

Lecture 3: Water Softening

Water Treatment Technology

**Water Resources Engineering
Civil Engineering
ENG 6305**

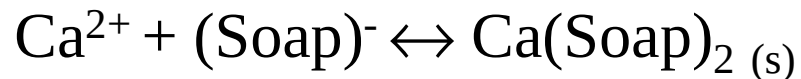
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Water Softening

1. Hardness definition:

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

- ü Dose form a foam or lather well and cause soap scum



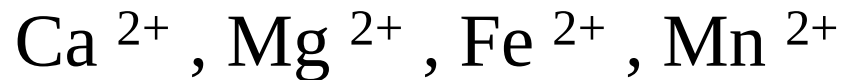
This increase the amount of soap needed for washing

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



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



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 CaCO_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

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E. Formation of Hardness

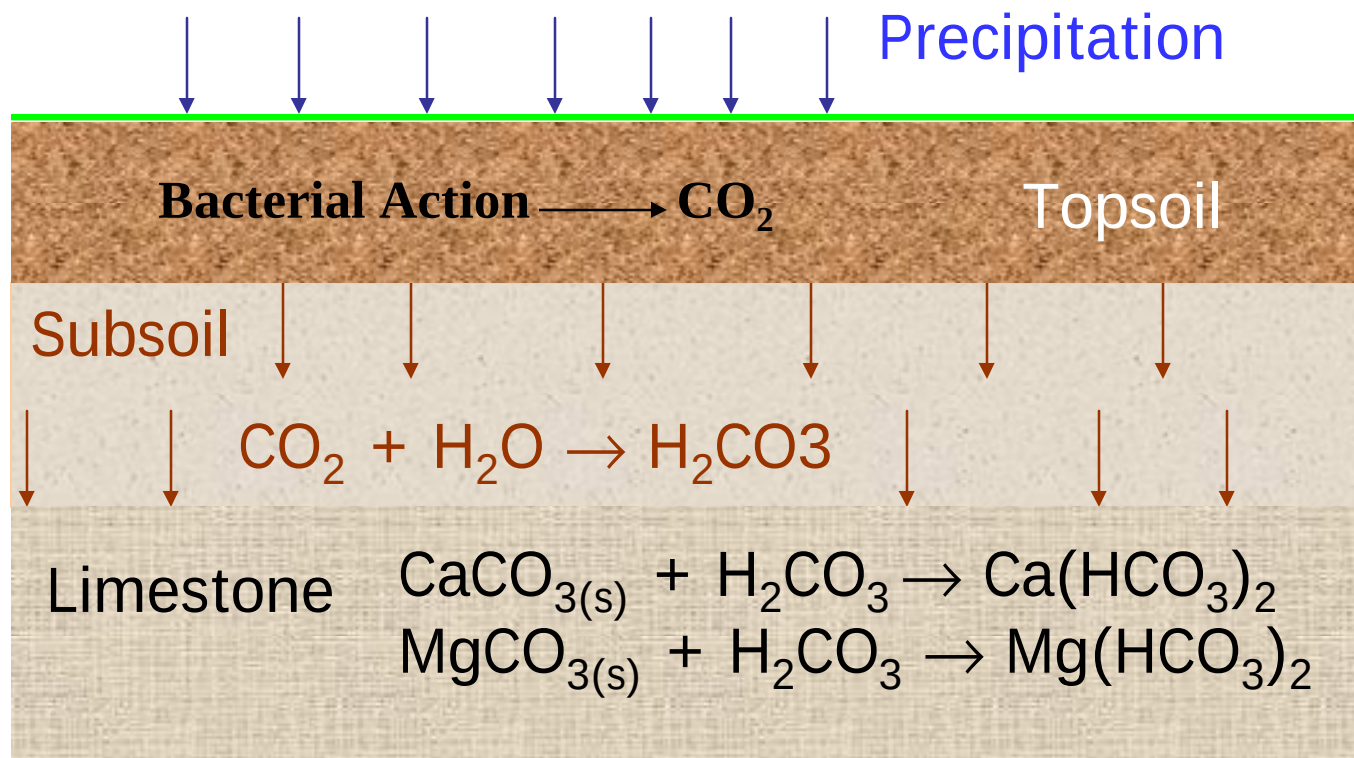


Fig. 3.1

Water Softening

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-}
 - $\text{NCH} = \text{TH} - \text{CH}$

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F. Hardness Units

Total Hardness = $\sum (\text{Ca}^{2+} + \text{Mg}^{2+})$

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

a.
$$\text{mg/L as CaCO}_3 = (\text{mg/L as species}) \frac{\text{EW of CaCO}_3}{\text{EW of species}}$$

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+} :

$$MW = 24.3 \frac{g}{mole}$$

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

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

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

$$EW = \frac{MW}{\text{Valance}}$$

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

Water Softening

b) Finding the EW for CaCO_3 :

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

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

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

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

$$\text{mg/L as CaCO}_3 = (\text{mg/L as species}) \frac{\text{EW of CaCO}_3}{\text{EW of species}}$$

Mg²⁺ conc.

$$(\text{Mg}^{2+}) \text{ in mg/L as CaCO}_3 = (10 \text{ mg/L as Mg}^{2+}) \frac{50 \text{ mg/meq}}{12.15 \text{ mg/meq}} \longrightarrow 41.15 \text{ mg/L as CaCO}_3$$

NAME	SYMBOL OR FORMULA	ATOMIC OR MOLECULAR WEIGHT	EQUIVALENT WEIGHT
Aluminum	Al^{3+}	27.0	9.0
Calcium	Ca^{2+}	40.1	20.0
Carbon	C	12.0	
Hydrogen	H^+	1.0	1.0
Magnesium	Mg^{2+}	24.3	12.2
Manganese	Mn^{2+}	54.9	27.5
Nitrogen	N	14.0	
Oxygen	O	16.0	
Phosphorus	P	31.0	
Sodium	Na^+	23.0	23.0
Ammonium	NH_4^+	18.0	18.0
Bicarbonate	HCO_3^-	61.0	61.0
Carbonate	CO_3^{2-}	60.0	30.0
Hydroxyl	OH^-	17.0	17.0
Hypochlorite	OCl^-	51.5	51.5
Nitrate	NO_3^-	62.0	62.0
Orthophosphate	PO_4^{3-}	95.0	31.7
Sulfate	SO_4^{2-}	96.0	48.0
Aluminum hydroxide	$\text{Al}(\text{OH})_3$	78.0	26.0
Calcium bicarbonate	$\text{Ca}(\text{HCO}_3)_2$	162	81.0
Calcium carbonate	CaCO_3	100	50.0
Calcium sulfate	CaSO_4	136	68.0
Carbon dioxide	CO_2	44.0	22.0
Ferric hydroxide	$\text{Fe}(\text{OH})_3$	107	35.6
Hydrochloric acid	HCl	36.5	36.5
Magnesium carbonate	MgCO_3	84.3	42.1
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	58.3	29.1
Magnesium sulfate	MgSO_4	120	60.1
Sodium sulfate	Na_2SO_4	142	71.0

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b.
$$\text{eq/L} = \frac{\text{g/L as ion}}{\text{EW of the ion}} \quad \text{or} \quad \text{meq/L} = \frac{\text{mg/L as ion}}{\text{EW of the ion}}$$

$$\text{eq/L} = \frac{\text{g/L as Compound or Radical}}{\text{EW of the Compound or Radical}}$$

or

$$\text{meq/L} = \frac{\text{mg/L as Compound or Radical}}{\text{EW of the Compound or Radical}}$$

Example 3.3 : for example 3.1 find the concentration of Mg^{2+} as meq/L .

$$\text{meq/L} = \frac{\text{mg/L as ion}}{\text{EW of the ion}}$$

$$(\text{Mg}^{2+}) \text{ concentration} = \frac{10 \text{ mg/L as } (\text{Mg}^{2+})}{12.15 \text{ mg/meq}}$$

$$= 0.82 \text{ meq/L}$$

Mg²⁺ conc.

