

## **Engineering Chemistry BT-101**

### **Module 2 Boiler problem & softening methods**

**Topics** - Boiler troubles (Sludge & Scale, Priming & Foaming, Boiler Corrosion, Caustic Embrittlement), Softening methods (Lime-Soda, Zeolite and Ion Exchange Methods) .

#### **Boiler Troubles**

On using hard water, alkaline or acidic water in the boiler the following problems may occur. They are known as boiler problems or boiler troubles.

1. Scale and Sludge
2. Boiler Corrosion
3. Priming & Foaming
4. Caustic Embrittlement

#### **1. Scale and Sludge**

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate, it is called sludge. On the other hand, if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called scale.

#### **Sludge**

Sludge is a soft, loose and slimy precipitate formed within the comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow or at bends. Sludge's are formed by substances which have greater solubility in hot water than in cold water, e.g.,  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , etc.

#### **Disadvantages of Sludge Formation :**

1. Sludges are poor conductor of heat, so they tend to waste a portion of heat generated.
2. If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
3. 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.

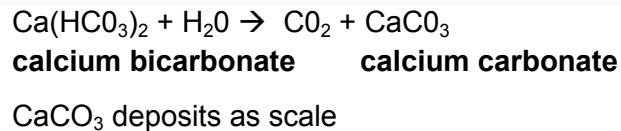
#### **Prevention of Sludge Formation :**

- (1) By using well softened water,
- (2) By frequently blow-down operation', i.e drawing off a portion of the concentrated water.

### **Scale**

Scales are hard deposits, which stick very firmly to the inner surfaces of the boiler. Formation of scales may be due to;

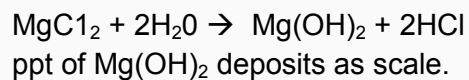
#### **a.Decomposition of calcium bicarbonate**



#### **b.Deposition of Calcium Sulphate**

CaSO<sub>4</sub> is soluble in cold water. As temperature rises solubility of CaSO<sub>4</sub> decreases and it forms hard scale.

#### **c.Hydrolysis of magnesium salts**



**d.Presence of silica (SiO<sub>2</sub>)** Silica combines with calcium or magnesium salts to form silicates which deposit as scales.

### **Disadvantages of scale formation :**

- (1) Wastage of fuel :** Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, excessive or over heating is carried out and this causes increase in fuel consumption.
- (2) Lowering of boiler safety :** Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.
- (3) Decrease in efficiency :** Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially. This results in decrease in efficiency of boiler.

### **Removal of scales :**

- (i) With the help of scraper or piece of wood or wire brush, if they are loosely adhering.

- (ii) By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water), if they are brittle.
- (iii) By dissolving them by adding them chemicals, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes.
- (iv) By frequent blow-down operation, if the scales are loosely adhering.

#### **Prevention of Scales Formation:**

(1) External treatment includes efficient 'softening of water' (i.e. removing hardness producing constituents of water).

(2) Internal treatment : In this process (also called sequestration), an ion is prohibited to exhibit its original character by 'complexing' or converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to boiler water either or to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

Internal treatments methods are, generally, followed by 'blow-down operation', so that an accumulated sludge is removed. Important internal conditioning/treatment methods are;

- (i) Colloidal conditioning : (ii) Phosphate conditioning : (iii) Carbonate conditioning (iv) Calgon conditioning (v) Treatment with sodium aluminate ( $\text{NaAlO}_2$ )

#### **Differences between sludges and scales**

<b>Sludge</b>	<b>Scale</b>
1. Sludges are soft and non-adherent deposits.	1. Scales are hard deposits which stick very firmly to the inner surface of the boiler.
2. Sludges can be removed easily.	2. Scales are very difficult to remove.
3. Sludges can transfer heat to some extent and are less dangerous.	3. Scales are bad conductors of heat and are more dangerous.
4. Sludges are formed by salts like $\text{MgCl}_2$ and $\text{CaCl}_2$ .	4. Scales are formed by salts like $\text{CaSO}_4$ and $\text{Mg(OH)}_2$
5. Can be removed by blow down operation	5. Cannot be removed by blow down operation

2. **Boiler corrosion** - The decay of boiler material by chemical or electrochemical attack by its environment .

