Islamic University of Gaza -Environmental Engineering Department

Water Treatment

EENV 4331

Lecture 6: Softening

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6. Hardness and Softening in water Treatment

6.1 Definition of hardness:

A. Hardness is the term often used to characterize a water that :

- Dose not form a foam or lather well and cause soap scum

  $Ca^{2+} + (Soap)^{-} \leftrightarrow Ca(Soap)_{2\ (s)}$ (soap scum)

  This increase the amount of soap needed for washing

- cause scaling on pipes and hot boilers.
- cause valves to stick due to the formation of calcium carbonate crystals
- leave stains on plumbing fixtures

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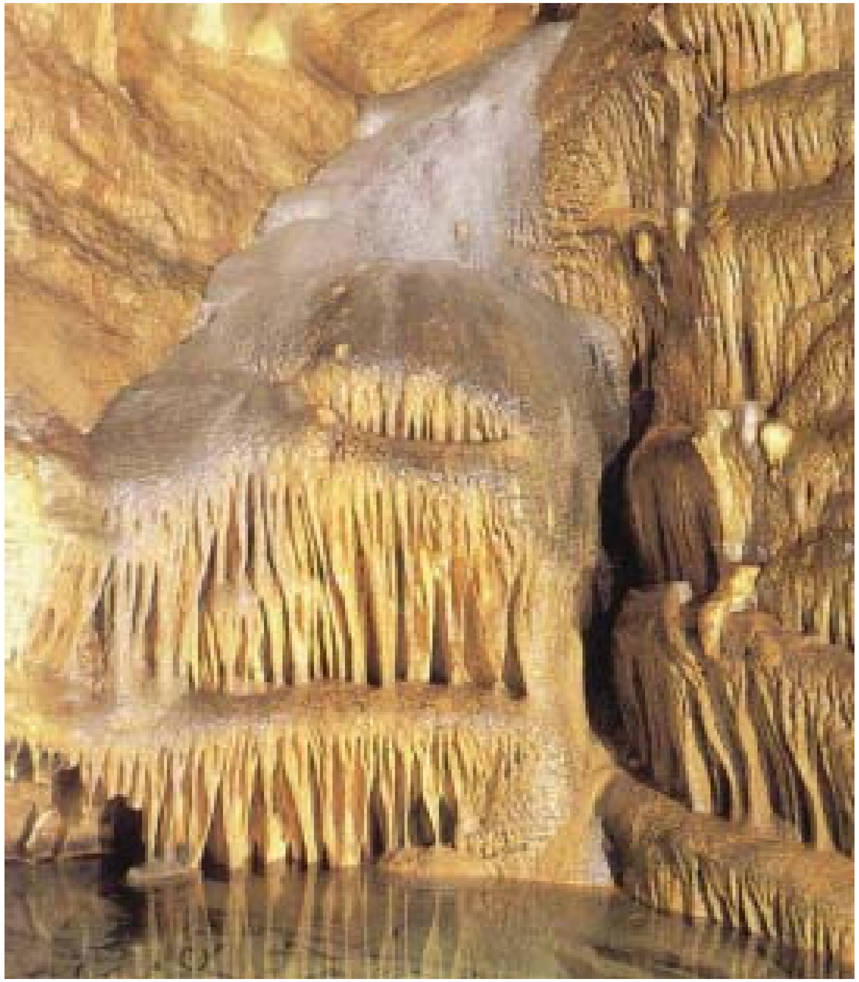

Figure 6.1:
Scaling due to calcium and magnesium precipitation

6. Hardness and Softing in water Treatment

B. Hardness is defined as the sum of the divalent metal cations (in consistent units) existing in water such as :

Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+}

Practically most hardness is due to Ca^{2+} , Mg^{2+} ions (the predominant minerals in natural waters)

C. Total Hardness = Ca^{2+} hardness+ Mg^{2+} hardness

where the concentration of each ion is in consistent units such as mg/L as Ca CO_3, or meq/L.

