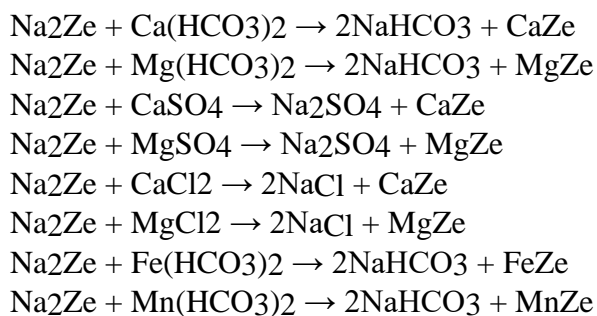
by adding sodium sulphate to boiler water. Na<sub>2</sub>SO<sub>4</sub> also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented if Na<sub>2</sub>SO<sub>4</sub> is added to boiler water so that the ratio of [Na<sub>2</sub>SO<sub>4</sub> conc.] and [NaOH conc.] is kept as 1:1, 2:1 and 3:1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

### Softening Methods

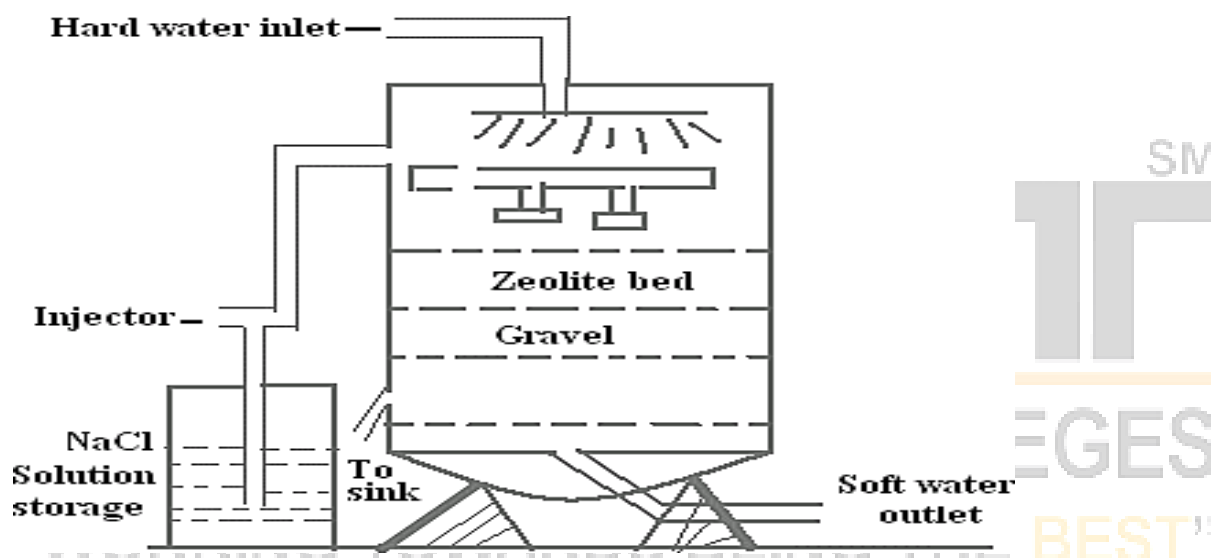
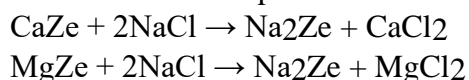
#### I. Zeolite/Permutit process:

Zeolite is micro-porous inorganic mineral. For odour removal and the softening of hard water generally sodium zeolites are used. It is capable of exchanging its sodium ions with hardness causing cations reversibly. It is hydrated sodium aluminosilicates and its chemical formula is Na<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>.xSiO<sub>2</sub>.yH<sub>2</sub>O here x may be 2-10 and y may be 2-6. Zeolites are of two types natural and synthetic. The natural zeolites are generally non or less porous while synthetic zeolites are more porous, glassy, gelatinous and have higher softening capacity than natural zeolites. Zeolites are characteristically soft to moderately hard, light in density, insoluble in water but can act as base exchangers in contact with water containing cations. Hence these can remove Ca<sup>2+</sup> and Mg<sup>2+</sup> ions from water when hard water is passed through it.

Zeolite process for water softening: When Ca<sup>2+</sup> and Mg<sup>2+</sup> ions containing hard water is passed through a bed of sodium zeolite, the sodium ions are replaced by the calcium and magnesium ions.



When all sodium ions are replaced by calcium and magnesium ions, the zeolite becomes inactive. Then the zeolite needs to be regenerated. zeolite can be easily regenerated by passing brine solution (10% NaCl) through the bed of inactivated zeolite. The following reactions are taken place and form Na<sub>2</sub>Ze.