#### **Disadvantages**

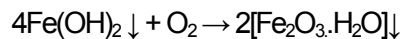
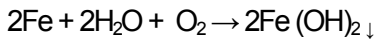
- Leaks in boiler
- Boiler wall may become weak
- Increased cost of repairs and maintenance

### Causes

#### a) By dissolved oxygen :-

Source: Water usually contains about 8ml of dissolved oxygen per litre at room temperature.

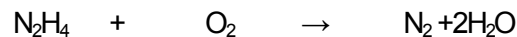
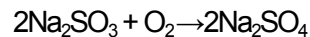
Reaction of corrosion : Boiler wall made of Fe, reacts with dissolved oxygen to produce rust.



Rust

### Removal of dissolved oxygen

By adding Chemicals



Hydrazine

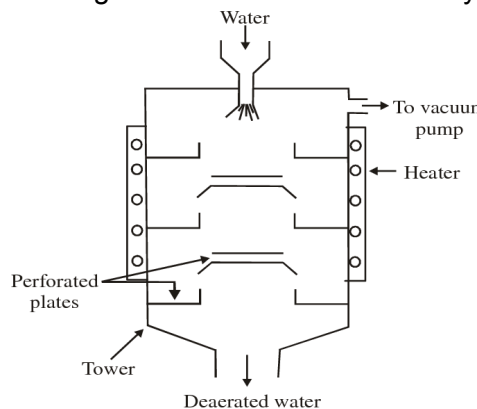
Using hydrazine is ideal method to remove  $\text{O}_2$  because it produces  $\text{N}_2$  which is harmless.

#### b) By dissolved $\text{CO}_2$

Dissolved  $\text{CO}_2$  reacts with water to form  $\text{H}_2\text{CO}_3$  (carbonic acid) which causes boiler corrosion

### Removal of $\text{CO}_2$

By mechanical deaeration - Water is sprayed over hot metallic plates which causes removal of dissolved gases. The gases are then sucked out by vacuum pump.



**Mechanical Deaerator**

### **3. Priming and Foaming**

**Priming** is the carryover of droplets of water in the steam (foam and mist). It is process of formation of wet steam.

#### **Disadvantages of Priming**

**Priming** lowers the energy efficiency of the steam and leads to the deposit of salt crystals on the super heaters and in the turbines.

#### **Causes**

- Priming may be caused by improper construction of boiler or high steam velocity
- Priming is sometimes increased by impurities in the boiler-water.
- Sudden boiling
- Sudden foaming

#### **Prevention**

- Avoiding high water levels, excessive boiler loads, and sudden boiling.

#### **Foaming**

Formation of stable bubbles above the surface of water is called foaming. These bubbles are carried over by steam leading to excessive priming and actual water level in the boiler cannot be known.

#### **Causes**

It is caused by presence of soluble impurities like alkali metal salts and oil.

#### **Control**

- Foaming can be controlled by action of anti-foaming agents like synthetic polyamides
- The most common measure to prevent foaming and priming is to maintain the concentration of solids in the boiler water at low levels.

### **4. Caustic Embrittlement**

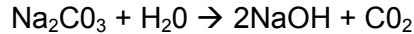
Caustic Embrittlement formation of brittle cracks in the boiler shell due to the accumulation of caustic substances.

#### **Causes**

- Presence of alkali-metal carbonates and bicarbonates in feed water.
- Sodium carbonate is used in softening of water by lime soda process, due to this some sodium carbonate may be left behind in the water.

### Process

$\text{Na}_2\text{CO}_3$  used for softening of water & some of which remain unreacted



As Conc. of NaOH increases, water flows into minute hair cracks by capillary action. As water evaporates, conc. of NaOH increases further and react with iron of boiler, (thereby dissolving Iron of boiler as Sodium ferroate), which causes Embrittlement. This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail.etc.

### Prevention :

1. Use of  $\text{Na}_3\text{PO}_4$  instead of  $\text{Na}_2\text{CO}_3$
2. By adding tanin & lignin that blocks the hair cracks.
3. By adding  $\text{Na}_2\text{SO}_4$  that also blocks the crack.

### Softening Methods

Hard water can be made by the following methods

1. Ion exchange process
2. Lime Soda process
3. Zeolite / Permutit Process

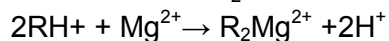
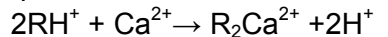
**Ion exchange process** :- Ion exchange resin are insoluble crosslinked ,long chain polymers with a microporous structure,and the functional group attached to the chain are responsible for the ion exchanging properties.Resin containing acidic functional group ( $\text{COOH}$  etc) are capable of exchanging their  $\text{H}^+$  Ion with other cations, which comes in their contact,where as those containing basic functional group ( $-\text{NH}_2$ ) are capable of exchanging their anions with other anions, which comes in their contact.