Water Softening

F. 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:

- $\text{Alkalinity} = (\text{HCO}_3^-) + (\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+)$
- 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:

$$10^{-10.33} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}, \quad 10^{-14} = [\text{H}^+] \cdot [\text{OH}^-], \quad [\text{H}^+] = 10^{-\text{pH}}$$

Where the concentrations are moles/ L in these three equations

Various Forms of alkalinity and CO₂ relative to pH in water at 25 °C.

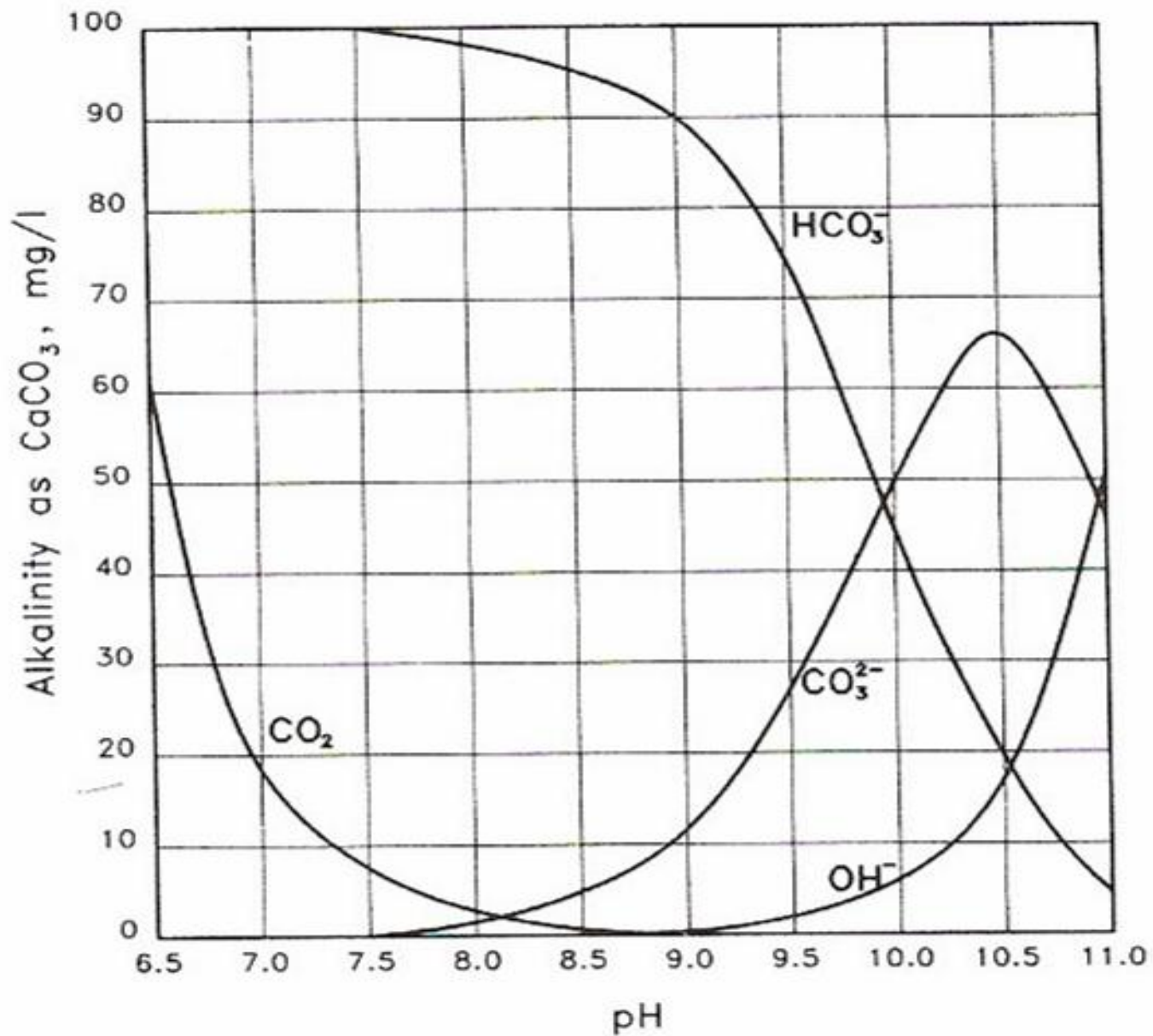


Fig. 3.1

Water Softening

Example 3.3

- 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

Water Softening

Example 3.3 ..cont'

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

Note : Examples 3.1 and 3.2 are sample calculations for Mg²⁺ in this Example

Water Softening

Example 3.3 ..cont'

Check The ionic balance:

$$\Sigma(\text{cations}) = \Sigma(\text{anions})$$

$$175.6 = 175.6 \quad \text{mg/L as CaCO}_3 \quad \text{O.K}$$

$$3.51 = 3.23 \quad \text{meq/L} \quad \text{O.K}$$

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** = $\Sigma (\text{Ca}^{2+}) + (\text{Mg}^{2+}) = 99.8 + 41.2$

$$\text{TH} = 141 \text{ mg/L as CaCO}_3$$

$$\text{or} \longrightarrow \text{TH} = 1.995 + 0.823 = 2.818 \text{ meq/L}$$

Water Softening

Example 3.3 ..cont'

- Alkalinity = $(\text{HCO}_3^-) + (\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+)$

a. Since pH = 7.2 $\rightarrow$
 $[\text{H}^+] = 10^{-\text{pH}} = 10^{-7.2} \text{ mole/L} = 10^{-7.2} \text{ g/L}$

$$\boxed{\text{eq/L} = \frac{\text{g/L as ion}}{\text{EW of the ion}}} = \boxed{\text{eq/L} = \frac{10^{-7.2} \text{ g H}^+/\text{L}}{1 \text{ g/eq}}} \longrightarrow \boxed{(\text{H}^+) = 10^{-7.2} \text{ eq/L}}$$

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

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

c. $(\text{HCO}_3^-) = 1.80 \text{ meq/L} = \underline{1.80 \cdot 10^{-3} \text{ eq/L}}$ from this example calculations as in the table.

$$\text{g/L as HCO}_3^- = \text{EW} \cdot \text{eq/L} = (61 \text{ g/eq}) \cdot 1.80 \cdot 10^{-3} \text{ g/L} = 109.8 \cdot 10^{-3} \text{ g/L}$$

$$[\text{HCO}_3^-] = (109.8 \cdot 10^{-3} \text{ g/L}) / (61 \text{ g/mole}) = \underline{1.80 \cdot 10^{-3} \text{ mole/L}}$$

Water Softening

Example 3.3 ..cont'

d. Find the carbonate concentration:

$$10^{-10.33} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \longrightarrow 10^{-10.33} = \frac{10^{-7.2} \times [CO_3^{2-}]}{1.8 \times 10^{-3}} \longrightarrow$$

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

$$\text{CO}_3^{2-} \text{ in } \boxed{\text{eq/L} = \frac{79.8 \times 10^{-6} \text{ g/L}}{30 \text{ g/eq}}} = 2.66 \times 10^{-6} \text{ eq/L}$$

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

$$\text{Alkalinity} = 1.801 \times 10^{-3} \times 1000 \times 50 = 90.1 \text{ mg/L as CaCO}_3$$

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.