**Merits of Zeolite Process:**

Used equipment is compact.

It removes the hardness upto 10 ppm.

The process automatically adjusts itself for variation in hardness of incoming water.

This process does not involve any type of precipitation, thus, no problem of sludge formation occurs.

**Demerits of Zeolite Process:**

The outgoing water (treated water) contains more sodium salts.

This method only replaces Ca<sup>+2</sup> and Mg<sup>+2</sup> ions by Na<sup>+</sup> ions.

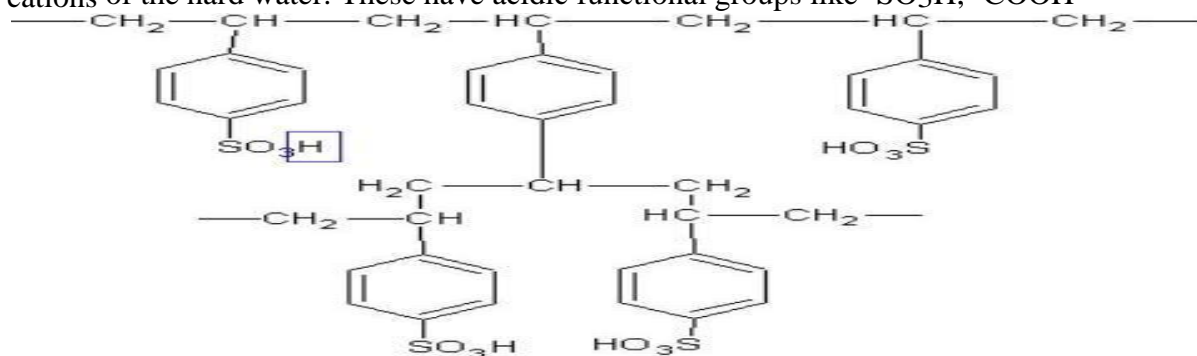
High turbidity water cannot be softened efficiently by zeolite process.

## II. Ion exchange process Or Demineralization process Or Deionization process:

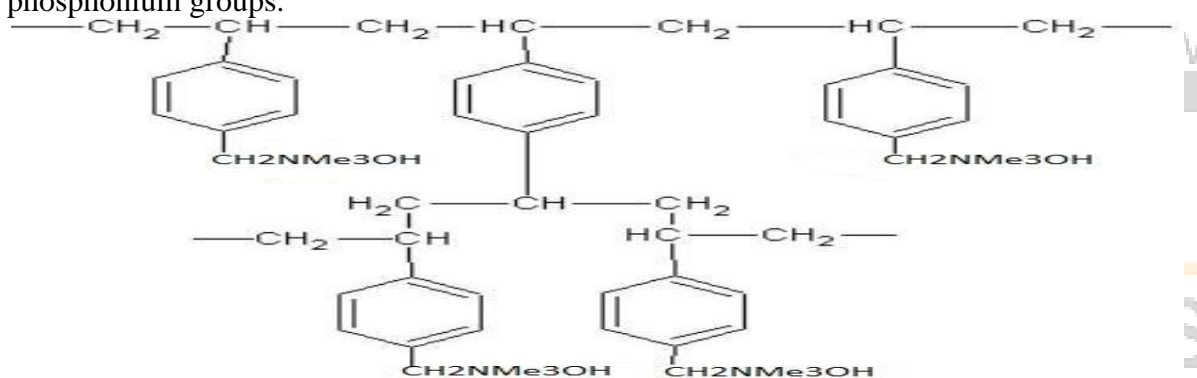
Ion exchange resins are insoluble, micro porous, cross linked, long chain, higher molecular weight, functional group containing organic copolymers. The functional groups attached to the chains are involved in the ion-exchanging properties.

Types of ion exchanger;

Cation exchange resins (RH<sup>+</sup>): These are usually styrene divinyl benzene copolymers which on carboxylation or sulphonation become capable of exchanging their H<sup>+</sup> ions with the cations of the hard water. These have acidic functional groups like -SO<sub>3</sub>H, -COOH



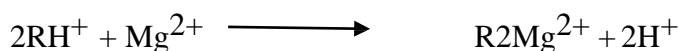
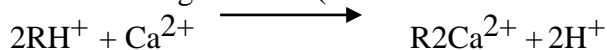
Anion exchanger resins (ROH<sup>-</sup>): These are usually styrene divinyl benzene or amine formaldehyde copolymers which on treatment with dilute NaOH solution become capable to exchange their OH<sup>-</sup> anions with complex anions in water. These resins contain basic functional groups like amino, quaternary ammonium or tertiary sulphonium or quaternary phosphonium groups.