Cation exchange resin ( $\text{RH}^+$ ) :- These are mainly styrene divinyl benzene copolymers,which on sulphonation ,or carboxylation become capable to exchange their hydrogen ions with the cations in water.

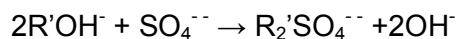
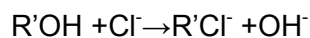
Anion exchange resin( $\text{ROH}^-$ ) :- These are amine formaldehyde copolymers which contain amino or quaternary ammonium group as an integral part of resin matrix, these after treatment with dil. NaOH solution become capable to exchange  $\text{OH}^-$  ion with anions in water.

### Process

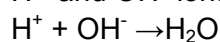
The hard water is passed through cation exchange column, which remove all cations from it and equivalent amount of  $H^+$  ions are released from the column to water, Thus



After cation exchange column, hard water is passed through anion exchange column, which remove all anions like  $Cl^-$  etc present in the water and equivalent amount of  $OH^-$  is released from column in to water

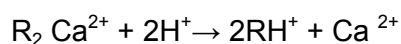


$H^+$  and  $OH^-$  ions combine to produce water molecule

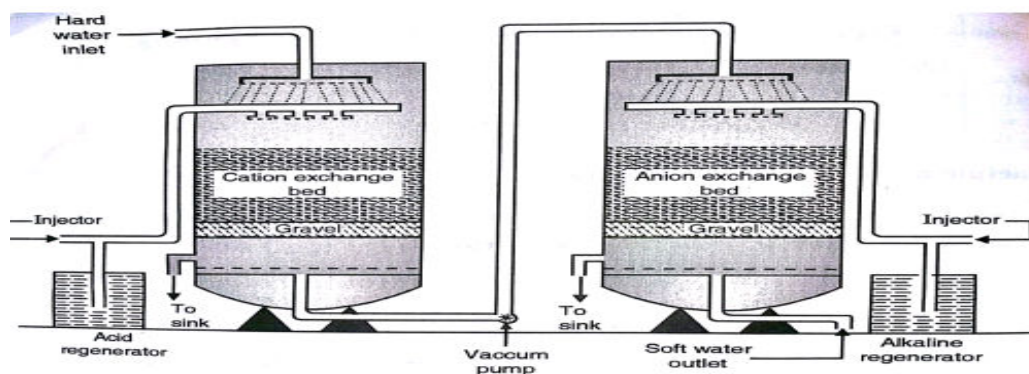
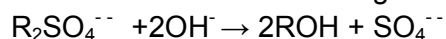


### Regeneration

When capacities of cation and anion exchanger to exchange  $H^+$  ion and  $OH^-$  ion respectively are lost then they are said to be exhausted and are regenerated by passing Dil. HCl in cation exchange column, further column is washed with deionised water and washing are passed to sink.



Anion exchange column is regenerated by passing dil NaOH, further the column is washed with deionised water and washings are passed to sink



### **Advantages**

- No prior knowledge of hardness is required
- It is fast process
- Water with very low residual hardness (0-2 ppm) is obtained

### Disadvantages

- Capital cost of equipment is high
- Chemical are costly

## 2. Permutit Method / Zeolite Method

Permutit method is also known as the zeolite method for water softening.

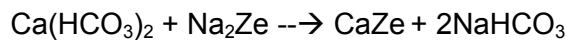
### Definition and principle

Zeolite are hydrated aluminosilicates of sodium. They are are capable of exchanging their  $\text{Na}^+$  ions with hardness producing cations present in water. An example of the of a zeolite is:  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ . Zeolite can be written as  $\text{Na}_2\text{Ze}$

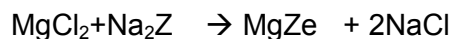
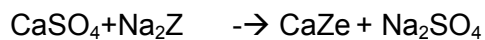
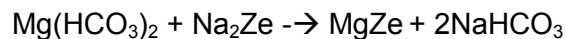
### Process

For softening of water by zeolite process, hard water is allow to flow at a specified rate through a bed of zeolite. Zeolite holds sodium ion loosely and can be represented as  $\text{Na}_2\text{Ze}$ , where Ze represents insoluble radical frame work.