Water Softening

Example 3.3 ..cont'

- 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:

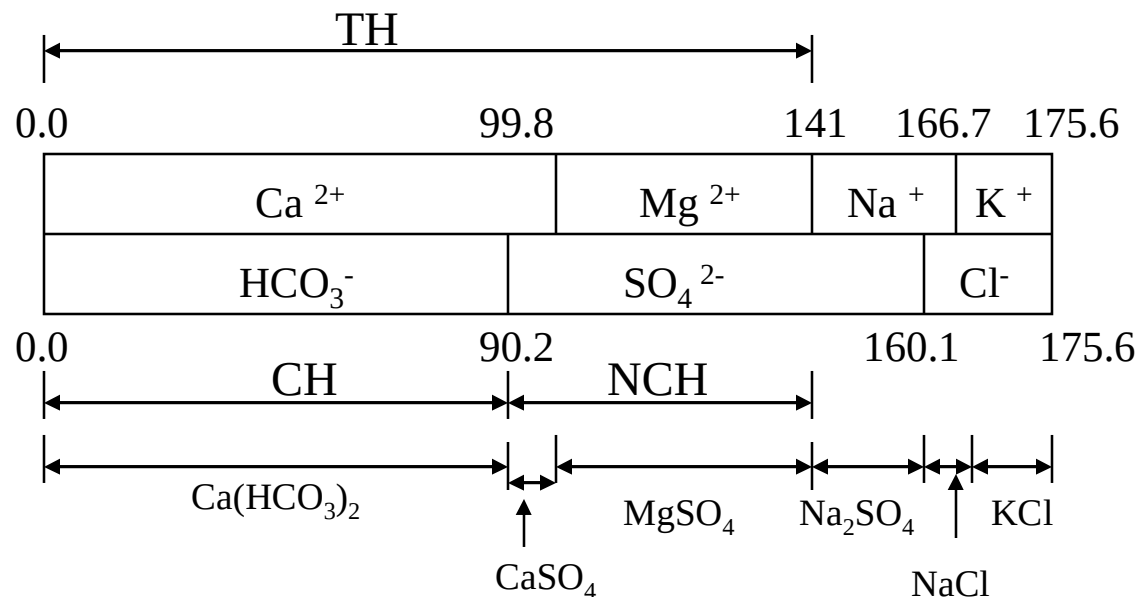
NCH = TH - CH

= 141 - 90.1 = 50.9 mg/L as CaCO_3

Water Softening

Example 3.3 ..cont'

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

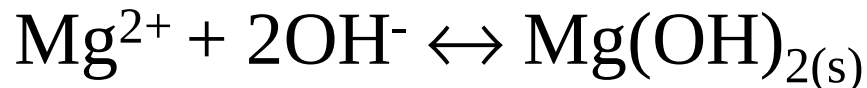
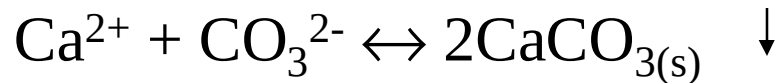


Note: the chemicals at the lower line of the bar graph is called the hypothetical combination of positive and negative ions in the water sample

Water Softening

2. Softening definition:

- a) **Softening** is the chemical processes in which hardness causing ions (Ca^{2+} , Mg^{2+}) are removed from water either completely or partially.
- b) Softening may be achieved 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 $\text{Mg}(\text{OH})_2$:



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

Water Softening

- 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 $\text{Mg}(\text{OH})_2$ we need to raise the pH to 10.3 by the addition of Lime [$\text{Ca}(\text{OH})_2$]. The addition of the OH^- will convert HCO_3^- to CO_3^{2-}
- h) To precipitate $\text{Mg}(\text{OH})_2$ 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 [$\text{Ca}(\text{OH})_2$] is consumed to remove CO_2 which is necessary to raise the pH.

Water Softening

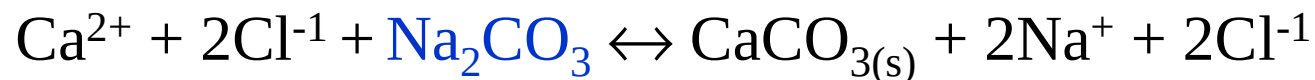
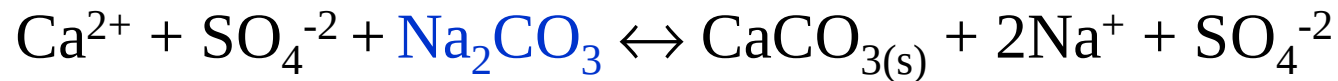
3. Chemistry of Lime- Soda Ash Softening

3.1) softening reactions

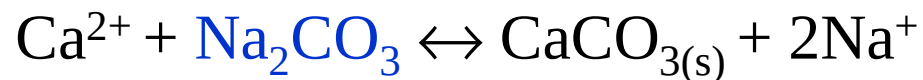
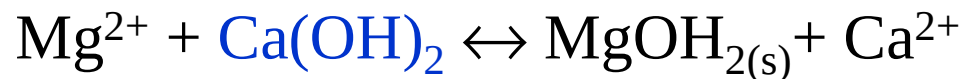
- Neutralization of carbonic acid
[To raise the pH we need first to neutralize any acid in the water]
$$\text{CO}_2 + \text{Ca(OH)}_2 \leftrightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O}$$
- Precipitation of CH due to **calcium**:
[To raise the pH to 10.3 all the HCO_3^- is converted to CO_3^{2-}]
$$\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{Ca(OH)}_2 \leftrightarrow 2\text{CaCO}_{3(s)} + 2\text{H}_2\text{O}$$
- Precipitation of CH due to **magnesium**
[To raise the pH to 11 add more lime]
$$\text{Mg}^{2+} + 2\text{HCO}_3^- + \text{Ca(OH)}_2 \leftrightarrow \text{Mg}^{2+} + \text{CO}_3^{2-} + \text{CaCO}_{3(s)} + 2\text{H}_2\text{O}$$
$$\text{Mg}^{2+} + \text{CO}_3^{2-} + \text{Ca(OH)}_2 \leftrightarrow \text{MgOH}_{2(s)} + \text{CaCO}_{3(s)}$$

Water Softening

- Removal of NCH due to calcium



- Removal of NCH due to magnesium



Water Softening

3.2) Softening process limitations:

1. Lime-Soda softening cannot produce a water completely free of hardness because of the solubility of CaCO_3 and $\text{Mg}(\text{OH})_2$, 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 .

Water Softening

3.3) Chemicals requirements:

According to the softening chemical reactions:

- Lime is added at the ratio of 1:1 for each carbonate hardness compound except for $\text{Mg}(\text{HCO}_3)$ the ratio is 2:1 [i.e. 2 lime for each 1 $\text{Mg}(\text{HCO}_3)$].
- 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 $\text{Mg}(\text{OH})_2$ remaining after softening.
- The units of the chemicals are either in meq/L or mg/L CaCO_3
- Example 3.4 illustrates the chemical requirements calculations.

