SOFTENING

Water Treatment

Zerihun Alemayehu

INTRODUCTION

- Sedimentation, coagulation and filtration → suspended solids
- **Chemical precipitation:** The removal of dissolved objectionable substances from water by the addition of some chemicals to convert them into insoluble substances
- ***Softening*** is the removal of ***hardness*** from water.
- Measurements of hardness are given in terms of the calcium carbonate equivalent.

DEGREE OF HARDNESS

Mg/L as $CaCO_3$	Degree of hardness
0-75	Soft
75-150	Moderately hard
150-300	Hard
> 300	Very hard

- Water softening is needed when hardness is above 150-200 mg/L;
- Hardness 50-80 is acceptable in treated water.

TYPES OF HARDNESS

Carbonate hardness compounds (temporary hardness)	Non-carbonate hardness compounds (permanent hardness)
Calcium carbonate ($CaCO_3$)	Calcium sulfate ($CaSO_4$)
Magnesium carbonate ($MgCO_3$)	Magnesium sulfate ($MgSO_4$)
Calcium bicarbonate ($Ca(HCO_3)_2$)	Calcium chloride ($CaCl_2$)
Magnesium bicarbonate ($Mg(HCO_3)_2$)	Magnesium chloride ($MgCl_2$)
Calcium hydroxide ($Ca(OH)_2$)	
Magnesium hydroxide ($Mg(OH)_2$)	

Total Hardness

- Total Hardness (*TH*) = $[Ca^{2+}]$ + $[Mg^{2+}]$as mg/L of $CaCO_3$
- Total Hardness (as $CaCO_3$) = (eq/L of cation charge) x (50g $CaCO_3$/Charge eq) x 1000mg/g
- TH = CH +NCH

SOFTENING METHODS

- Boiling
  - Boiling reduces only calcium carbonate hardness but not non-carbonate hardness.
  - $Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$
- Lime treatment
- Lime-soda process
- Ion-exchange method

SOFTENING CHEMISTRY

- $Ca_2^+ + CO_3^{2-} \rightleftharpoons CaCO_3$ (s) → pH must be raised to 10.3
- $Mg_2^+ + 2OH^- \rightleftharpoons Mg(OH)_2$ (s) → pH must be raised to 11
- We have to provide CO_3^{2+} if no HCO_3^- is present.
- We increase conc. Of CO_3^{2-}/OH^- by addition of chemicals, and derive the reactions to the right.
- $HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_20$
- Source of OH^- →$CaO + H_2O \rightleftharpoons Ca(OH)_2$ + heat
- When carbonate ions must be provided we used soda ash (Na_2CO_3)

Lime Treatment

- Addition of lime to hardwater converts soluble bicarbonate into insoluble $CaCO_3$.
- If CO_2 is present in water, some amount of lime is required to neutralize it.
- CO_2: $CO_2 + Ca(OH)_2 \leftrightarrow CaCO_3 \downarrow + H_20$
- Calcium carbonate hardness:

  $Ca(HCO_3)_2 + Ca(OH)_2 \leftrightarrow 2\ CaCO_3\downarrow + 2\ H_2O$
- Magnesium carbonate hardness:

  $Mg(HCO_3)_2 + Ca(OH)_2 \leftrightarrow CaCO_3\downarrow + MgCO_3 + 2\ H_2O$
- Excess lime treatment:

  $MgCO_3 + Ca(OH)_2 \leftrightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow$
- Noncarbonate hardness:

  $MgSO_4 + Ca(OH)_2 \leftrightarrow Mg(OH)_2 \downarrow + CaSO_4$

  $MgCl_2 + Ca(OH)_2 \leftrightarrow Mg(OH)_2 \downarrow + CaCl_2$

PROCESS LIMITATIONS

- Lime-soda softening cannot produce a water completely free of hardness because of
  - the solubility of $CaCO_3$ and $Mg(OH)_2$
  - The physical limitation of mixing and contact
  - The lack of sufficient time for reactions to go completion.
- Thus,
  - Min Ca hardness = 30 mg/l as $CaCO_3$
  - Min Mg Hardness = 10 mg/l as $CaCO_3$
  - Our goal is from 75 to 120 mg/L as $CaCO_3$
  - Add min. excess lime of 20 mg/L as $CaCO_3$
  - Max Mg = 40 mg/L as $CaCO_3$

