ENGINEERING CHEMISTRY
Chapter: Water Treatment

LIME – SODA PROCESS

Hardness

- Hardness is defined as sum of divalent metallic cations existing in water such as; Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}

- Practically most hardness is due to Ca^{2+} and Mg^{2+} ions (the predominant minerals in natural waters)
- Total Hardness = Ca^{2+} hardness+ Mg^{2+}hardness where the concentration of each ion is in consistent units such as mg/L as $CaCO_3$ equivalent hardness.

Types of Hardness

1. Carbonate Hardness is because of presence of HCO_3^- and CO_3^{2-} of Ca^{2+} and Mg^{2+} ; Carbonate hardness is also known as temporary hardness as it can be removed by boiling.
2. Non- Carbonate Hardness is associated with Cl^- and SO_4^{2-} of Ca^{2+} and Mg^{2+} and is often termed as Permanent Hardness

Water Softening

- Water softening or reduction of hardness is generally accomplished through Chemical Precipitation or Ion Exchange Process.
- Chemical precipitation is accomplished by converting calcium hardness to Calcium Carbonate and magnesium hardness to magnesium hydroxide.
- This is generally practiced either by Lime- Soda process.

Lime - Soda Process

- Chemical precipitation is one of the more common methods used to soften water.
- Chemicals normally used are lime (calcium hydroxide, $Ca(OH)_2$) and soda ash (sodium carbonate, Na_2CO_3).
- Lime is used to remove chemicals that cause carbonate hardness. Soda ash is used to remove chemicals that cause non-carbonate hardness.
- When lime and soda ash are added, hardness-causing minerals form nearly insoluble precipitates. Calcium hardness is precipitated as calcium carbonate ($CaCO_3$). Magnesium hardness is precipitated as magnesium hydroxide ($Mg(OH)_2$.
- These precipitates are then removed by conventional processes of coagulation/flocculation, sedimentation, and filtration. Because precipitates are very slightly soluble, some hardness remains in the water--usually about 50 to 85 mg/l (as $CaCO_3$).

- At room temperature, the ppt. formed are very fine. They do not settle down easily and cause difficulty in filtration. The fine ppt of $CaCO_3$ and $Mg(OH)_2$ eventually result in after deposition, later in the pipes and boiler tubes, producing scales.
- To eliminate this problem small amount of coagulants like Alum, Aluminium sulphate $Al_2(SO_4)_3$, or Sodium Aluminate $NaAlO_2$ are added, they hydrolyse to precipitate of Aluminium hydroxide which entraps the fine ppt and helps in the formation of coarse ppt.

Lime Requirement

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

- $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$
- $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO3 + Mg(OH)_2 + 2H_2O$
- $MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$

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

- $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$
- $MgSO_4 + Na_2CO_3 \rightarrow MgCO_3 + Na_2SO_4$
- $MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$
- $2NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O$
- $2KHCO_3 + Ca(OH)_2 \rightarrow 2CaCO_3 + K_2CO_3 + 2H_2O$

- $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$

- $2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$
- $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

- $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$
- $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaSO_4$

- $FeSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Fe(OH)_2$

- $AI2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2AI(OH)_3$

- $NaAlO_2 + 2H_2O \rightarrow AI(OH)_3 + NaOH$

- $2NaOH + CaCl_2 \rightarrow Ca(OH)_2 + 2NaCl$

Conclusions:

1. Half mole of lime is required for the removal of one mole of HCl and bicarbonates of Na+ and K+ each.

2. One mole of lime is required for the removal of one mole of temporary hardness of Ca^{2+}, , permanent hardness of Mg^{2+}, CO_2, $FeSO_4$, H_2SO_4 each.

3. Two moles of lime is required for the removal of one mole of temporary hardness of Mg^{2+}, .

4. Three moles of lime is required for the removal of one mole of $Al_2(SO_4)_3$.

5. NaOH produced by $NaAlO_2$ reacts with hardness causing salts and produces lime. Hence its hardness must be subtracted from the lime requirement.

6. During the treatment of lime to remove the permanent hardness of Mg^{2+}, , acids and alums the permanent hardness of Ca^{2+}, is generated in water. Hence they require both lime and soda treatment.