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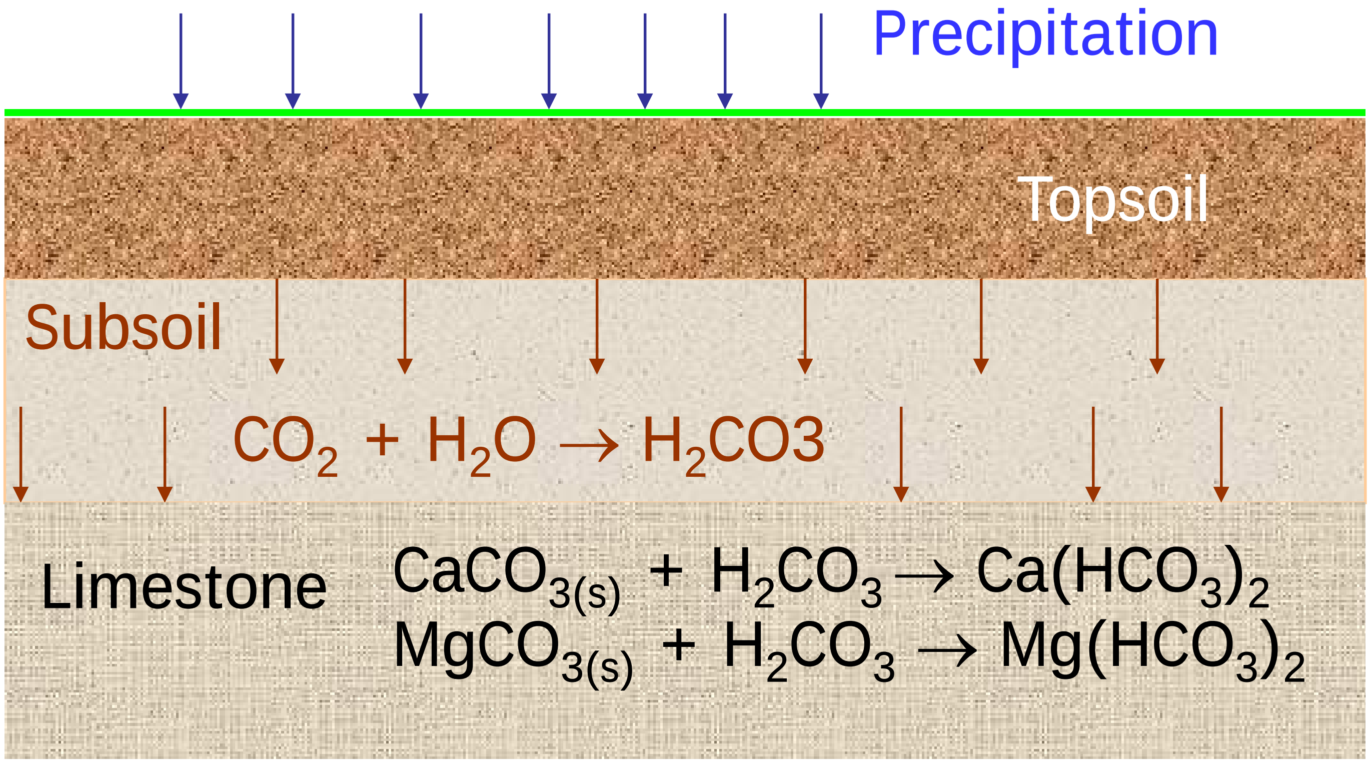
D. Hard water classification

Description	Hardness range (mg/L as $CaCO_3$)
Soft	0 - 75
Moderately hard	75 - 100
Hard	100 - 300
Very hard	> 300

6. Hardness and Softening in water Treatment

E. Formation of Hardness



6. Hardness and Softening in water Treatment

F. Carbonate and non carbonate Hardness

- Carbonate Hardness (CH)
  - Ca^{2+}, Mg^{2+} associated with HCO_3^-, CO_3^{2-}
  - Often called "temporary hardness" because heating the water will remove it. When the water is heated, the insoluble carbonates will precipitate and tend to form bottom deposits in water heaters.
- Non-Carbonate Hardness (NCH)
  - Ca^{2+}, Mg^{2+} associated with other ions, Cl^-, NO_3^-, SO_4^{2-}
  - NCH = TH – CH

6. Hardness and Softening in water Treatment

F. Hardness Units

Total Hardness = ∑ ($Ca^{2+} + Mg^{2+}$)

