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Program : **B.Tech**

Subject Name: **Engineering Chemistry**

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Semester: **1st**



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UNIT II: BOILER PROBLEMS & SOFTENING METHODS

BOILER WATER (WATER FOR STEAM GENERATION)

A boiler is a closed vessel in which water under pressure is transferred into steam by the application of heat. In the boiler furnace, the chemical energy in the fuel is converted into heat, and it is the function of the boiler to transfer this heat to the contained water in the most efficient manner. The boiler should also be designed to generate high quality steam for plant use. A boiler must be designed to absorb the maximum amount of heat released in the process of combustion. This heat is transferred to the boiler water through radiation, conduction and convection.

Steam utilization. Steam is generated for the following plant uses:

- (i) Turbine drive for electric generating equipment, blowers and pumps,
- (ii) Heating for direct contact for equipment and comfort,
- (iii) Process for direct contact with products; direct contact sterilization and noncontact for processing temperatures.

Water is mainly used in boilers for the generation of steam (for industries and power houses). For such 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:

- (i) Its hardness should be below 0.2 ppm.
- (ii) Its caustic alkalinity (due to OH^-) should be between 0.15 and 0.45 ppm.
- (iii) Its soda alkalinity (due to Na_2CO_3) should be 0.45 – 1 ppm.

Excess of impurities, if present, in boiler feed water generally cause the following problems:

Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.

BOILER PROBLEM:

1. SLUDGE & SCALE FORMATION
2. PRIMING & FOAMING
3. CARRY OVER
4. BOILER CORROSION
5. CAUSTIC EMBRITTLEMENT

1. 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 walls, it is called as *scale*.

SULDGE: 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_3 , MgCl_2 , CaCl_2 , MgSO_4 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 removed (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:-

- (i) Sludges are poor conductors of heat, so they tend to waste a portion of heat generated and thus decrease the efficiency of boiler.
- (ii) 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:-

- (i) By using softened water
- (ii) By frequently '**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.

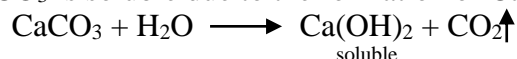
SCALES: Scales are hard deposits firmly sticking to the inner surfaces of the boiler. They are difficult to remove, even with the help of hammer and chisel, and are the main source of boiler troubles.

(i) *Decomposition of 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_3 is soluble due to the formation of Ca(OH)_2



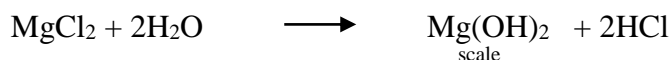
(iii) *Deposition of calcium sulphate:-*

The solubility of CaSO_4 in water decreases with increase in temperature. 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 $k_{\text{sp}} < k_{\text{ionic prod.}}$ and less availability of water molecules for solvation at high temperature.

Consequently, 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 SiO_2 is present, it may deposit as calcium silicate (CaSiO_3) and / or magnesium silicate (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:

(i) *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:

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

(ii) *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.

(iii) *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.

(iv) *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.

Removal of Scales:

Scales are removed by mechanical methods (*i – iii*) and / or by chemical methods (*iv*)

(i) If the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush,

(ii) *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).

(iii) *If the scales are loosely adhering, they can also be removed* by frequent blow-down operation. Blow-down operation is partial removal of hard water through a ‘tap’ at the bottom of the boiler, when extent of hardness in the boiler becomes alarmingly high. ‘Make-up’ water is addition of fresh softened water to boiler after blow down operation.

(iv) *If the scales are adherent and hard*, they can be removed by dissolving them by adding chemicals e.g., CaCO_3 scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be removed by adding EDTA, since the Ca – EDTA complex is highly soluble in water.