PROCESS LIMITATIONS

- Excess lime needed for Mg to be removed
  - < 20 mg/L excess lime = 20 mg/L as CaCO3
  - From 20 to 40 mg/L = equal to Mg to be removed
  - >40 = 40 mg/L as CaCO3

Chemical addition	Reason
Lime = CO_2	Destroy H_2CO_3
Lime = HCO_3^-	Raise pH; convert HCO_3^- to CO_3^{2-}
Lime = Mg^{2+} to be removed	Raise pH; precipitate $Mg(OH)_2$
Lime = required excess	Derive reaction
Soda = noncarbonate hardness to be removed	Provide CO_3^{2-}

EXAMPLE

- From the water analysis presented below, determine the amount of line and soda (in mg/L as $CaCO_3$) necessary to soften the water to 80.00 mg/L hardness as $CaCO_3$.

Water composition (mg/L)		
Ca^{2+}: 95.20	CO_2: 19.36	HCO_3^-: 241.46
Mg^{2+}: 13.44		SO_4^{2-}: 53.77
Na^+: 25.76		Cl^-: 67.81

SOLUTION

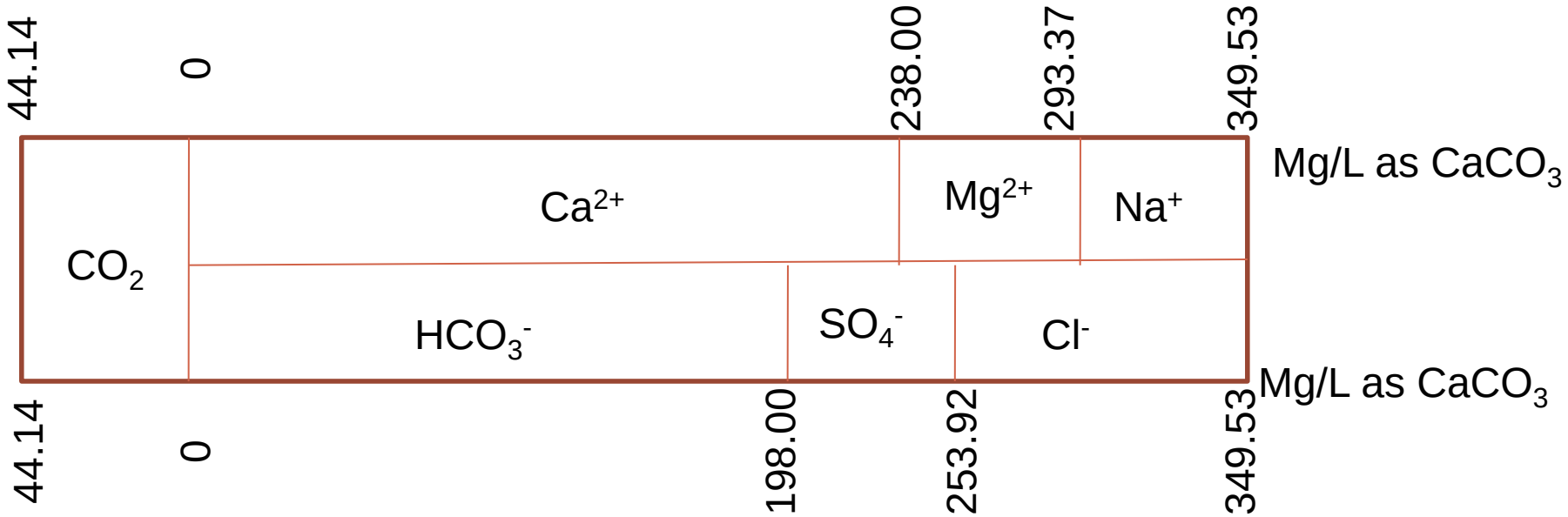
- First convert the elements and compounds to $CaCO_3$ equivalents.

50

Ion	mg/L as ion	EW $CaCO_3$/EW ion	mg/L as $CaCO_3$
Ca^{2+}:	95.20	2.50	238.00
Mg^{2+}:	13.44	4.12	55.37
Na^{+}:	25.76	2.18	56.16
HCO_3^{-}:	241.46	0.820	198.00
SO_4^{2-}:	53.77	1.04	55.92
Cl^{-}:	67.81	1.41	95.61
CO_2:	19.36	2.28	44.14

SOLUTION...