The hardness unit is the same as that consistent unit used for both of the above ions. The most used units are:

$$\boxed{\text{mg/L as } CaCO_3 = (\text{mg/L as species})\frac{\text{EW of } CaCO_3}{\text{EW of species}}}$$

Where,

EW = equivalent weight

Species = Ion or Radical or Compound

Radical: such as CO_3^{2-}, SO_4^{2-}

Compounds: such as CO_2, $CaSO_4$

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$$EW = \frac{MW}{\text{Electrical Charge}}$$ → For radicals and compounds

$$EW = \frac{MW}{\text{Valance}}$$ → For ions

MW = molecular weight of the Species

Example 3.1 : a) **Find the EW of Mg^{2+} that has a concentration of 10 mg/L as the ion in water.** b) **Find the EW of $CaCO_3$** c) **find concentration of Mg^{2+} as mg/L $CaCO_3$.**

a) **Finding the EW for Mg^{2+} :**

$$MW = 24.3 \frac{g}{mole} \longrightarrow MW = 24.3 \frac{mg}{mmole}$$

$$\text{Valance (n)} = \frac{2\ eq}{mole} \longrightarrow \text{Valance (n)} = \frac{2\ meq}{mmole}$$

$$EW = \frac{MW}{\text{Valance}} \longrightarrow EW = \frac{24.3\ mg}{mmole} \cdot \left[\frac{1}{2\ \ meq/mmole}\right] \longrightarrow EW = 12.15 \frac{mg}{meq}$$

6. Hardness and Softening in water Treatment

b) Finding the EW for $CaCO_3$:

$$MW = 100 \frac{g}{mole} \longrightarrow MW = 100 \frac{mg}{mmole}$$

$$\text{Electrical charge (n)} = \frac{2 \text{ eq}}{mole} \longrightarrow \text{Electrical charge} = \frac{2 \text{ meq}}{mmole}$$

$$EW = \frac{MW}{\text{Electrical Charge}} \longrightarrow EW = \frac{100 \text{ mg}}{mmole} . [\frac{1}{2 \text{ meq/mmole}}] \longrightarrow EW = 50 \frac{mg}{meq}$$

D) Finding the Mg^{2+} concentration as $CaCO_3$:

$$\boxed{\text{mg/L as } CaCO_3 = (\text{mg/L as species}) \frac{\text{EW of } CaCO_3}{\text{EW of species}}}$$

Mg $^{2+}$ conc.

$$(Mg2+) \text{ in mg/L as } CaCO_3 = (10 \text{ mg/L as Mg } 2+) \frac{50 \text{ mg/meq}}{12.15 \text{ mg/meq}} \longrightarrow 41.15 \text{ mg/L as } CaCO_3$$