The essential differences between sludges and scales are summarized as follows:

<i>S.No.</i>	<i>Sludges</i>	<i>Scales</i>
1.	Sludges are soft, loose and slimy precipitate.	Scales are hard deposits.
2.	They are non-adherent deposits and can be easily removed.	They stick very firmly to the inner surface of boiler and are very difficult to remove.
3.	Formed by substances like CaCl_2 , MgCl_2 , MgSO_4 , MgCO_3 etc.	Formed by substance like CaSO_4 , Mg(OH)_2 etc.
4.	Formed at comparatively colder portions of the boiler.	Formed generally at heated positions of the boiler.
5.	They decrease the efficiency of boiler but are less dangerous.	Decrease the efficiency of boiler and chances of explosions are also there.
6.	Can be removed by blow-down operation.	Cannot be removed by blow-down operation.

Priming and Foaming

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*.

Priming refers to the propulsion of water into the steam drum by extremely rapid, almost explosive boiling of the water at the heating surfaces.

The moisture contamination in the steam is expressed in percentage by weight of steam.

For example, if steam contains 0.2% moisture, its steam quality will be reported as $100 - 0.2 = 99.8\%$.

Priming is caused by:

- (i) The presence of considerable quantities of dissolved solids (mainly due to suspended impurities and due to dissolved impurities in water).
- (ii) Steam velocities high enough to carry droplets of water into the steam pipe;
- (iii) Sudden boiling;
- (iv) Faulty design of boiler.

Priming can be avoided by:

- (i) Controlling rapid change in steaming velocities,
- (ii) The proper design of boilers (maintaining low water levels in boilers)
- (iii) Ensuring efficient softening and
- (iv) Filtration of the boiler-water carried over to the boiler.
- (v) 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 oils and alkalis react to form scaps, which greatly lowers the surface tension of water, and thus increase the foaming tendency of the liquid.

With respect to foaming, water can be following grades:

- (i) *Foaming water.* It is that water which produces foam even in two days, if blowing off operation is not done.
- (ii) *Semi-Foaming water.* It is that water which does not produce any foam in locomotive boilers for two days.
- (iii) *Non-Foaming water.* It is that water which does not produce any foam in locomotive boilers for one week.

Foaming can be avoided by: (i) the addition of anti-foaming agents, which act by count enacting the reduction in surface tension. For example addition of castor oil (which spreads on the surface of water and therefore) neutralizes the surface tension reduction. (ii) The removal of foaming agent (oil) from boiler water.

Traces oils are generally introduced in boiler feed water through the lubricating materials used for pumps etc. Oils can be removed by the addition of aluminum compounds, like *sodium aluminate* and *aluminium sulphate* which is hydrolyzed to form aluminium hydroxide flocks which entrap oil drops. The flocks of $\text{Al}(\text{OH})_3$ containing oil droplets are removed by filtration through anthracite filter bed.

Carry Over: The phenomenon of carrying of water along with impurities by steam is called “carry over”. This is mainly due to priming and foaming.

Priming and foaming usually occur together.

They are objectionable, usually occur together.

- (i) 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.
- (ii) Dissolved salts may enter the parts of other machinery, thereby decreasing their life;
- (iii) The maintenance of the boiler pressure becomes difficult because of improper judgment of actual height of water column.

Boiler Corrosion

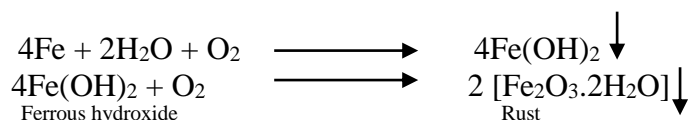
Boiler corrosion is “decay” or “disintegration” of boiler body material either due to chemical or electrochemical reaction with its environment.

The disadvantages of corrosion are:

- (i) Shortening of boiler life,
- (ii) Leakages of the joints and rivets;
- (iii) Increased cost of repairs and maintenance

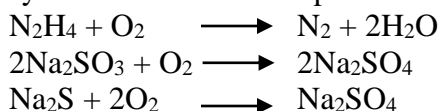
Corrosion in boilers is due to the following reasons:

(1) **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:

- (i) By adding hydrazine or sodium sulphate 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.