- Draw a bar chart



SOLUTION...

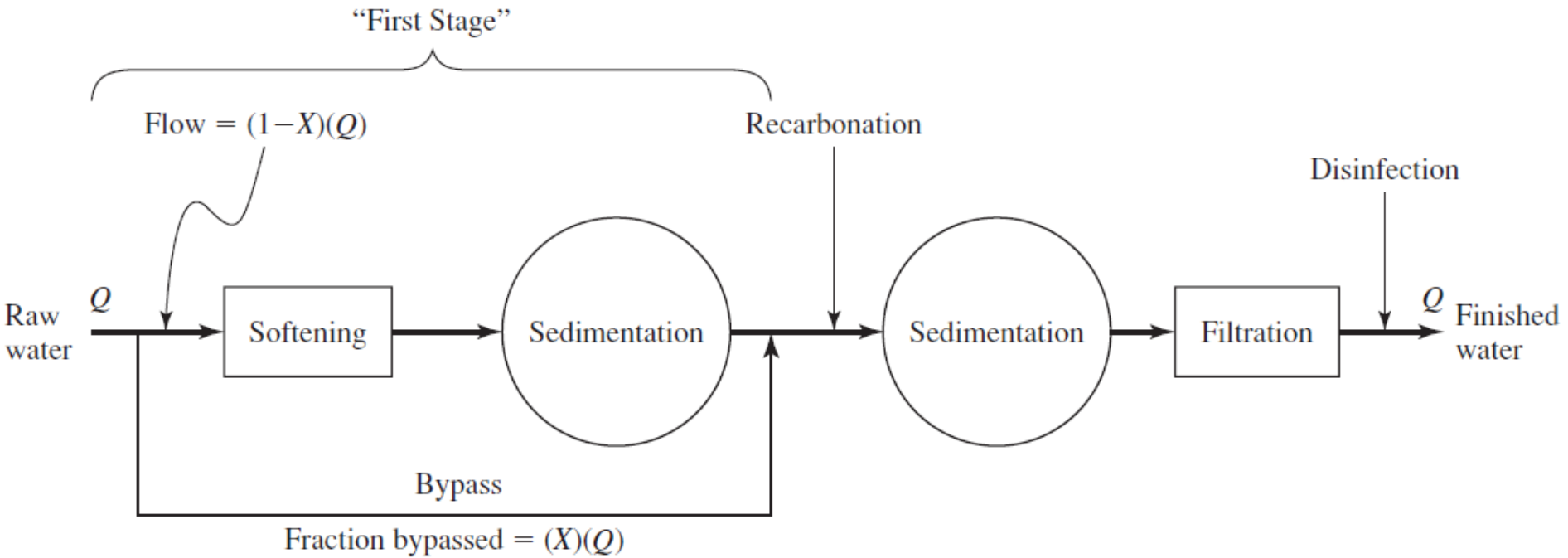
- From the bar chart we notice that
- Total hardness (TH) = 293.37 mg/L
- The carbonate hardness (CH) = 198.00 mg/L
- The noncarbonate hardness (NCH) = TH – CH
- NCH = 293.37 – 198.00 = 95.37 mg/L

SOLUTION...

Chemical addition	Dose (mg/L as CaCO3)
Lime = CO_2	44.14
Lime = HCO_3^-	198.00
Lime = Mg^{2+} - 40 = 55.37 - 40	15.37
Lime = excess	20
Total lime required	**277.51**

- NCH needed to be removed
  - NCH_{left} = Final hardness (80.00 mg/L) – CH_{left} due limitations (40.00 mg/L):
  - NCH_f = 80.00 – 40.00 mg/L
  - Thus, 40.00 mg/L may be left
- $NCH_{removed} = NCH_{initial} – NCH_{left}$
  - NCH_R = 95.37 – 40.00 = 55.37 mg/L
  - Thus, soda to be added is 55.37 mg/L as CaCO3

Split Treatment



OTHER TREATMENT METHODS

- Ion exchange
- Fluoridation
- Iron & Manganese removal
- Activated Carbon Adsorption
- Air striping
- Dissolved air floatation
- Aeration
- Reverse osmosis and Nanofiltration
- Membrane filtration