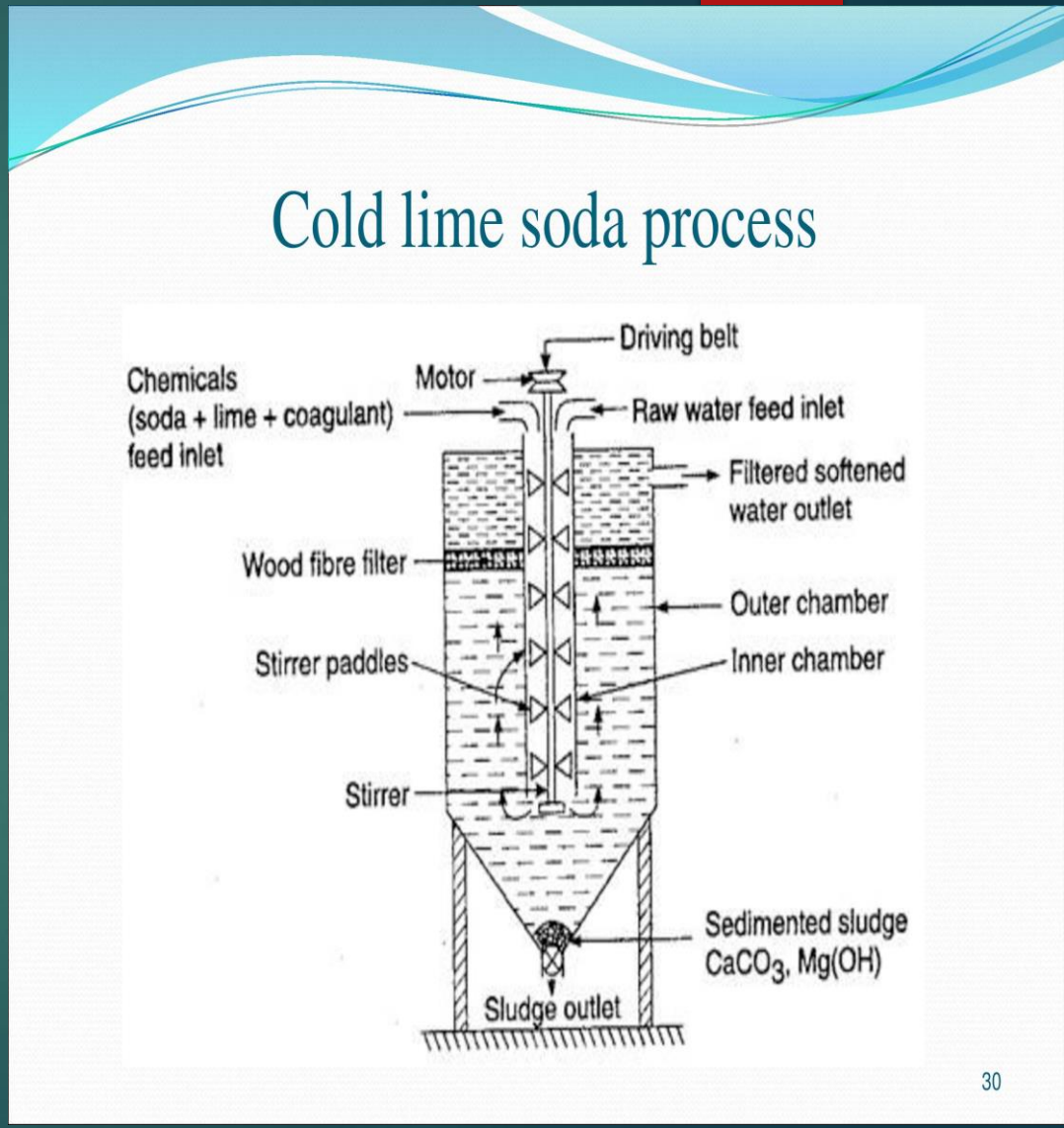
Lime Requirement = 74/ 100 ([temp. hardness of Ca^{2+}, + 2 x temp. hardness of Mg^{2+}, + permanent hardness of Mg^{2+}, + CO_2 + HCl + H_2SO_4 + $NaHCO_3$ + $FeSO_4$ + $Al2(SO_4)_3$ – $NaAlO_2$]

- **Soda Requirement** = 106/100 [permanent hardness of Ca^{2+}, + permanent hardness of Mg^{2+}, + HCl + H_2SO_4 + $FeSO_4$ + $Al_2(SO_4)_3$ - $NaHCO_3$]

* All in terms of chemical equivalents of CaCO3.