- (a) 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.
- (b) Excess hydrazine must not be used because excess of it decomposes to give NH_3 , which causes corrosion of some alloys like brass etc. used in condenser tubes.



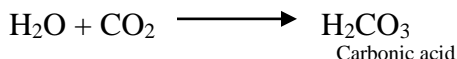
On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate is formed. Under high pressure it decomposes giving SO_2 . The SO_2 enters the steam pipes and appears as corrosive sulphurous acid (H_2SO_3) in steam condensate. So as a rule a very low concentration of 5-10 ppm of Na_2SO_3 in the boiler is maintained, rather adding it intermittently.

- (ii) *By mechanical de-aeration.* This process consists of spraying water over preheated perforated plates stacked in a degasifier. Removal of dissolved O_2 is ensured by applying high temperature and vacuum.

(2) **Carbon dioxide.** There are two sources of CO_2 in boiler water, viz. dissolved CO_2 in raw water and CO_2 formed by decomposition of bicarbonates in H_2O according to the equation:



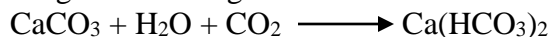
Carbon dioxide in presence of water forms carbonic acid which has a corrosive effect on the boiler material like any other acid.



CO_2 can be removed by:

- (i) Mechanical de-aeration along with O_2 .

(ii) Filtering water through lime-stone



But this method increases hardness

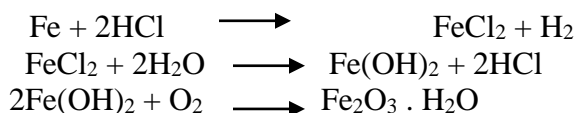
(iii) Addition of appropriate quantity of ammonium hydroxide



(3) **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_2 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.

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_2CO_3 is still present in the softened water. In high pressure boilers Na_2CO_3 decomposes to give sodium hydroxide and CO_2 , 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 ferrote (Na_2FeO_2).

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



Further dissolution of iron takes place because of

- (i) The precipitation of Fe_3O_4 , and
- (ii) The regeneration of NaOH.

This causes embrittlement of boiler walls more particularly 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:

- (i) by using sodium phosphate as softening reagent, instead of sodium carbonate in external treatment of boiler water.
- (ii) 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.
- (iii) by adding sodium sulphate to boiler water:

Na_2SO_4 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_2SO_4 is added to boiler water so that the ratio:

$\frac{[\text{Na}_2\text{SO}_4 \text{ conc.}]}{[\text{NaOH conc.}]}$ 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

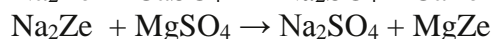
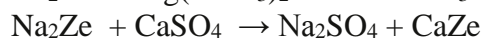
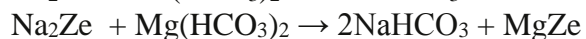
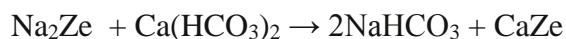
Zeolite process

Zeolite is micro-porous mineral which is used as catalyst in many industrial purposes such as water purification and air purification. The zeolites are hydrated alumino silicates and general composition $\text{Al}_x\text{Si}_y\text{O}_{2(x+y)}$ (without water molecules). Zeolites are two types natural and synthetic or artificial. The natural zeolite that is used for water softening is gluconites or greensand. Permutit is the synthetic zeolite that is most used in water softening and its chemical formula is $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, n\text{SiO}_2, x\text{H}_2\text{O}$. These are used as ion exchanger and odor removal in water softener. Permutit are more porous, glassy, and have higher softening capacity than greensand.

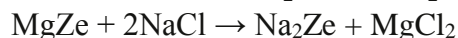
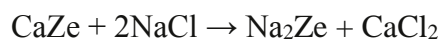
Zeolites are characteristically soft to moderately hard, light in density, insoluble in water but can act as base exchangers in contact with water containing cations. Hence these can remove Ca^{2+} and Mg^{2+} ions from water when hard water is passes through.