Water Softening

4. Process variation in Lime Soda-Ahs softening:

There are three basic schemes for water softening:

- Excess lime treatment
- Selective Calcium removal
- Split treatment

Water Softening

4.1) Excess lime treatment:

- Carbonate hardness associated with Ca^{2+} can be effectively removed to the practical limit of CaCO_3 (30 mg/L as CaCO_3) by adding the stoichiometric addition of lime.
- Precipitation of hardness (CH or NCH) associated with Mg^{2+} as $\text{Mg}(\text{OH})_2$ needs in addition to the stoichiometric addition of lime to an excess lime of 62.5 mg/L as CaCO_3 , without it $\text{Mg}(\text{OH})_2$ will not precipitate. In fact this excess lime raise the pH to 11.
- Excess lime treatment reduces the total hardness to 40 mg/L as CaCO_3 (i.e., 30 mg/L CaCO_3 and 10 mg/L $\text{Mg}(\text{OH})_2$ as CaCO_3)
- The excess lime treatment is usually achieved in a two stage system as shown in the Figure 3.3

Water Softening

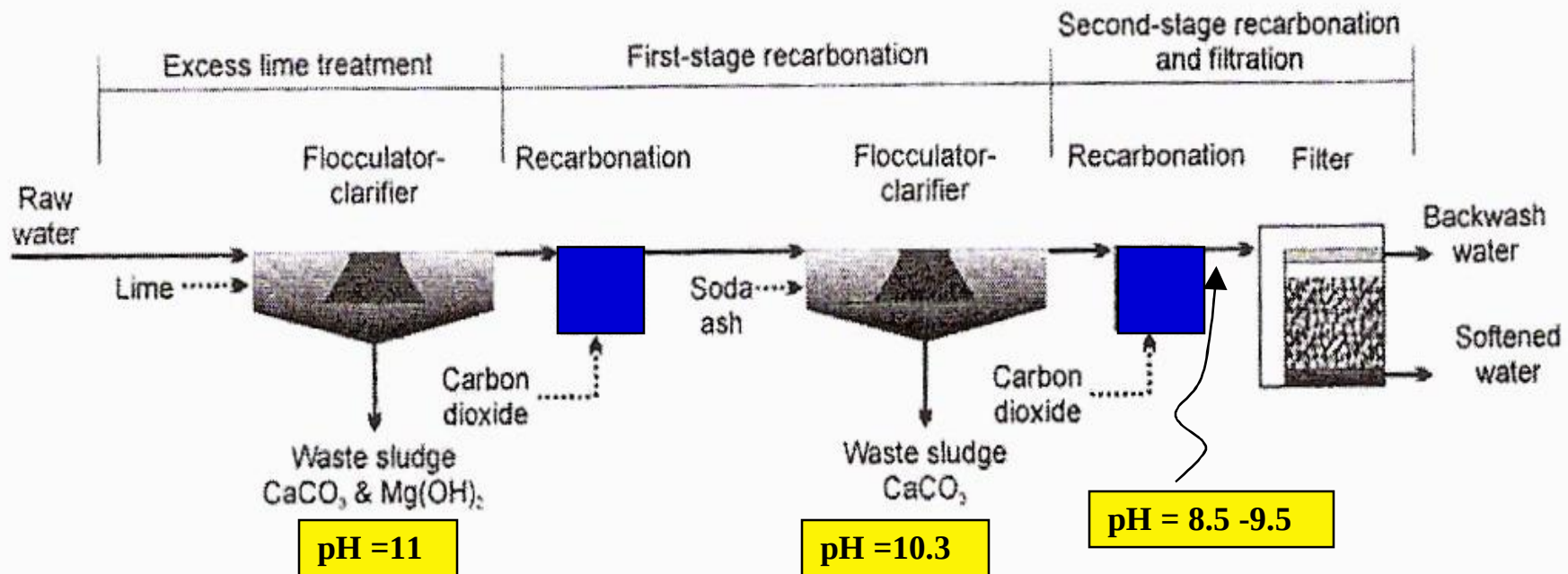
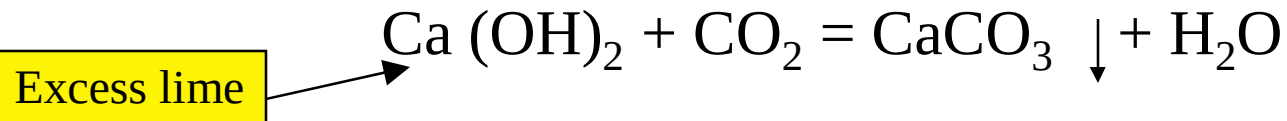


Fig. 3.3 Schematic diagram of a two stage excess lime softening water treatment plant

Water Softening

- The system is composed of :
 - Rapid mixer,
 - Flocculator/sedimentation tank,
 - recarbonation tank,
 - Rapid mixer
 - Second stage Flocculator/sedimentation tank
 - second stage recarbonation tank
 - Filtration tank
- In the first stage only lime is added to the system through a rapid mixer this will raise the pH to 11. CaCO_3 and $\text{Mg}(\text{OH})_2$ will precipitate in this stage.
- **Recarbonation** is implemented to reduce the pH to 10.3 before entering the second stage. This reduction occurs due to the removal of the excess lime added in the first stage:



Water Softening

- In the **second stage** only Soda Ash is added to the system through a rapid mixer . CaCO_3 will precipitate in this stage from the excess lime and from the NCH reaction .
- **Recarbonation** is implemented after the second stage Flocculator /sedimentation to reduce the pH in the range of 8.5-9.5 to stabilize the water by converting some of the Ca CO_3 and Mg (OH)_2 residual to bicarbonate :



- **Recarbonation** is achieved in a tank in which carbon dioxide is injected either in liquid form or in the gaseous form generated in the tank using a special burner as Shown in Figure 3.4.