When the water passes through the zeolite the hardness causing ions ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  etc.) are retained by the zeolite as  $\text{CaZe}$  and  $\text{MgZe}$  respectively, while the outgoing water contains equivalent amount of sodium salts. The block diagram and chemical reactions taking place in zeolite softener are:



Zeolite



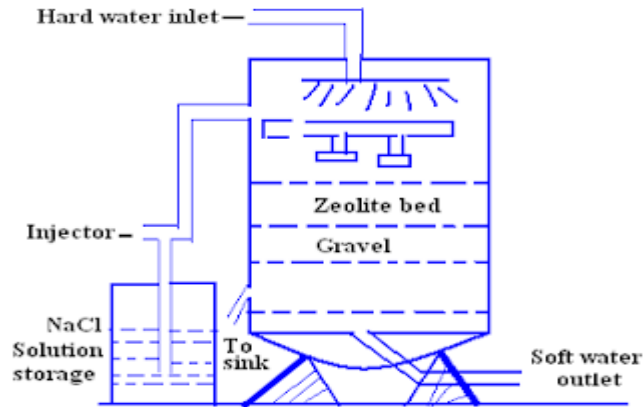
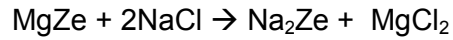
### Regeneration

After some time, when the zeolite is completely changed into calcium and magnesium zeolites, then it gets exhausted (saturated with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions) and it ceases to soften water. It can be regenerated and reused by treating it with a 10% brine (sodium chloride) solution.





Exhausted zeolite                      Regenerated zeolite



#### Merits of Zeolite Process:

- It removes the hardness almost completely (about 10 ppm hardness only).
- The process is fast and equipment occupies less space
- 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.
- High turbidity water cannot be softened efficiently by zeolite process.

### 3 Lime Soda Process of Water Softening

**Lime-soda principle:** The basic principle in this method is to convert all the soluble hardness causing constituents into insoluble precipitates by appropriate chemical reactions. In this process, a suspension of calcium hydroxide (lime ( $\text{Ca}(\text{OH})_2$ ) and sodium carbonate (soda ( $\text{Na}_2\text{CO}_3$ )) is added to water in calculated quantities based on the concentration of impurities. By this process soluble magnesium and calcium salts are removed as calcium carbonate and magnesium hydroxide precipitated. After removal of this precipitated, we obtain soft water.

#### Reactions involved in treatment:

- 1)  $\text{Ca (OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$
- 2)  $\text{Ca (OH)}_2 + \text{Ca (HCO}_3)_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$
- 3)  $\text{Ca (OH)}_2 + \text{Mg(HCO}_3)_2 \rightarrow \text{MgCO}_3 + \text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$
- 4)  $\text{Mg}^{+2} + \text{Ca (OH)}_2 \rightarrow \text{Mg (OH)}_2 + \text{Ca}^{2+}$
- 5)  $\text{Ca}^{+2} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$
- 6)  $\text{CO}_2 + \text{Ca (OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
- 7)  $2\text{H}^+ + \text{Ca (OH)}_2 \rightarrow \text{Ca}^{+2} + 2\text{H}_2\text{O}$
- 8)  $\text{Fe}^{2+} + \text{Ca (OH)}_2 \rightarrow \text{Ca}^{+2} + \text{Fe (OH)}_2$
- 9)  $\text{Al}_2 (\text{SO}_4)_3 + 3\text{Ca (OH)}_2 \rightarrow 3\text{CaSO}_4 + 2\text{Al (OH)}_3$
- 10)  $3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{Na}_2\text{SO}_4 + 3\text{CaCO}_3$

### **Process**

Raw water along with calculated amount of lime and soda are added in a large tank. Cold lime soda method also requires coagulants for producing thick precipitate so that it filters easily. The precipitate formed is separated from water to obtain soft water.

### **Advantages of Lime-soda process**

1. The pH of soft water is higher which prevents corrosion of the distribution pipes.
2. Amount of impurities such as iron and manganese are also decreased.
3. Water produced after treatment is of alkaline nature so amount of micro organism are reduced.
4. It is very economical method.

### **Disadvantages of Lime-Soda process:**

1. This process cannot be used for domestic purpose because it is difficult to find amount of lime-soda required.
2. Skilled and careful supervision is required for efficient and economical operation.