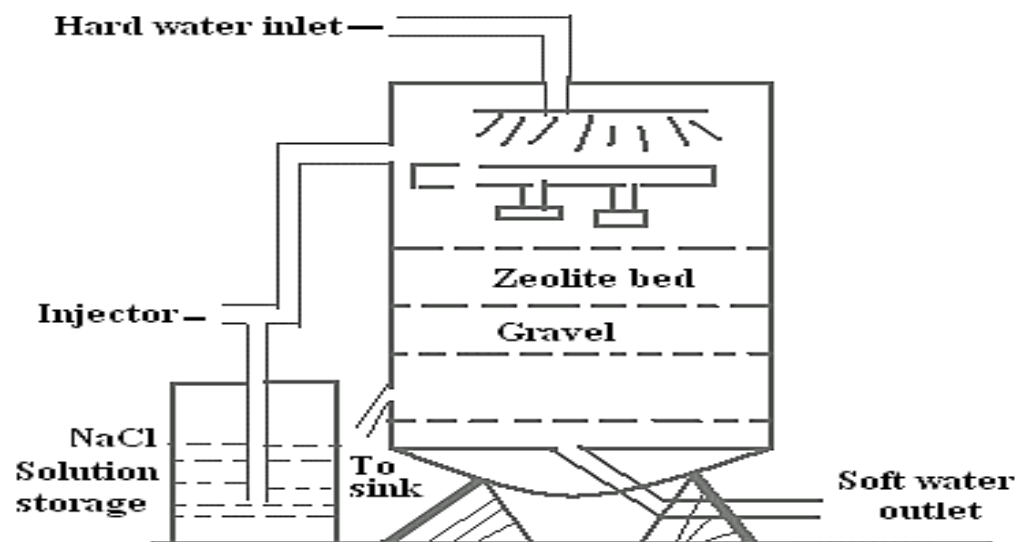
Zeolite process for water softening

Zeolite process for water softening has become a commercial success for the reason that zeolite can be easily regenerated. When Ca^{2+} and Mg^{2+} ions containing hard water is passes through a bed of sodium zeolite, the sodium ions are replace 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. Brine solutions are passing through the bed of inactivated zeolite. The following reactions are taken place and form Na_2Ze





Merits of Zeolite Process:

It removes the hardness almost completely (about 10 ppm hardness only).

The process automatically adjust 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^{+2} and Mg^{+2} ions by Na^{+} ions.

High turbidity water cannot be softened efficiently by zeolite process.

Ion exchange process Or Demineralization process Or Deionization process

Ion exchanger resin are insoluble, cross linked, long chain higher molecular weight organic polymers which are permeable due to their micro porous structure, and the functional groups attached to the chains are involved in the ion-exchanging properties.

Types of ion exchanger resins

Cation exchanger resins (RH^{+}) : These are usually styrene divinyl benzene copolymers which on carboxylation or sulphonation become capable of exchanging their H^{+} ions with the cations of the solution. These have acidic functional groups like SO_3H^{+} , $-\text{COOH}^{-}$ or OH^{-}

Anion exchanger resins (ROH^{-}) : These are usually styrene divinyl benzene or amine formaldehyde copolymers which on treatment with dilute NaOH solution become capable to exchange their OH^{-} anions with anions in water. Which contains basic functional groups like quaternary ammonium or quaternary 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

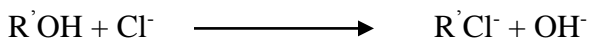
(Anion exchanger). H^+ and OH^- ions released from cation exchanger and anion exchanger columns get combined to produce water molecule.