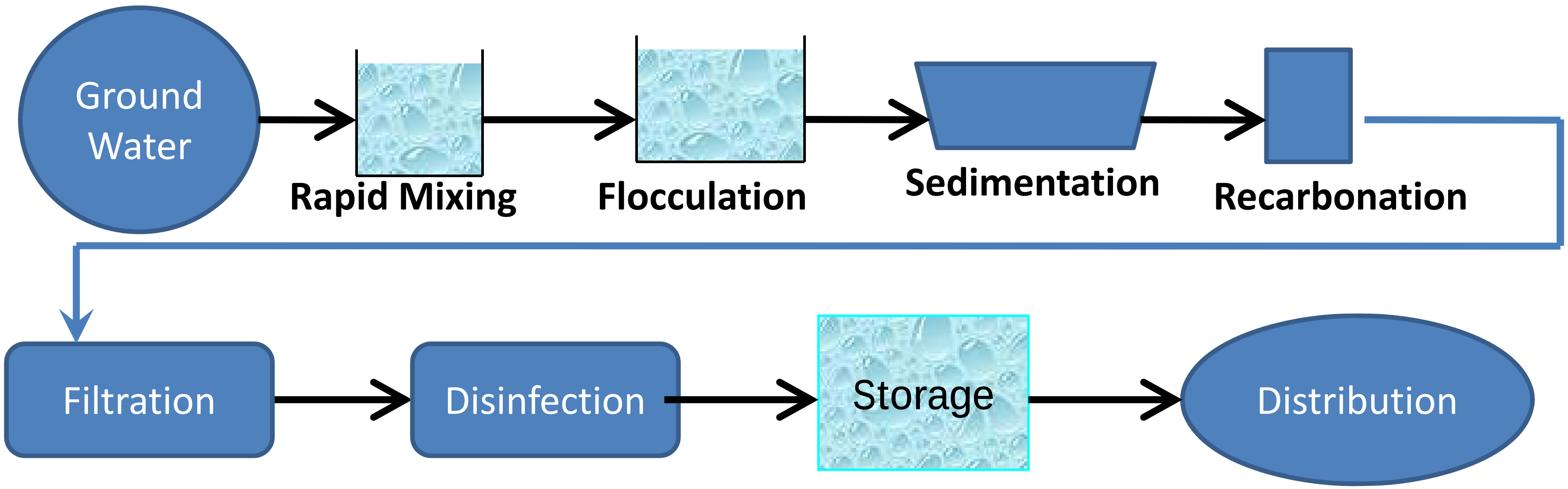


Figure 6.2: Softening Treatment Plant Single stage softening

6. Hardness and Softening in water Treatment

6.2 Relation between Alkalinity and hardness:

A. Definition of Alkalinity

Alkalinity is a very important parameter in water chemistry and related very closely to hardness and softening process. The following equation is used to measure the alkalinity in water:

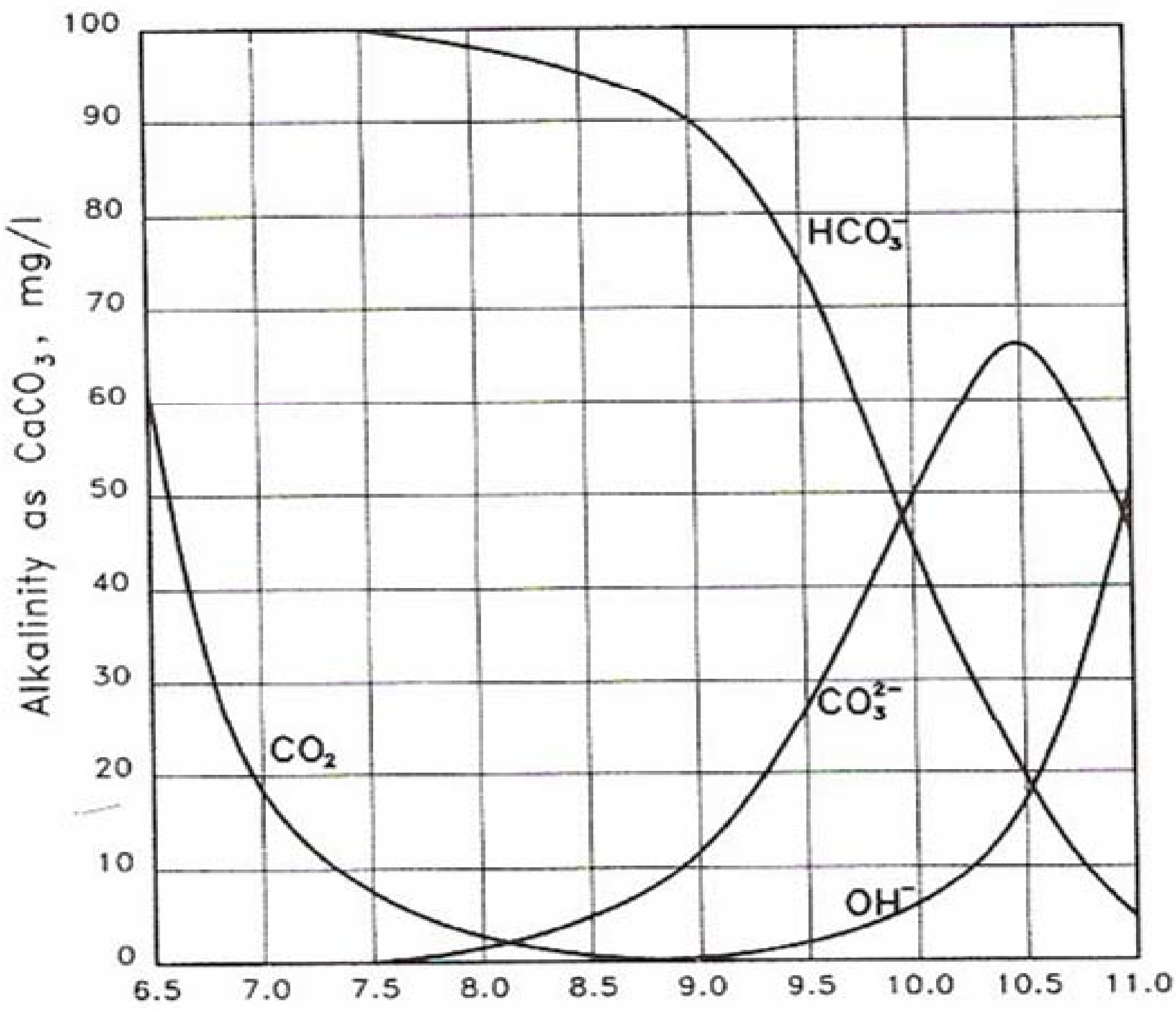
- **Alkalinity = (HCO_3^-) + (CO_3^{2-}) + (OH^-) - (H^+)**

