CE 370

Lime-Soda Softening

Definition

- **Lime-Soda Softening**:

  is a process used in water treatment to remove Hardness from water.

- **What is Hardness**:

  Hardness of water is a measure of its capacity to precipitate soap and is caused mainly by the presence of divalent cations of calcium (Ca^{+2}) and magnesium (Mg^{+2}). Other multivalent cations also cause water hardness such as Fe^{+3}, Sr^{+2}, Zn^{+2}, Mn^{+2}.

Types of Hardness

- **Total Hardness (TH)**

  Hardness caused by calcium ions and magnesium ions. Calcium and magnesium are normally the only significant minerals that cause hardness, so it is generally assumed that:

  Total Harness (TH) = Ca^{+2} hardness + Mg^{+2} hardness

Types of Hardness

- **Carbonate Hardness (CH):**

  Carbonate hardness is caused primarily by the bicarbonate salts of calcium and magnesium, which are calcium bicarbonate, $Ca(HCO_3)_2$, and magnesium bicarbonate $Mg(HCO_3)_2$. Calcium and magnesium combined with carbonate (CO_3) also contribute to carbonate hardness.

- **Non-Carbonate Hardness (NCH):**

  Non-carbonate hardness is a measure of calcium and magnesium salts other than carbonate and bicarbonate salts. These salts ate calcium sulfate ($CaSO_4$), calcium chloride ($CaCl_2$), magnesium sulfate ($MgSO_4$), and magnesium chloride ($MgCl_2$). Therefore, non-carbonate hardness is hardness exceeding carbonate hardness.

Types of Hardness

If the total hardness (TH) is greater than alkalinity (ALK), then:

Carbonate Hardness (CH) = alkalinity (ALK)

Non-carbonate Hardness (NCH) = total hardness – carbonate hardness (CH)

If the total hardness (TH) is less than alkalinity (ALK), then:

Carbonate Hardness (CH) = total hardness (TH)

Non-carbonate Hardness (NCH) = 0

Hardness - Example

Problem:

A sample of water has 210 mg/l alkalinity, 330 mg/l total hardness and 290 mg/l calcium hardness. Find out the following?

a) Magnesium hardness

b) Carbonate hardness

c) Non-carbonate hardness.

Solution:

a) Mg hardness = TH – Ca hardness = 330-290 = 40 mg/l

Since TH is greater than Alk

b) Carbonate hardness = ALK = 210 mg/l

c) Non-Carbonate hardness = TH – CH = 330-210 = 120 mg/l

Water Hardness

- Public tolerance of hardness varies, however, a level ranging from 60 to 120 mg/l as $CaCO_3$ is generally acceptable.
- Disadvantages of hardness
  - excessive soap consumption during laundering
  - scale-formation in hot water heaters and pipes.
- The use of synthetic detergents and pipe linings can overcome those problems.

Hardness Ranges

Hardness Concentration (mg/l)	Degree of Hardness
0 – 60	Soft
60 – 120	Moderately Hard
120 – 180	Hard
180 and Over	Very Hard

Lime-Soda Softening

- In this process Calcium and Magnesium ions are precipitated by the addition of lime ($Ca(OH)_2$) and soda ash (Na_2CO_3). Following are the reactions that takes place in this process:
  - As slacked lime is added to a water, it will react with any carbon dioxide present as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O ....(1)$$

  - The lime will react with carbonate hardness as follows:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O .....(2)$$

$$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 \downarrow + 2H_2O .....(3)$$

Lime-Soda Softening

- The product magnesium carbonate in equation 3 is soluble. To remove it, more lime is added:

$$Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 \downarrow + Mg(OH)_2 \downarrow .....(4)$$

- Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:

$$Ca(OH)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(OH)_2 \downarrow .....(5)$$

- Lime addition removes only magnesium hardness and calcium carbonate hardness. In equation 5 magnesium is precipitated, however, an equivalent amount of calcium is added. The water now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5. Soda ash is added to remove calcium non-carbonate hardness

$$Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3 \downarrow .....(6)$$

Lime-Soda Softening

- To precipitate $CaCO_3$ requires a pH of about 9.5; and to precipitate $Mg(OH)_2$ requires a pH of about 10.8, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.

- The amount of lime required:

  lime (meq/l) = carbon dioxide (meq/l) + carbonate hardness (meq/l) + magnesium ion (meq/l) + 1.25 (meq/l)

- The amount of soda ash required:

  soda ash (meq/l) = non-carbonate hardness (meq/l)

Lime-Soda Softening

- After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate. Recarbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:

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

$$CO_2 + Mg(OH)_2 \rightarrow MgCO_3 + H_2O$$

Further recarbonation, will bring the pH to about 8.5 and stablize the calcium carbonate as the following:

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2$$

It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

Lime

- Lime is commercially available in the forms of:
  - quicklime
  - hydrated lime
- Quicklime
  - available in granular form
  - contains minimum of 90% CaO
  - magnesium oxide is the primary impurity
- Hydrated Lime
  - contains about 68% CaO
- Slurry lime is written as $Ca(OH)_2$.

Example 8.3 (from text)

- **Problem:**

  A water that is to be softened by lime-soda process has the following concentrations:

CO_2	8 mg/l
Ca^{+2}	65 mg/l
Mg^{+2}	32 mg/l
HCO^-_3	260 mg/l

  Determine the CaO and soda ash required per million liters if the purities are 85 and 95%, respectively. Use meq/l as the basis of computations for Alkalinity and hardness, instead of mg/l as $CaCO_3$

- **Solution:**
  - Calculate the concentrations in meq/l.

    for CO_2:

    MW = 12+2(16) = 44 g/mole Valence (Z) = 2 eq/mole

    eq. wt. = 44/2 = 22 g/eq or 22 mg/ meq

    Concentration, meq/l = 8/22 = 0.36 meq/l

Example 8.3 (from text)

– The following Table can be constructed:

Ion	Conc., mg/l	Conc., meq/l
CO_2	**8**	**0.36**
Ca^{+2}	**65**	**3.25**
Mg^{+2}	**32**	**2.67**
HCO^-_3	**260**	**4.26**

Total hardness (TH) = $Ca^{+2} + Mg^{+2}$ = 3.25 + 2.67 = 5.92 meq/l

Alkalinity = HCO^-_3 = 4.26 meq/l

TH is greater than Alk, therefore:

carbonate hardness (CH) = alk = 4.26 meq/l

non-carbonate hardness = TH – CH = 5.92- 4.26 = 1.66 meq/l

Lime requirement = CO_2 + CH + Mg^{+2} + excess

= 0.36 + 4.26 + 2.67 + 1.25 = 8.54 meq/l

The soda ash requirement = NCH = 1.66 meq/l

Example 8.3 (from text)

– **Calculate requirement of lime (CaO) and soda ash (Na_2CO_3) in kg per million liters.**

eq. wt. CaO = (40+16)/2 = 28 mg/meq

eq. wt. Na_2CO_3 = (2(23)+12+3(16))/2 = 53 mg/meq

CaO required = 8.53 meq/l × 28 mg/meq = 239.0 mg/l

Na_2CO_3 required = 1.66 meq/l × 53 mg/meq = 88.0 mg/l

Lime per million liters = 239 mg/l × 10^{-6} kg/mg × 10^6 *l*/ML × 1/0.85 = 281.2 kg/ML

Soda per million liters = 88 mg/l × 10^{-6} kg/mg × 10^6 *l*/ML × 1/0.95 = 92.6 kg/ML