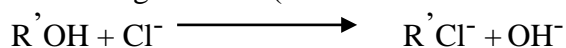
Ion exchange process

It is a two stage process, the water first passes through the column containing hydrogen exchanger (Cation exchanger) and then through second column containing hydroxyl exchanger (Anion exchanger). H<sup>+</sup> and OH<sup>-</sup> ions released from cation exchanger and anion exchanger columns get combined to produce water molecule.

Cation exchange resins : (RH<sup>+</sup> = Cation exchange resin)

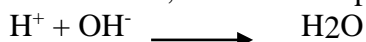


Anion exchange resins : (R'OH<sup>-</sup> = Anion exchange resin)



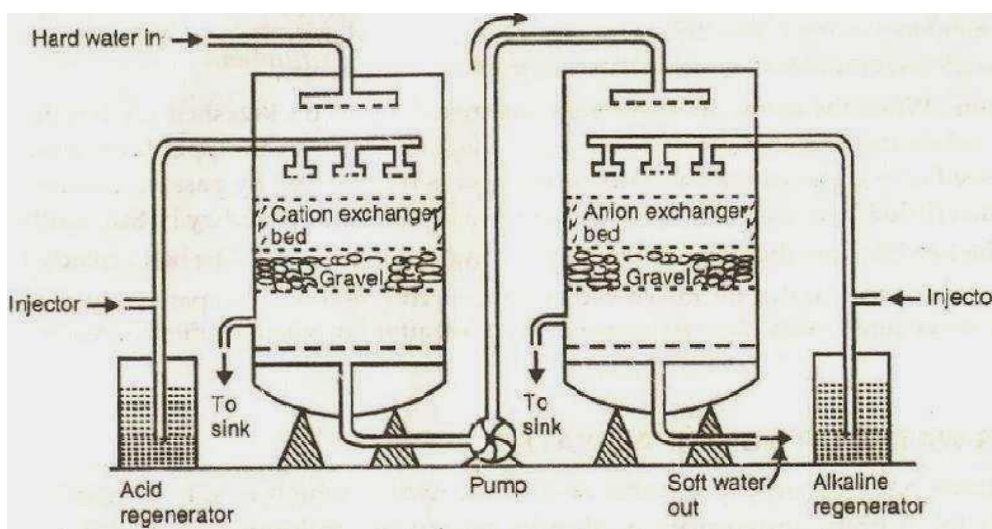
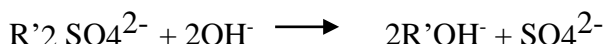


$H^+ + OH^-$  ions, combine and produce water



Regeneration of exhausted resins: After some time the cation and anion exchanging resins lose the capacity to remove complex cations and anions respectively, they are then said to be exhausted. When the resins are exhausted, the supply of water is stopped. The exhausted cation exchanger is regenerated by passing dilute HCl or H<sub>2</sub>SO<sub>4</sub> Solution and exhausted anion exchange resin is regenerated by passing dilute NaOH solution.

Regeneration Chemical reaction



The columns are washed with deionised water and washing (which contain  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$ ,  $Cl^-$  ions) are passed to sink or drain. The regenerated resins are again used.

Advantages: Highly acidic or alkaline water also can be softened by this process.

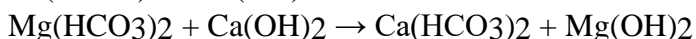
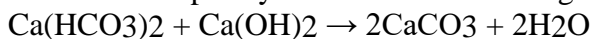
It produces water of low hardness (up to 2 ppm).

If the output water is passed through de-gassifier, then the gaseous impurities like O<sub>2</sub>, CO<sub>2</sub> also get expelled, to get water of distilled water standard.

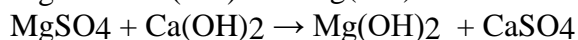
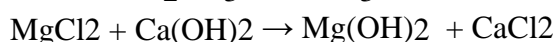
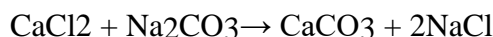
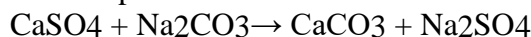
Disadvantages: Costly equipment, exchangers and costly chemicals are needed for regeneration. Turbid water can not be used as it decreases the efficiency of resins. It can be operated only small scale purification of water.