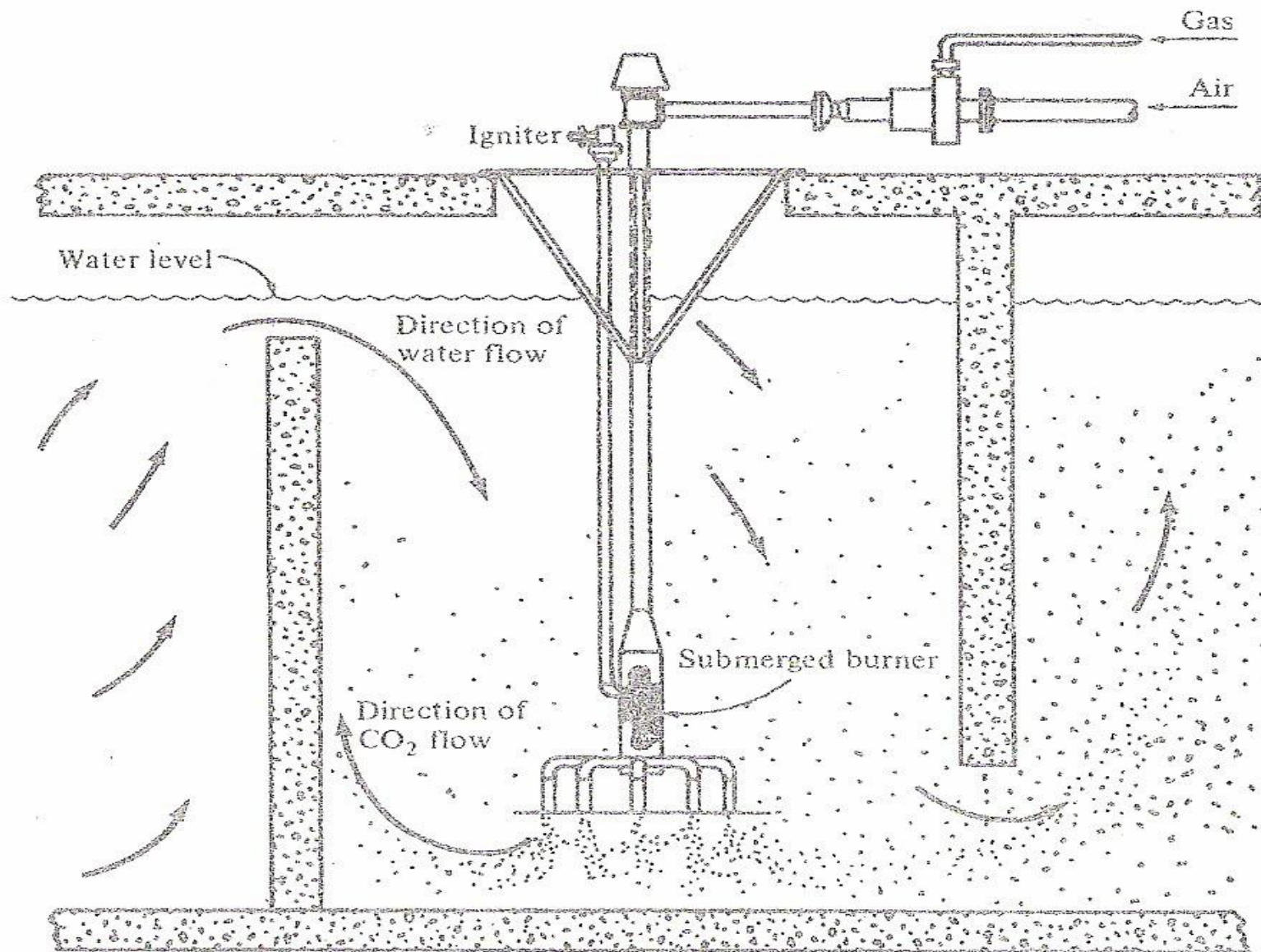


Fig. 3.4 Submerged burner for recarbonation

Water Softening

- The first stage removes the following:
 - CH hardness associated with Ca^{2+}
 - CH and NCH associated with Mg^{2+}
 - Recarbonation reduces pH from 11 to 10.3
- The Second stage removes the following:
 - NCH hardness associated with Ca^{2+} that is originally existing in water
 - NCH hardness associated with Ca^{2+} that was created from the first stage.
 - Recarbonation reduces pH from 10.3 to the range 8.5-9.5

Water Softening

Example: 3.4

A water with the ionic characteristics shown below is to be softened to the minimum possible hardness by the two stage lime-soda-ash **excess lime process**. Calculate the required chemical quantities in meq/L. Draw a bar diagram of the finished water. Assume that 0.6 meq/L CaCO_3 and 0.2 meq/L $\text{Mg}(\text{OH})_2$ will be in the effluent of the second stage before recarbonation. Assume also that 0.2 meq/L $\text{Mg}(\text{OH})_2$ and 0.2 meq/L of the 0.6 CaCO_3 will be converted to HCO_3^- by second stage recarbonation to reach water stability.

		3.4	6.4	7.4
	Ca^{2+}	Mg^{2+}	Na^{2+}	
CO_2	HCO_3^-		SO_4^{-2}	
0.6	0.0	4.9	7.4	

Solution:

Lime = $0.6 + 3.4 + 2(4.9 - 3.4) + (6.4 - 4.9) + \text{excess lime}$
 = $8.5 + 1.25 = 9.75 \text{ meq/L}$

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

Water Softening

Example: 3.4 Cont'

CO₂:

1st stage recarbonation = 1.25 meq/ L [to remove the excess lime]

2nd stage recarbonation = 0.2 meq/L [to convert 0.2meq/L of CaCO₃ to Ca(HCO₃)]
+ (0.20 x 2) meq/L [to convert all Mg(OH)₂ to Mg(HCO₃)]= 0.60 meq/L]

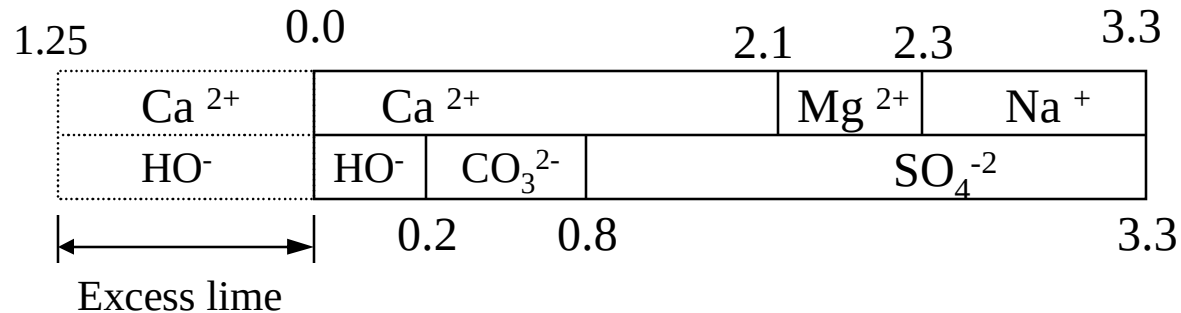
Total CO₂ needed = 1.25+0.6 = 1.85 meq/L

Na⁺:

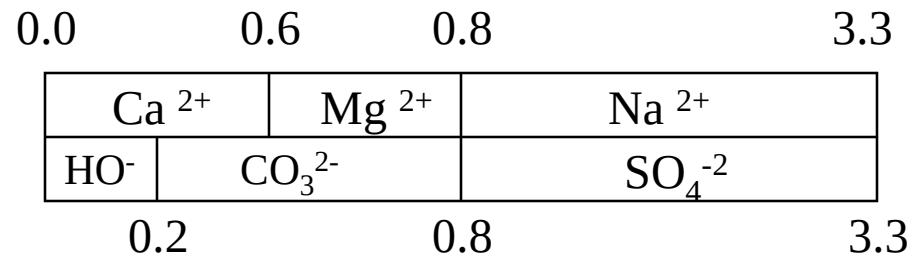
- The addition of soda ash adds to the water an equal amount of Na⁺.
- Since we added 1.5 meq/L soda ash, this will add 1.5 meq/L Na⁺
- The original concentration existing in the raw water is 1.0 meq/L .
Total Na⁺ = 1 + 1.5 = 2.5 meq/L Na⁺.