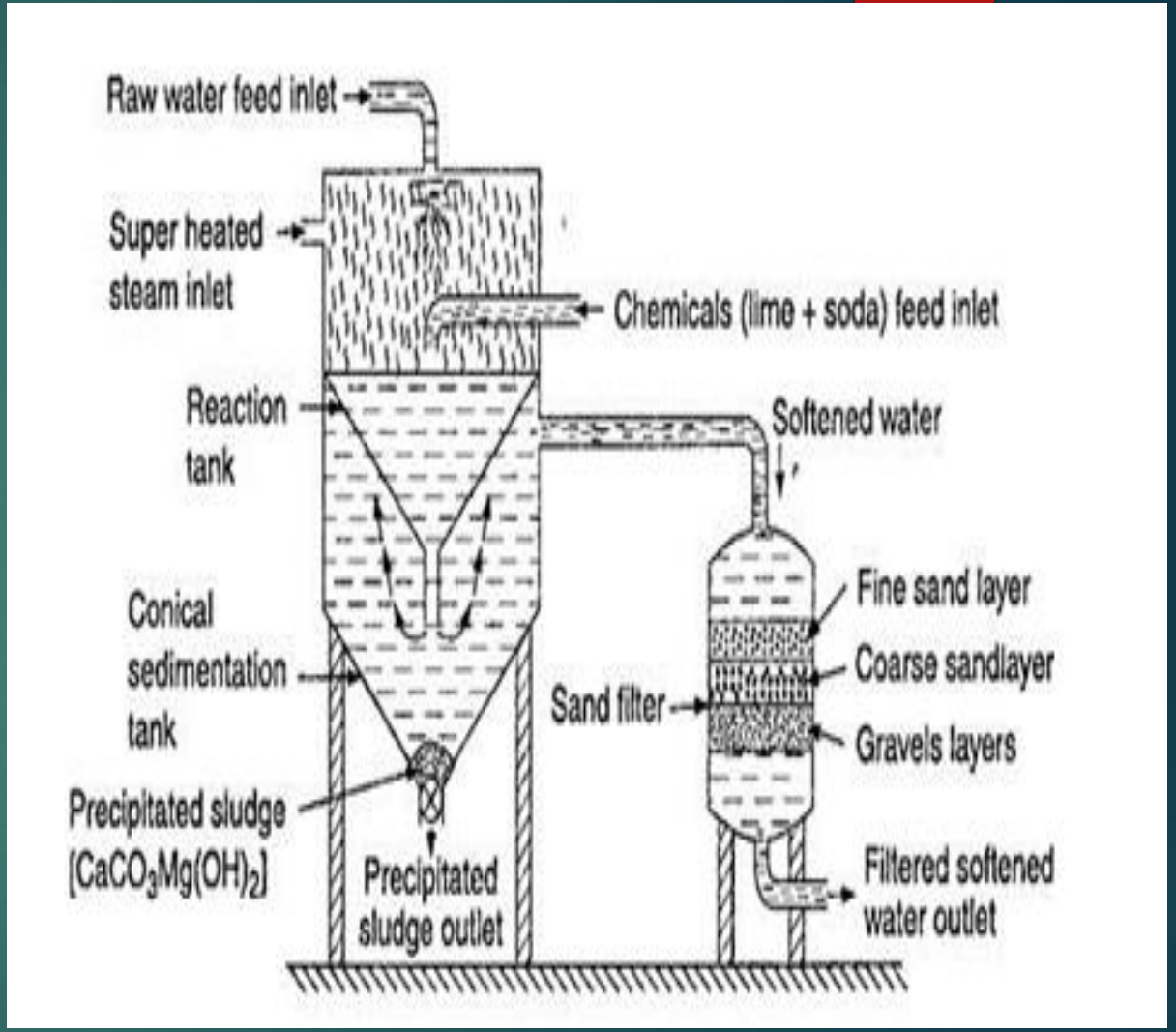
There are two types of lime-soda process; cold lime soda process and hot lime soda process.

- **Cold lime soda process -**
  In the cold lime soda process the reactions take place at normal temperature.
- Calculated quantities of lime and soda are added to the reaction tank.
- Ppt formed is very fine and scattered and is difficult to filter.
- To make the ppt coarse and easily filtrable, coagulants are added. Such as Aluminium Sulphate, Ferrous Sulphate, Sodium Aluminate.
- The residual hardness of the treated water is approx. 50-60 ppm.



Hot lime soda process

- the reactions take place at higher temperature near about boiling point of water (94 – 100 oC)
- Coarse ppt. is formed at high temperature which can be easily filtered off.
- Hence, coagulant is not required.
- The residual hardness of the treated water is approx. 15 – 30 ppm.



Advantages of Hot Lime- Soda process

- This process is more rapid. The process completes in 15 minutes. Whereas cold l process takes several hours to complete.
- The softening capacity of this process is several times higher than the cold process because elevated temperature accelerates the chemical reactions and reduces the viscosity of the water. This increases the rate of aggregation of the particles. Hence, both the settling rates and filtration rates are increased.
- The sludge and the ppt formed settles down rapidly and no coagulant is required.
- Residual hardness is low.
- Quantity of chemicals required is low.

Advantages of Lime- Soda process

- This process is very economical.
- Treated water is alkaline and hence has less corrosion tendencies.
- Iron and manganese are also removed to some extent.
- Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.

Disadvantages of Lime- Soda process

- It requires careful operation and skilled supervision for economical and efficient softening.
- Sludge disposal is a problem.
- The treated water contains soluble salts like sodium sulphate and cannot be used in high pressure boilers.