3. It creates the problem of disposal of sludge.
4. The hardness of water is not completely removed.

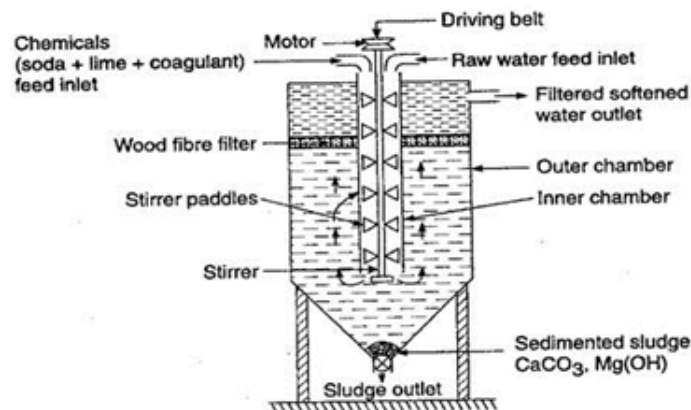
### Types of Lime Soda Method

A) Cold Lime Soda Method B) Hot Lime Soda Method

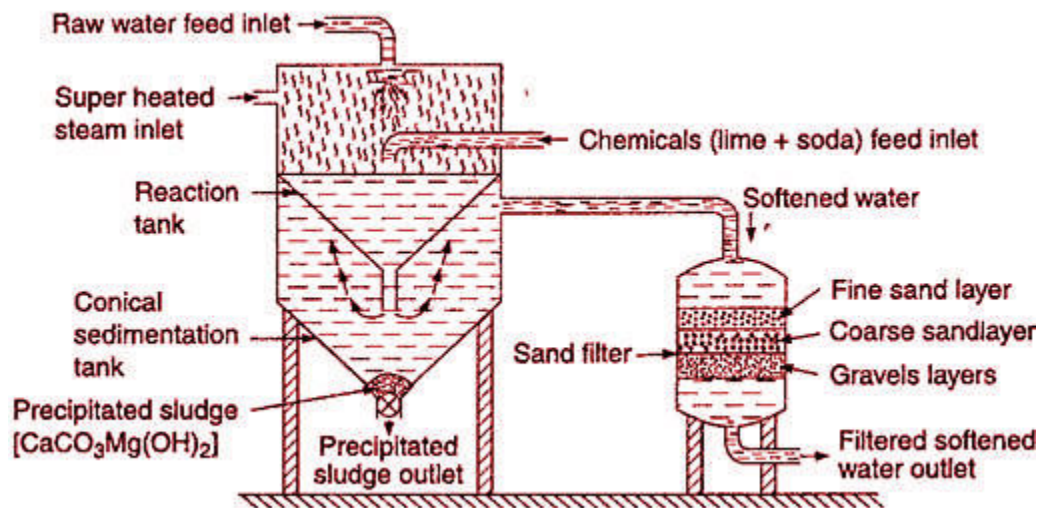
Difference between hot and cold lime soda method

Cold lime soda process	Hot lime soda process
1. It is carried out at room temperature (25-30°C)	1. It is carried out at high temperature (95-100°C)
2. It is a slow process	2. It is a rapid process
3. Use of coagulant is a necessary	3. No coagulant required
4. Filtration is not easy	4. Filtration is easy as viscosity of water is low
5. Residual hardness is 60 ppm	5. Residual hardness is 15—30 ppm
6. Dissolved gases are not removed	6. Dissolved gases are removed
7. It has low softening capacity	7. It has high softening capacity

In the **cold lime soda process** the reactions take place at normal temperature. The raw water is passed into a tank with a continuous flow, at the same time a calculated amount of chemical mixture of lime and soda and coagulant are also added and then thoroughly mixed with a stirrer in this inner tank. Afterward this precipitate formed is allowed to settle. When the settlement becomes complete the water is passed by continuous up-flow process into another tank which is called outer tank. Then soft water is obtained.



**Continuous Cold Lime Soda Method**



### Continuous Hot Lime Soda Method

In the **hot lime soda process** the reactions take place at higher temperature near about boiling point of water. The chemical mixing process is same as the cold lime soda process, but steam is applied in mixture tank. As a result precipitation becomes almost complete very quickly. This process is more effective than cold lime soda process. Soft water is filtered through a separate filter.

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