III. Soda lime process: It is the most common and economic water softening method. It is very useful for the treatment of large volumes of hard water. Addition of lime i.e. Ca(OH)<sub>2</sub> and soda i.e. Na<sub>2</sub>CO<sub>3</sub> to the hard water precipitates calcium as the carbonate, and magnesium as its hydroxide. The amounts of the two chemicals required are easily calculated from the analysis of the water and stoichiometry of the reactions. The lime-soda method uses lime, Ca(OH)<sub>2</sub> and soda ash, Na<sub>2</sub>CO<sub>3</sub> to precipitate hardness from solution.

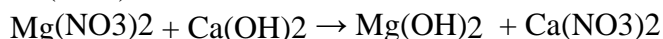
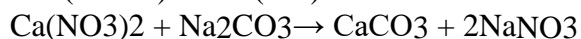
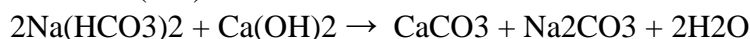
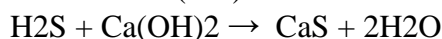
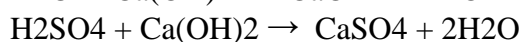
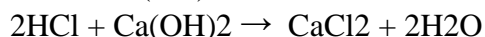
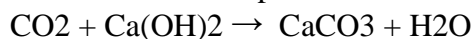
In case of Temporary hardness the following reactions are take places:



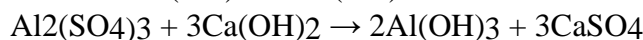
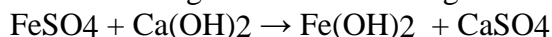
In case of permanent hardness the following reactions are take places:



In case of other impurities the following reactions are take places:



In case of coagulants the following reactions are take places:



There are two types of lime-soda processes; cold lime soda process and hot lime soda process.

**Cold Lime soda process:** When the chemicals (L Or S) are added to hard water at room temperature, the process is known as cold lime soda process. At room temperature, the precipitates are finely divided and do not settle easily so small quantity of coagulant is also added to water which help in the formation of coarse precipitates.



Cold lime soda process provides water containing a residual hardness of 50-60 ppm.

**Hot Lime soda process:** When the chemicals are added to higher temperature (80<sup>o</sup> C to 150<sup>o</sup> C) the process is known as Hot lime soda process. Hot L-S Method is proffered over the Cold L-S Method because in hot lime soda method at higher temperature the reactions are fast, precipitation is more complete, settling rate and filtration rates are increased. As a result the precipitate and sludge formed settle rapidly and coagulants are not required and also chemicals needed are in smaller quantities than that of cold L-S process. Dissolved gases are eliminated from water to a certain extent. The softened water recovered from hot L-S process has hardness of about 15 to 30 ppm.

Therefore, Lime requirement for softening

$$= \frac{74}{100} \left[ \frac{\text{T.H of Ca}^{2+} + 2 \times \text{T.H of Mg}^{2+} + \text{P.H of (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+}{\text{HCO}_3^-} \right] \times \text{Vol. of water (L)}$$

T.H = temporary hardness

P.H = Permanent Hardness

Soda requirement for softening

$$= \frac{106}{100} \left[ \text{P.H of (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{H}^+ - \text{HCO}_3^- \right] \times \text{Vol. of water (L)}$$

Diagram of Cold L-S Method;

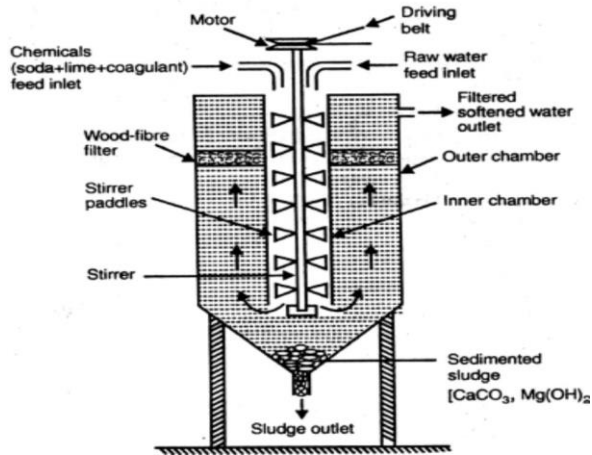
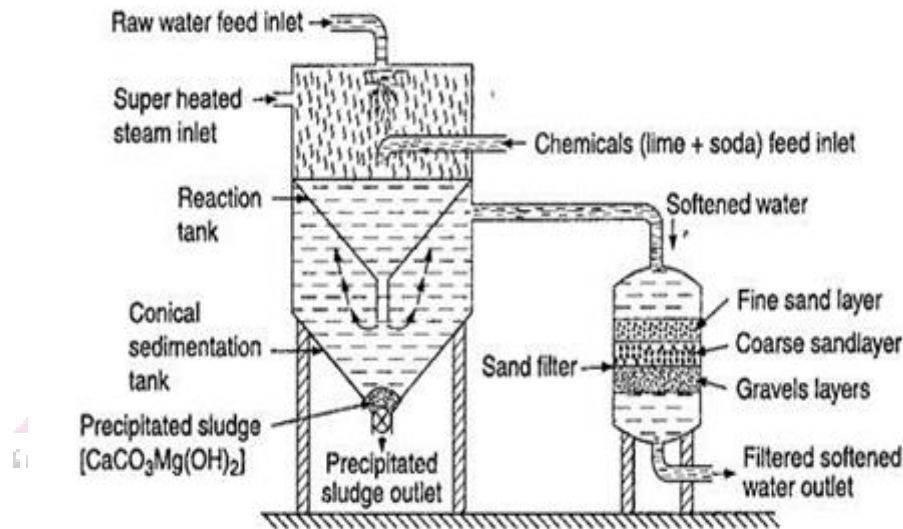