Water Softening

Example: 3.4 Cont'



Bar graph of the water before recarbonation and before adding Soda -Ash



Bar graph of the water after adding Soda –Ash and 1st stage recarbonation

Water Softening

Example: 3.4 Cont'

	0.6	0.8	3.3
Ca ²⁺	Mg ²⁺	Na ⁺	
CO ₃ ²⁻	HCO ₃ ⁻	SO ₄ ⁻²	
0.0	0.4	0.8	3.3

Bar graph of the finished water after and 2nd stage recarbonation

The remaining hardness:

Calcium hardness = 0.6 meq/L = 30 mg/L as CaCO₃

Calcium hardness = 0.2 meq/L = 10 mg/L as CaCO₃

TH remaining = 0.8 meq/L = 10 mg/L as CaCO₃

Water Softening

4.2) Selective Calcium removal:

- Magnesium hardness is expensive to remove.
- Only Magnesium hardness in excess of 40 mg/L as CaCO_3 (0.8 meq/l) needs to be removed.
- For waters having an Mg^{2+} hardness less or equal to 40 mg/L CaCO_3 , only Ca^{2+} hardness needs to be removed.
- to remove only Ca^{2+} , we add lime needed to remove Ca^{2+} , and do not add excess lime. In this way no Mg^{2+} removal occurs.
- Soda Ash may be needed if NCH associated with Ca^{2+} is to be removed.
- That's way this treatment is called selective.
- This treatment is achieved in a single stage system as that shown in [Figure 3.5](#)

Water Softening

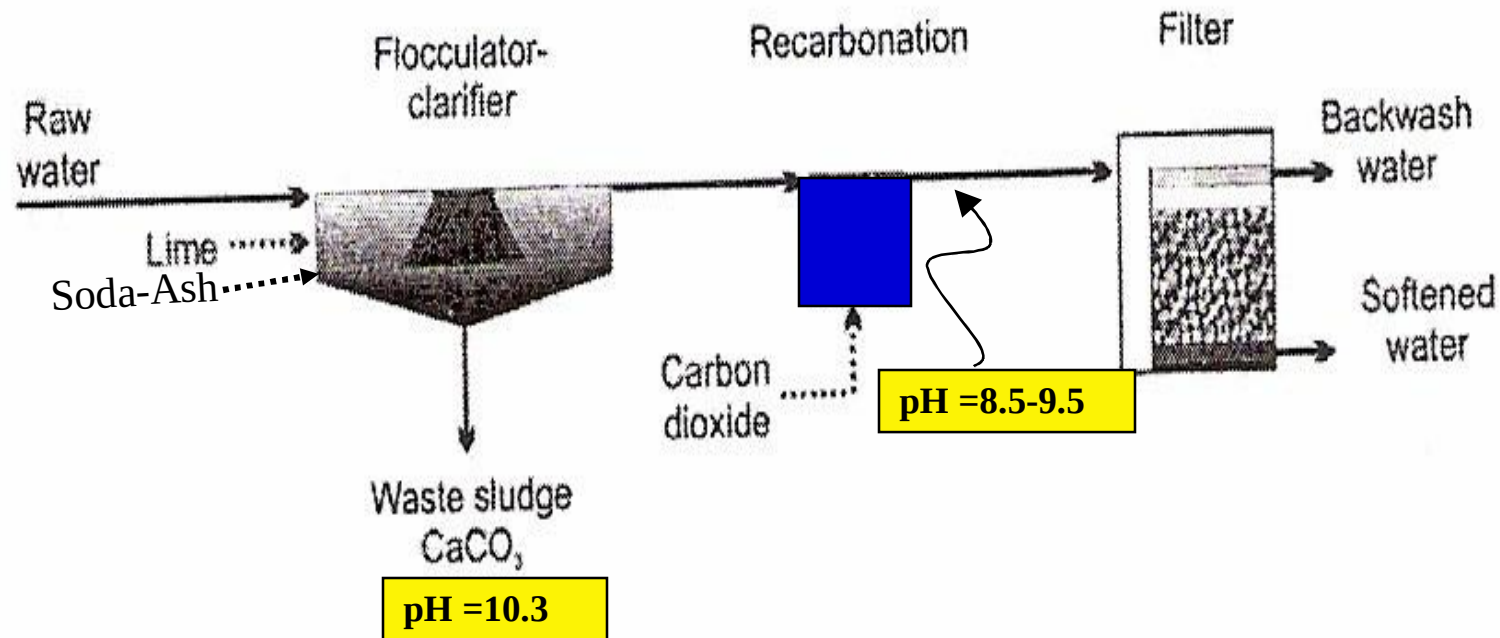


Fig. 3.5 Schematic diagram of a single stage softening water treatment plant

Water Softening

Example: 3.5

A water with the ionic characteristics shown below is to be softened by **selective calcium process**. Calculate the required chemical quantities in meq/L. Draw a bar diagram of the finished water.

0.4	0.0	3.5	4.3	4.6
CO ₂	Ca ²⁺		Mg ²⁺	Na ²⁺
	HCO ₃ ⁻	SO ₄ ⁻²	Cl ⁻¹	
0.4	0.0	2.3	4.3	4.6

Solution:

Since Mg²⁺ is 0.8 meq/L we can apply the **selective calcium treatment**.

Lime = $0.4 + 2.3 = 2.7$ meq/L [to remove CO₂ and Ca(HCO₃) only]
 = $2.7 \times 28 = 76$ mg/L CaO

Soda Ash = $3.5 - 2.3 = 1.2$ meq/L [to remove NCH, CaSO₄]
 = $1.2 \times 53 = 64$ mg/L Na₂CO₃

Water Softening

Example: 3.5 Cont'

CO₂:

For stability reasons it is desired to convert 0.3 out of the 0.6 meq/L CaCO₃ to Ca(HCO₃)₂ by recarbonation.

$$\begin{aligned}\text{Recarbonation} &= 0.3 \text{ meq/L CO}_2 \text{ [to convert 0.2 meq/L of CaCO}_3 \text{ to Ca(HCO}_3\text{)]} \\ &= 0.3 \times 22 = 6.6 \text{ mg/L CO}_2\end{aligned}$$

Na⁺:

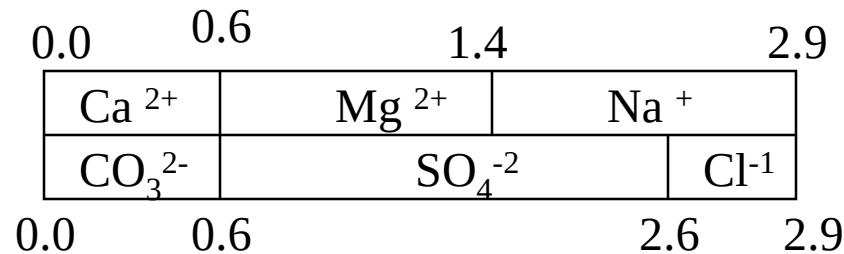
- The addition of soda ash adds to the water an equal amount of Na⁺.
- Since we added 1.2 meq/L soda ash, this will add 1.2 meq/L Na⁺
- The original concentration existing in the raw water is 0.3 meq/L .

$$\begin{aligned}\text{Total Na}^+ &= 0.3 + 1.2 = 1.5 \text{ meq/L Na}^+ \\ &= 1.5 \times 23 = 34.5 \text{ mg/L Na}^+\end{aligned}$$