- **Where the concentrations are in meq/L or mg/L as $CaCO_3$ Usually the (OH^-) and (H^+) are negligible.**
- **The relation between the** alkalinity species **is given by the following three equations:**

$$\boxed{10^{-10.33} = \frac{[H^+][CO^{2-}_3]}{[HCO3\text{-}]}} \quad , \quad \boxed{10^{-14} = \left[H^+\right] \bullet \left[OH^-\right]} \quad , \quad \boxed{\left[H^+\right] = 10^{-pH}}$$

Where the concentrations are moles/ L in these three equations

Various Forms of alkalinity and CO_2 relative to pH in water at 25 ^oC.



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Example 6.1:

A sample of water having a pH of 7.2 has the following concentrations of ions

Ca^{2+}	40 mg/L
Mg^{2+}	10 mg/L
Na^{+}	11.8 mg/L
K^{+}	7.0 mg/L
HCO_3^{-}	110 mg/L
SO_4^{2-}	67.2 mg/L
Cl^{-}	11 mg/L

- Construct a bar chart of the ions in term of mg/L $CaCO_3$
- Calculate the TH, CH, NCH, Alkalinity

6. Hardness and Softening in water Treatment

Example 6.1:

Ion	Conc. mg/L	M.W. mg/mmol	|n|	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as $CaCO_3$
Ca^{2+}	40.0	40.1	2	20.05	1.995	99.8
Mg^{2+}	10.0	24.3	2	12.15	.823	41.2
Na^{+}	11.8	23.0	1	23.0	.51	25.7
K^{+}	7.0	39.1	1	39.1	.179	8.95
HCO_3^{-}	110.0	61.0	1	61.0	1.80	90.2
SO_4^{2-}	67.2	96.1	2	48.05	1.40	69.9
Cl^{-}	11.0	35.5	1	35.5	.031	15.5

6. Hardness and Softening in water Treatment

Check The ionic balance:

Σ(cations) = Σ(anions)

175.6 = 175.6 mg/L as $CaCO_3$ O.K

3.51 = 3.23 meq/L O.K

Note: (error in the range of $\pm$ 10% is accepted)

Note: one check is enough (either as {mg/L as CaCO3 } or as {meq/L})

- Total Hardness = Σ $(Ca^{2+}) + (Mg^{2+})$= 99.8 + 41.2

  TH =141 mg/L as $CaCO_3$

  or TH= 1.995 + 0.823 = 2.818 meq/L

6. Hardness and Softening in water Treatment

- Alkalinity = $(HCO_3^-) + (CO_3^{2-}) + (OH^-) - (H^+)$

a. Since pH = 7.2 $\rightarrow$

$[H^+] = 10^{-pH} = 10^{-7.2}$ mole/L = $10^{-7.2}$ g/L

$$\boxed{eq/L = \frac{10^{-7.2}\ g\ H^+/L}{1\ g/eq}} \longrightarrow \boxed{(H^+) = 10^{-7.2}\ eq/L}$$

b. $$\boxed{10^{-14} = [H^+] \bullet [OH^-]} = \boxed{10^{-14} = 10^{-7.2} \bullet [OH^-]} \longrightarrow \boxed{[OH^-] = 10^{-6.8}\ mole/L}$$

$$\boxed{[OH^-] = 10^{-6.8}\ mole/L = 17 * 10^{-6.8}\ g/L} \longrightarrow \boxed{eq/L = \frac{17 * 10^{-6.8}\ g\ OH^-/L}{17\ g/eq}} \longrightarrow \boxed{(OH^-) = 10^{-6.8}\ eq/L}$$