Cation exchange resins :



(RH^+ = Cation exchange resin)

Anion exchange resins :

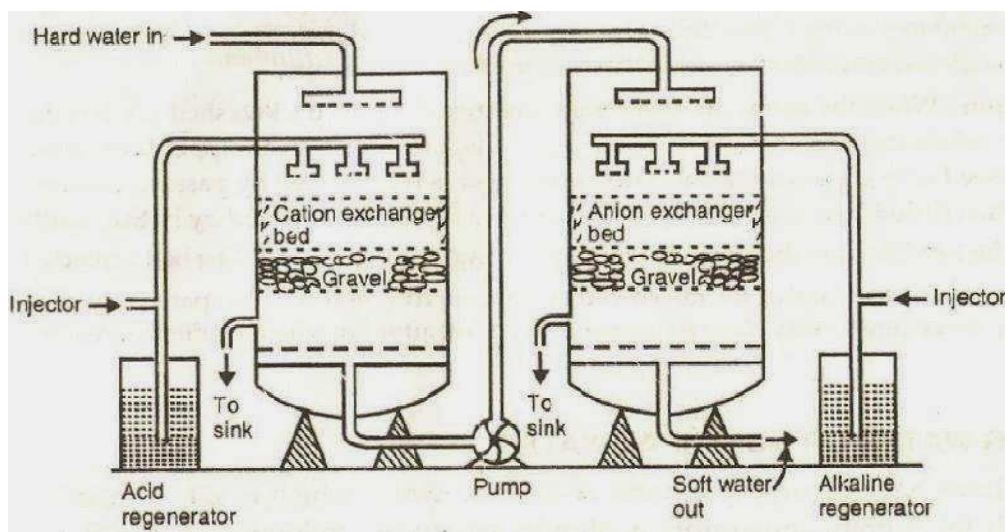


($\text{R}'\text{OH}^-$ = Anion exchange resin)

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



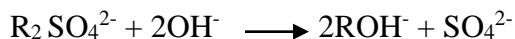
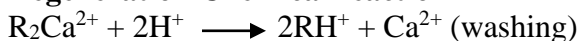
Ion exchange process Diagram



Regeneration of exhausted resins

After some time the cation and anion exchanging resins lose the capacity to remove H^+ ions and OH^- ions 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_2SO_4 Solution and exhausted anion exchanger 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-} , Na^+ 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_2 , CO_2 also get expelled, to get water of distilled water standard.

Disadvantages:

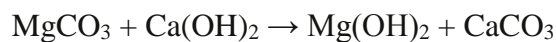
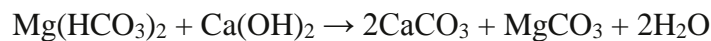
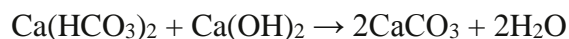
Costly equipment and costly chemicals are needed for regeneration.

Turbid water can not be used as it decreases the efficiency of resins.

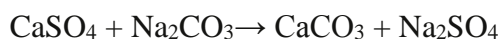
It can be operated only small scale purification of water.

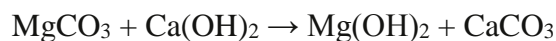
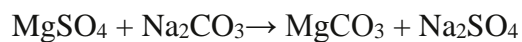
Soda lime is a process used in water treatment to remove **Hardness** from water. This process is now obsolete but was very useful for the treatment of large volumes of hard water. Addition of lime (CaO) and soda (Na_2CO_3) to the hard water precipitates calcium as the carbonate, and magnesium as its 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 uses lime, $Ca(OH)_2$ and soda ash, Na_2CO_3 , to precipitate hardness from solution. Carbon dioxide and carbonate hardness (calcium and Magnesium bicarbonate) are complexed by lime. In this process Calcium and Magnesium ions are precipitated by the addition of lime ($Ca(OH)_2$) and soda ash (Na_2CO_3).

temporary water hardness the following reactions are take places:



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





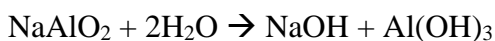
There are two type lime-soda process; cold lime soda process and hot lime soda process.

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, nor can they be easily filtered.

They 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° C to 150° C) the process is known as Hot lime soda process.

Why Hot L-S Method is proffered over the Cold L-S Method

- 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 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 has hardness of about 15 to 30 ppm.

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.
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