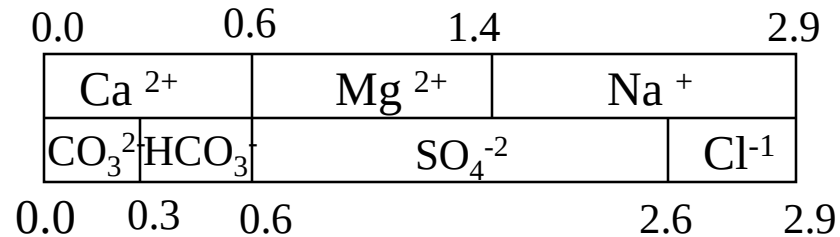
$$\begin{aligned}\text{Final hardness} &= \text{all the original Mg}^{2+} + 0.6 \text{ meq/L calcium hardness} \\ &= 0.8 \text{ meq/L Mg}^{2+} + 0.6 \text{ meq/L Ca}^{2+} = 1.4 \text{ meq/L} \\ &= 1.4 \times 50 = 70 \text{ mg/L CaCO}_3\end{aligned}$$

Water Softening

Example: 3.5 Cont'



Bar graph of the water after softening and before recarbonation



Bar graph of the finished water after recarbonation

Water Softening

4.3) Split Treatment:

- Split treatment consist of treating portion of the raw water by excess lime treatment and Then neutralizing the excess lime by the bicarbonate naturally existing in the untreated bypass flow (Figure 3.6).
- The first stage is operated to soften the water to the practical limits of 10 mg Mg^{+2}/L as CaCO_3 , and 30 mg Ca^{2+} /L as CaCO_3 .
- Magnesium concentration in the bypass will be the same as in the raw water.
- The finished water should have a final of 40 mg Mg^{+2}/L as CaCO_3 as desired by domestic water users and industries.
- Some advantages of Split Treatment:
 - * Reduces the chemical dosage of lime and CO_2 .
 - * No need for first stage recarbonation
 - * Reduce the capital cost of the first stage since only a portion of the water is treated and consequently the tanks are smaller.
 - * Allows us to leave a Mg^{2+} concentrations above the practical value of 10 mg Mg^{+2}/L as CaCO_3 usually we are forced to achieve in the conventional excess lime treatment.

Water Softening

-The Fraction Bypassed is calculated as :

$$X = \frac{Mg_f - Mg_i}{Mg_r - Mg_i}$$

Where, Mg_f = final magnesium concentration, mg/L $CaCO_3$
 Mg_i = magnesium concentration from the first stage, mg/L $CaCO_3$
 Mg_r = raw water magnesium concentration, mg/L $CaCO_3$

Water Softening

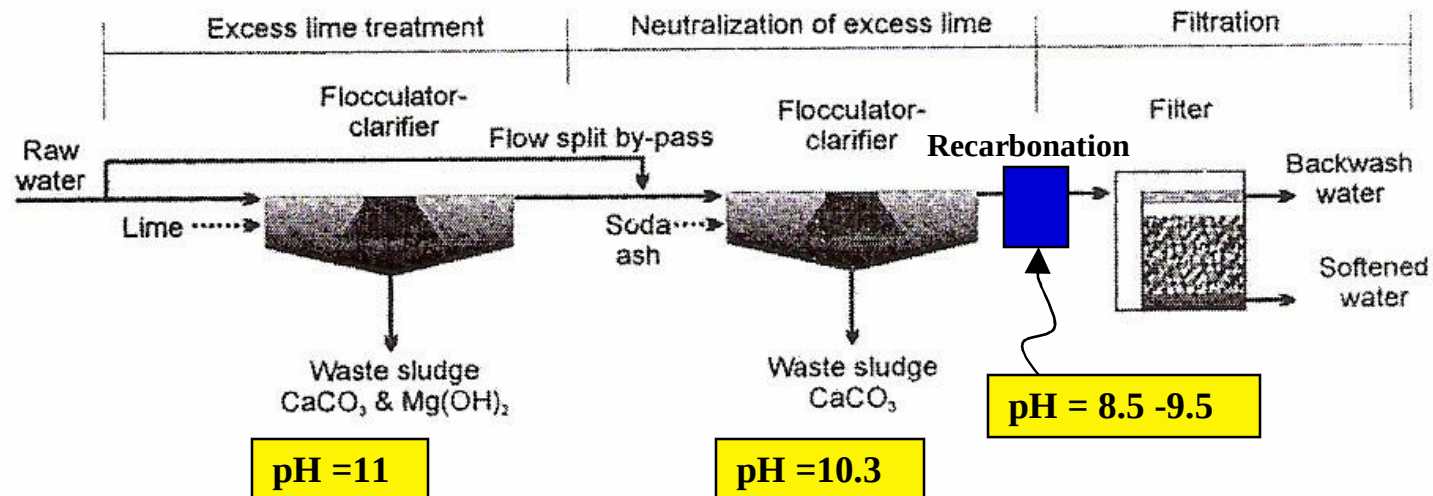


Fig. 3.6 Schematic diagram of a split system softening water treatment plant

Water Softening

Example: 3.6

For the water in example 3.4 use a split treatment to soften it. Calculate the required chemical quantities in meq/L. Draw a bar diagram of the finished water. Assume that the maximum permissible Magnesium hardness of 40 mg/L CaCO_3 and Calcium hardness in the range of 40-60 mg/L CaCO_3 . The expected magnesium hardness from the first stage split is 10 mg/L CaCO_3 .

	3.4	6.4	7.4
	Ca ²⁺	Mg ²⁺	Na ²⁺
CO ₂	HCO ₃ ⁻	SO ₄ ⁻²	
0.6 0.0	4.9	7.4	

Solution:

$$X = \frac{\text{Mg}_f - \text{Mg}_i}{\text{Mg}_r - \text{Mg}_i} \longrightarrow X = \frac{40 - 10}{3(50) - 10} = 0.214$$

$$1 - X = 1 - 0.214 = 0.786$$

Water Softening

Example: 3.6 Cont'

Solution:

Chemicals to be added

$$\begin{aligned}\text{A) Lime} &= 0.786 [(0.6 + 3.4 + 2(4.9 - 3.4) + (6.4 - 4.9))] \\ &= 6.681 \text{ meq/L [needed for the first stage treatment]}\end{aligned}$$

Lime = $0.214 [0.6 + 3.4] = 0.856 \text{ meq/L}$ [needed for removing the Ca^{2+} hardness and CO_2 from the bypass flow. However, this amount will be added to the first stage, and will act as an excess lime.]

Excess lime concentration in the first stage = $(0.856 / 0.786) = 1.09 < 1.25 \text{ meq/L}$
so additional amount is needed

$$= Y / 0.786 = 1.25 \longrightarrow Y = 0.983 \text{ meq/L}$$

$$= 0.214 [0.6 + 3.4 + Z] = 0.983 \longrightarrow Z = 0.593 \text{ meq/L}$$

Corrected lime for the bypass = $0.214 [0.6 + 3.4 + 0.593] = 0.983 \text{ meq/L}$

Excess lime concentration in the first stage = $(0.983 / 0.786) = 1.25 \text{ meq/L (OK)}$.