Diagram of Hot L-S Method;



Advantages: It is very economical process.  
 Less amount of coagulants are required.  
 Certain quantity of minerals is reduced from water.  
 The level of carbon dioxide can also be reduced using hot L-S Process.  
 Fe and Mn are also removed from the water.  
 The process increases the PH value of the treated water thereby corrosion of the distribution pipes is reduced.

Disdvantages: Sludge disposal is problem.  
 This can remove hardness only up to 15 ppm, which is not good for boilers.  
 Careful operations and skilled supervision are required for economical and efficient softening.

List of References;

Sr. No.	Title of the Book	Author/Publisher/Edition
1	Engineering Chemistry	rgpvnotes.in@gmail.com
2	Engineering Chemistry	Dara S.S & Singh A.K, S Chand & Co..
3	Engineering Chemistry	Jain & Jain, Dhanpat Rai & Co.
4	Engineering Chemistry	Chawla S. ,Dhanpat Rai & Co.

**Questions based on Unit II:**

1. A water sample has the following composition data:  $\text{Ca}(\text{HCO}_3)_2=40.5$  ppm,  $\text{Mg}(\text{HCO}_3)_2=146$  ppm,  $\text{CaCl}_2=111$  ppm,  $\text{MgCl}_2=95$  ppm,  $\text{CaSO}_4=68$  ppm,  $\text{MgSO}_4=60$  ppm. Calculate the quantity of lime (84%) and soda (90%) required for softening 100000 liters of water.
2. A water sample has the following composition data:  $\text{Ca}(\text{HCO}_3)_2=81$  ppm,  $\text{Mg}(\text{HCO}_3)_2=146$  ppm,  $\text{CaCl}_2=110$  ppm,  $\text{MgCl}_2=90$  ppm,  $\text{CaSO}_4=68$  ppm,  $\text{MgSO}_4=60$  ppm,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}=139$  ppm,  $\text{CO}_2=44$  ppm. Calculate the quantity of lime and soda required for softening one million liter of water.
3. Calculate the amount of lime(88.3% pure) and soda(99.2 % pure) required to soften one million liters of water containing the following impurities:-  
 $\text{CaCO}_3= 185$  mg/L,  $\text{CaSO}_4= 0.34$  mg/L,  $\text{MgCO}_3= 0.42$  mg/L,  $\text{MgCl}_2= 0.76$  mg/L,  $\text{MgSO}_4= 0.90$ mg/L,  $\text{NaCl}= 2.34$  mg/L,  $\text{SiO}_2=2.34$
4. A zeolite softener was completely exhausted and was regenerated by passing 100 L of brine solution containing 200g/L of NaCl. How many litres of water of hardness 500 ppm can be softened by this softener?
5. Hardness of 20,000 L of water sample was completely removed by Zeolite softener. The zeolite softener required 60 L of brine solution containing 1500 g/L of NaCl for regeneration. Calculate hardness of water sample.
6. What are boiler troubles? Explain causes, effects and preventive methods of scale and sludge formation.
7. Discuss Lime Soda process of softening hard water with the help of neat labeled diagram and chemical reactions involved in it?
8. What are ion-exchangers. Discuss softening of hard water by ion exchange method with the help of neat labeled diagram. Also write advantages and disadvantages of the process.

9. Discuss Zeolite method of softening hard water with diagram and chemical reactions involved in it? Also write advantages and disadvantages of the process.
  
10. Discuss boiler corrosion and carry over processes of boiler with causes, effects and preventive methods.