C. $\mathbf{(HCO_3^-)}$ = 1.80 meq/L = **$1.80 * 10^{-3}$ eq/L** from this example calculations as in the table.

g/L **as HCO_3^-** = EW * eq/L = (61 g/eq) * $1.80 * 10^{-3}$ g/L = $109.8 * 10^{-3}$ g/L

$\mathbf{[HCO_3^-]}$ = ($109.8 * 10^{-3}$ g/L)/(61g/mole) = **$1.80 * 10^{-3}$ mole/L**

6. Hardness and Softening in water Treatment

d. Find the carbonate concentration:

$$10^{-10.33} = \frac{[H^+][CO^{2-}_3]}{[HCO3-]} \longrightarrow 10^{-10.33} = \frac{10^{-7.2}\, x[CO^{2-}_3]}{1.8 \text{ x } 10^{-3}} \longrightarrow$$

$[CO_3^{2-}]$= 1.33 x 10^{-6} mole/L = 79.8 x 10^{-6} g/L

CO_3^{2-} in $$eq/L = \frac{79.8 * 10^{-6} \text{ g /L}}{30 \text{ g/eq}}$$ = 2.66 x 10^{-6} eq/L

Alkalinity = (1.80 x 10^{-3}) + (2.66 x 10^{-6}) + $10^{-6.8}$ - $10^{-7.2}$ = 1.801 x 10^{-3} eq/L

Alkalinity = 1.801 x 10^{-3} x 1000 x 50 = 90.1 mg/L as $CaCO_3$

Note: it is clear that the most effective form of alkalinity is bicarbonate, this is always true when the pH is 8.3 or less.

6. Hardness and Softening in water Treatment

- Carbonate Hardness

the portion of the hardness associated with carbonate or bicarbonate

- Alkalinity = 90.1 mg/L as $CaCO_3$

  TH = 141 mg/L as $CaCO_3$

  CH = 90.2 mg/L as $CaCO_3$

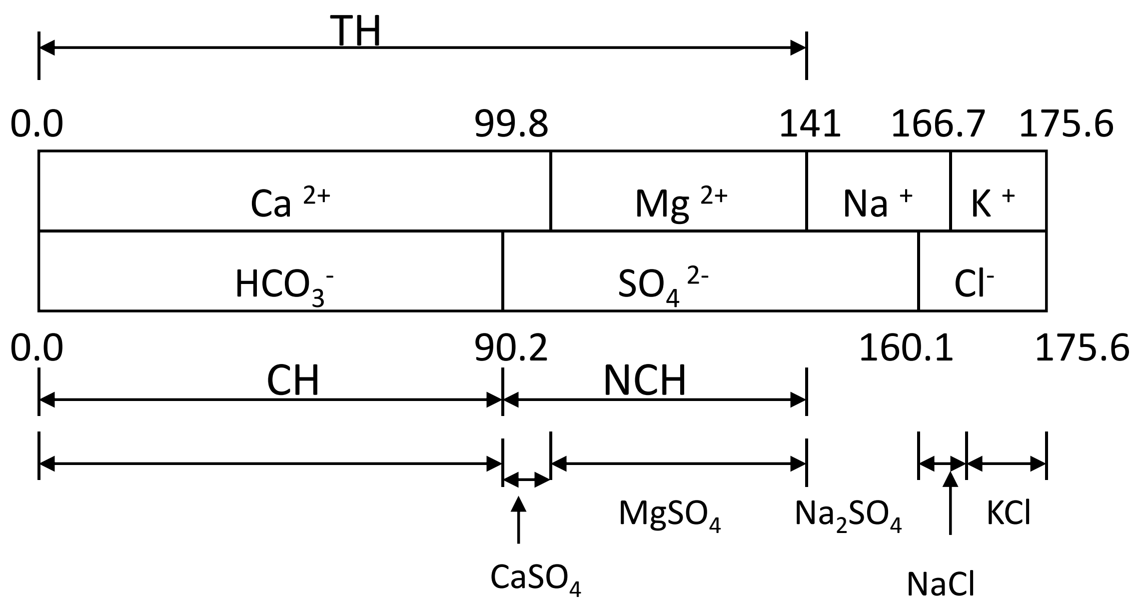
- Non-carbonate Hardness:

  NCH = TH - CH

  = 141 - 90.1= 50.9 mg/L as $CaCO_3$

6. Hardness and Softening in water Treatment

Construct the bar chart of the ions in term of mg/L $CaCO_3$



Note: the chemicals at the lower line of the bar graph is called the **hypothetical combination** of positive and negative ions in the water sample

6. Hardness and Softening in water Treatment

6.3 Softening definition:

a) Softening is the chemical processes in which hardness causing ions (Ca^{2+} , Mg^{2+}) are removed from water ether completely or partially.

b) Softening may be a chivied by chemical precipitation using the Lime- Soda Ash method or by ion exchange.

c) In the chemical precipitation method the objective is to produce $CaCO_3$ and $Mg(OH)_2$:

$$Ca^{2+} + CO_3^{2-} \leftrightarrow 2CaCO_{3(s)}$$

$$Mg^{2+} + 2OH^{-} \leftrightarrow Mg(OH)_{2(s)}$$

These two reactions are achieved by the addition of Lime [$Ca(OH)_2$] and Soda ash [Na_2CO_3] as will be shown.

6. Hardness and Softening in water Treatment

f) A common water treatment goal is to provide a water with a hardness in the range of 75 to 120 mg/L as $CaCO_3$

g) To precipitate $CaCO_3$ and $Mg(OH)_2$ we need to raise the pH to 10.3 by the addition of Lime $[Ca(OH)_2]$. The addition of the OH- will convert HCO_3^- to CO_3^{2-}

h) To precipitate $Mg(OH)_2$ we need to raise the pH to 11 by the addition of Soda ash $[\ Na_2CO_3]$. This will add the CO_3^{2-} ion needed to react with the remaining Ca^{2+}

i) Some of the added lime $[Ca(OH)_2]$ is consumed to remove CO_2 which is necessary to raise the pH.

6. Hardness and Softening in water Treatment

6.4 Chemistry of Lime- Soda Ash Softening

softening reactions

- Neutralization of carbonic acid

  [To raise the pH we need first to neutralize any acid in the water]

  $CO_2 + Ca(OH)_2 \leftrightarrow CaCO_{3(s)} + H_2O$
- Precipitation of CH due to calcium:

  [To raise the pH to 10.3 all the HCO_3^- is converted to CO_3^{2-}]

  $Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \leftrightarrow 2CaCO_{3(s)} + 2H_2O$
- Precipitation of CH due to magnesium

  [To raise the pH to 11 add more lime]

$Mg^{2+} + 2HCO_3^- + Ca(OH)_2 \leftrightarrow Mg^{2+} + CO_3^{2-} + CaCO_{3(s)} + 2H_2O$

$Mg^{2+} + CO_3^{2-} + Ca(OH)_2 \leftrightarrow MgOH_{2(s)} + CaCO_{3(s)}$

6. Hardness and Softening in water Treatment

6.4 Chemistry of Lime- Soda Ash Softening

- Removal of NCH due to calcium

$Ca^{2+} + SO_4^{-2} + Na_2CO_3 \leftrightarrow CaCO_{3(s)} + 2Na^{+} + SO_4^{-2}$

$Ca^{2+} + 2Cl^{-1} + Na_2CO_3 \leftrightarrow CaCO_{3(s)} + 2Na^{+} + 2Cl^{-1}$

- Removal of NCH due to magnesium

$Mg^{2+} + Ca(OH)_2 \leftrightarrow MgOH_{2(s)} + Ca^{2+}$

$Ca^{2+} + Na_2CO_3 \leftrightarrow CaCO_{3(s)} + 2Na^{+}$

6. Hardness and Softening in water Treatment

6.4 Chemistry of Lime- Soda Ash Softening

Softening process limitations:

1. Lime-Soda softening cannot produce a water completely free of hardness because of the solubility of $CaCO_3$ and $Mg(OH)_2$, limitations of mixing and reaction time .
2. Thus , the minimum calcium hardness that can be achieved is 30 mg/L as $CaCO_3$, the minimum Magnesium hardness that can be achieved is 10 mg/L as $CaCO_3$, this gives a minimum hardness of 40 mg/L as $CaCO_3$.
3. However, normally the water is treated to give a hardness in the range of 75 to 120 mg/L as $CaCO_3$.
4. An Excess lime beyond the stoichiometric amount is usually added to remove Mg^{2+} hardness . The minimum excess lime is usually 20 mg/L as $CaCO_3$, maximum excess lime is 62.5 mg/L as $CaCO_3$ (1.25 meq/L).
5. Mg^{2+} in excess of 40 mg/L as $CaCO_3$ is not desired as it forms scale in water heaters. Mg^{2+} is expensive to remove, so we only remove Mg^{2+} in excess of 40 mg/L as $CaCO_3$.

6. Hardness and Softening in water Treatment

6.4 Chemistry of Lime- Soda Ash Softening

Chemicals requirements:

According to the softening chemical reactions:

-Lime is added at the ratio of 1:1 for each carbonate hardness compound except for $Mg(HCO_3)$ the ratio is 2:1 [i.e. 2 lime for each 1 $Mg(HCO_3)$].

-Lime is also added at the ratio of 1:1 for each Magnesium NCH compound such as $MgSO_4$

-Soda ash is added at the ratio of 1:1 for each Magnesium or Calcium NCH compound such as $MgSO_4$, and $CaSO_4$.

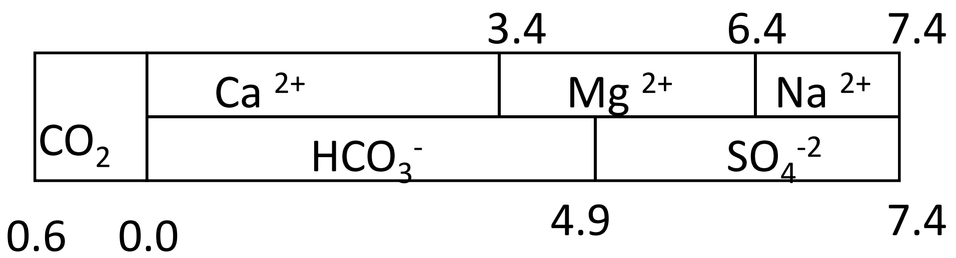
- CO_2 needed is 1:1 ratio with the excess lime added, and 1:1 ratio with $CaCO_3$ remaining after softening, 2:1 ratio with $Mg(OH)_2$ remaining after softening.
- The units of the chemicals are either in meq/L or mg/L $CaCO_3$
- Example 6.2 illustrates the chemical requirements calculations.

6. Hardness and Softening in water Treatment

6.5 Excess Lime Softening example

Example: 6.2

A water with the ionic characteristics shown below is to be softened to the minimum possible hardness by lime-soda-ash excess lime process. Calculate the required chemical quantities in meq/L. Draw a bar diagram of the softened water. Assume that a residual of $CaCO_3$ of 0.60 meq/L and a residual of $Mg(OH)_2$ of 0.20 meq/L will remain in the softened water.



6. Hardness and Softening in water Treatment

Example: 6.2 …….. continued

Solution:

Lime = 0.6+3.4+ 2(4.9-3.4)+ (6.4-4.9)+ excess lime

= 8.5 +1.25 = 9.75 meq/L

Soda Ash = 6.4-4.9 = 1.5 meq/L (to remove NCH, $MgSO_4^{2-}$)

Na^+ :

- The addition of soda ash adds to the water an equal amount of Na^+.
- Since we added 1.5 meq/L soda ash, this will add 1.5 meq/L Na^+
- The original concentration existing in the raw water is 1.0 meq/L .

Total Na^+ = 1 + 1.5 = 2.5 meq/L Na^+.

6. Hardness and Softening in water Treatment

Example: 6.2 …….. continued

0.0	0.6	0.8	3.3
Ca^{2+}	Mg^{2+}	Na^{2+}	
CO_3^{2-}	HO^-	SO_4^{-2}	
	0.6	0.8	3.3

Bar graph of the softened water