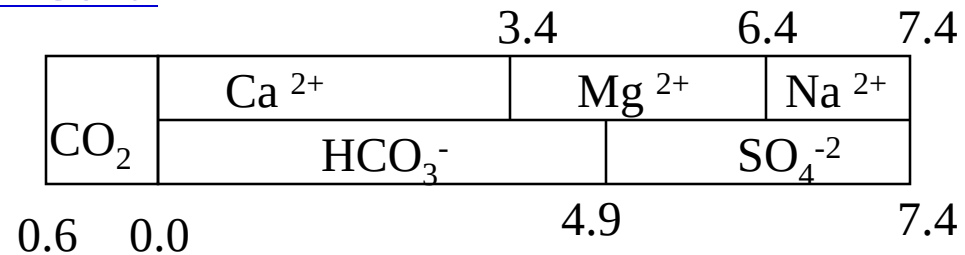
B) Soda Ash = See the lower Bar graph in slide 48, we need to remove CaSO_4
 $= 1.3 - 0.60 = 0.70 \text{ meq/L}$

Another method to calculate the needed Soda Ash:

$$\begin{aligned}\text{Soda ash} &= (\text{Raw water Mg}^{2+} \text{ concentration} - 0.80) \text{ meq/L Mg}^{2+} \text{ NCH} + \text{meq/L Ca}^{2+} \text{ NCH} \\ &= 1.50 - 0.80 + 0.0 \\ &= 0.70 \text{ meq/L}\end{aligned}$$

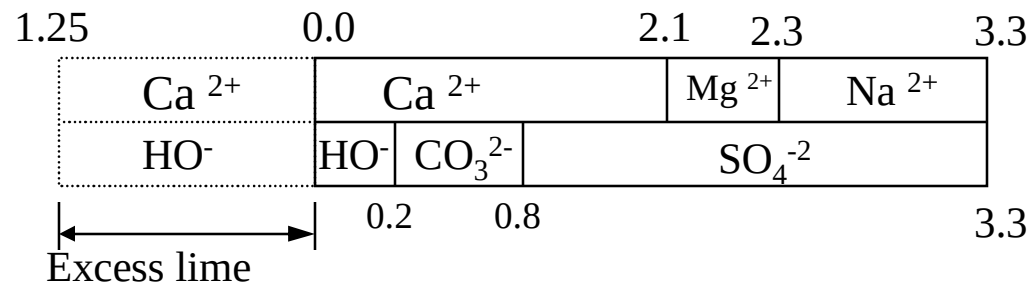
Water Softening

Example: 3.6 Cont'



A

Bar graph of the water in the Bypass line (Raw water)

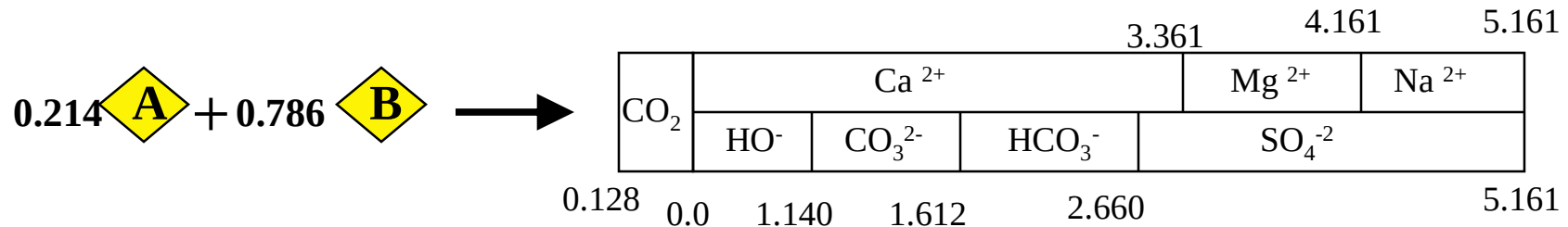


B

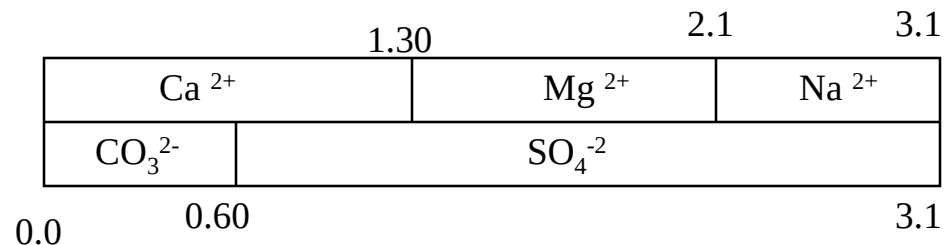
Bar graph of the water after the first stage split softening before blending and before adding Soda Ash

Water Softening

Example: 3.6 Cont'



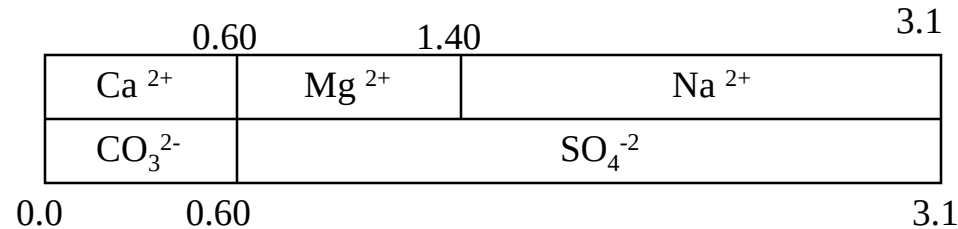
Bar graph of the water after blending and before reaction between the excess lime and before adding Soda Ash



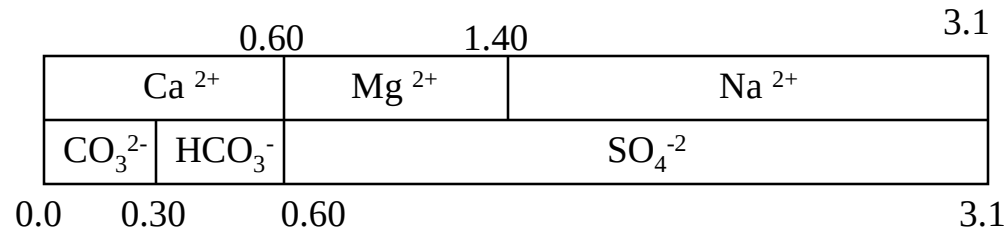
Bar graph of the water after blending and reaction between the excess lime and before adding Soda Ash

Water Softening

Example: 3.6 Cont'



Bar graph of the water after adding Soda Ash and before second stage carbonation



Bar graph of the finished water

Note :

$$\begin{aligned}
 \text{Remaining hardness} &= 0.60 \text{ Ca}^{2+} \text{ hardness} + 0.8 \text{ Mg}^{2+} \text{ hardness} = 1.40 \text{ meq/L} \\
 &= 0.60 \times 50 \text{ mg Ca}^{2+} / \text{L CaCO}_3 + 0.8 \text{ Mg}^{2+} \text{ mg/L CaCO}_3 \\
 &= 30 \text{ mg Ca}^{2+} / \text{L CaCO}_3 + 40 \text{ mg Mg}^{2+} / \text{L CaCO}_3
 \end{aligned}$$

$$\text{Remaining Hardness} = 70 \text{ mg /L CaCO}_3$$

Water Softening

5. Coagulation and Softening

- The softening precipitates [i.e. CaCO_3 and $\text{Mg}(\text{OH})_2$] may be more efficiently removed by adding a coagulant such as Alum.
- On the other hand, if both coagulation and softening are to be applied, (such as in hard turbid surface water), the coagulation process is more efficient due to the greater quantity of precipitate formed due to softening.
- That's why coagulation and lime soda-Ash softening have similar infrastructure (i.e. rapid mixer, Flocculator, sedimentation tank).