

Process Chemistry Relationships for Precipitative Softening and Recarbonation

Marvin Gnagy, P.E.
Water Resources Manager

*OTCO Water Workshop
March 23, 2010*

Agenda

- Alkalinity Species and Distribution
- Alkalinity / pH Relationships
- Titration Equation
- Calcium / Magnesium Solubilities

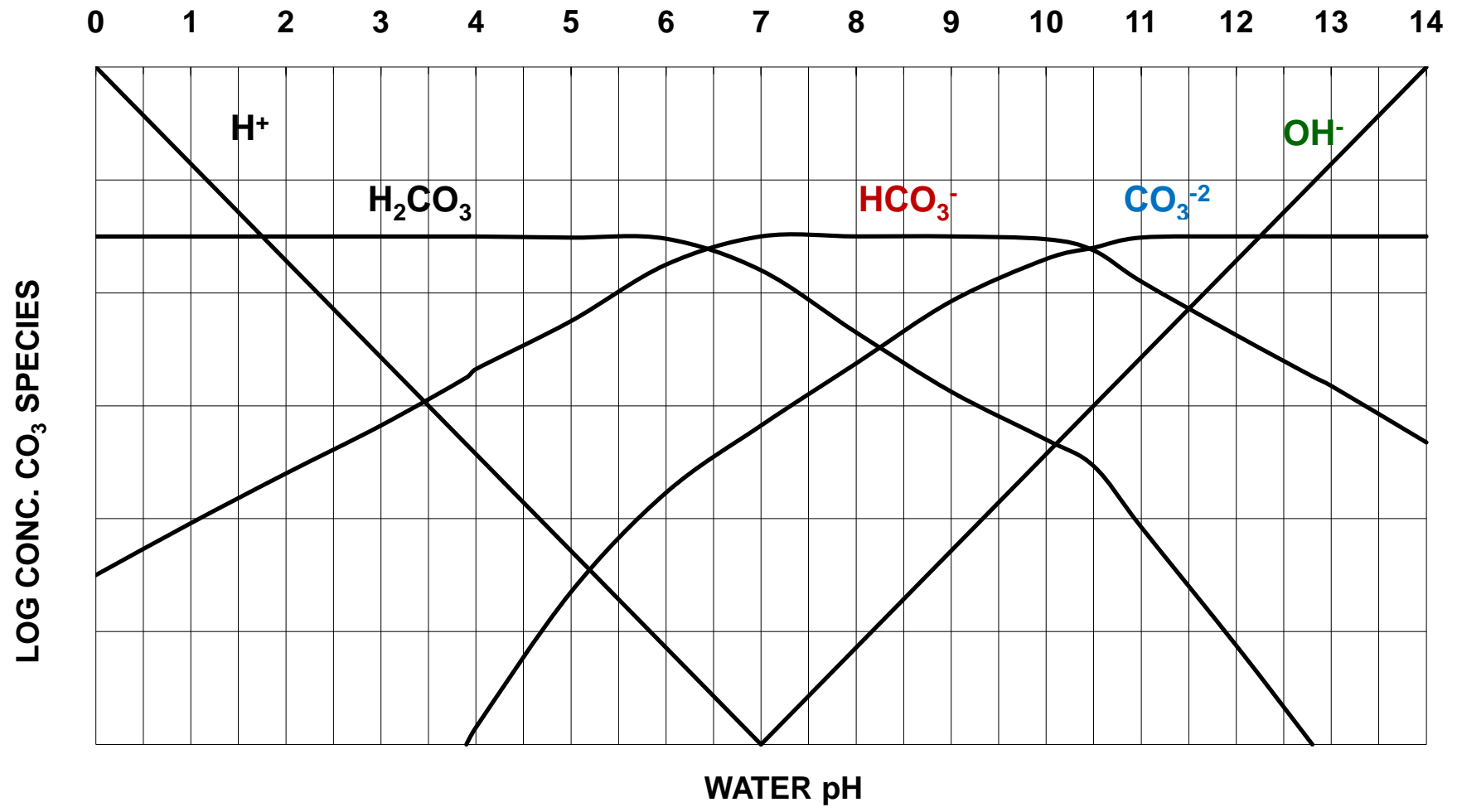
Agenda

- Magnesium Fouling Issues
- Softening Demand Curves
- CO₂ Determinations

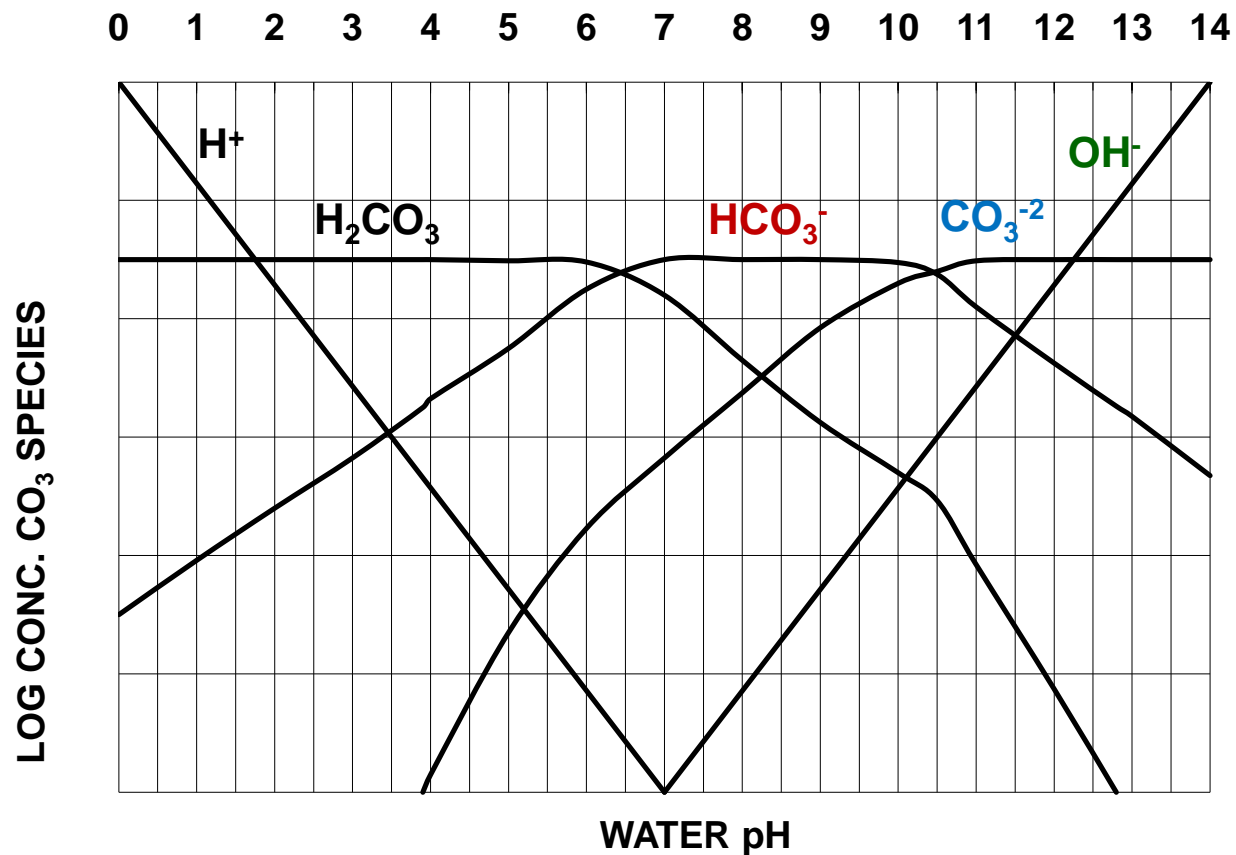
Agenda

- Coagulant Reaction Byproducts
- Recarbonation Chemistry
- CO₂ Dosage Determinations

Carbonate Equilibrium Diagram



Carbonate Equilibrium Diagram



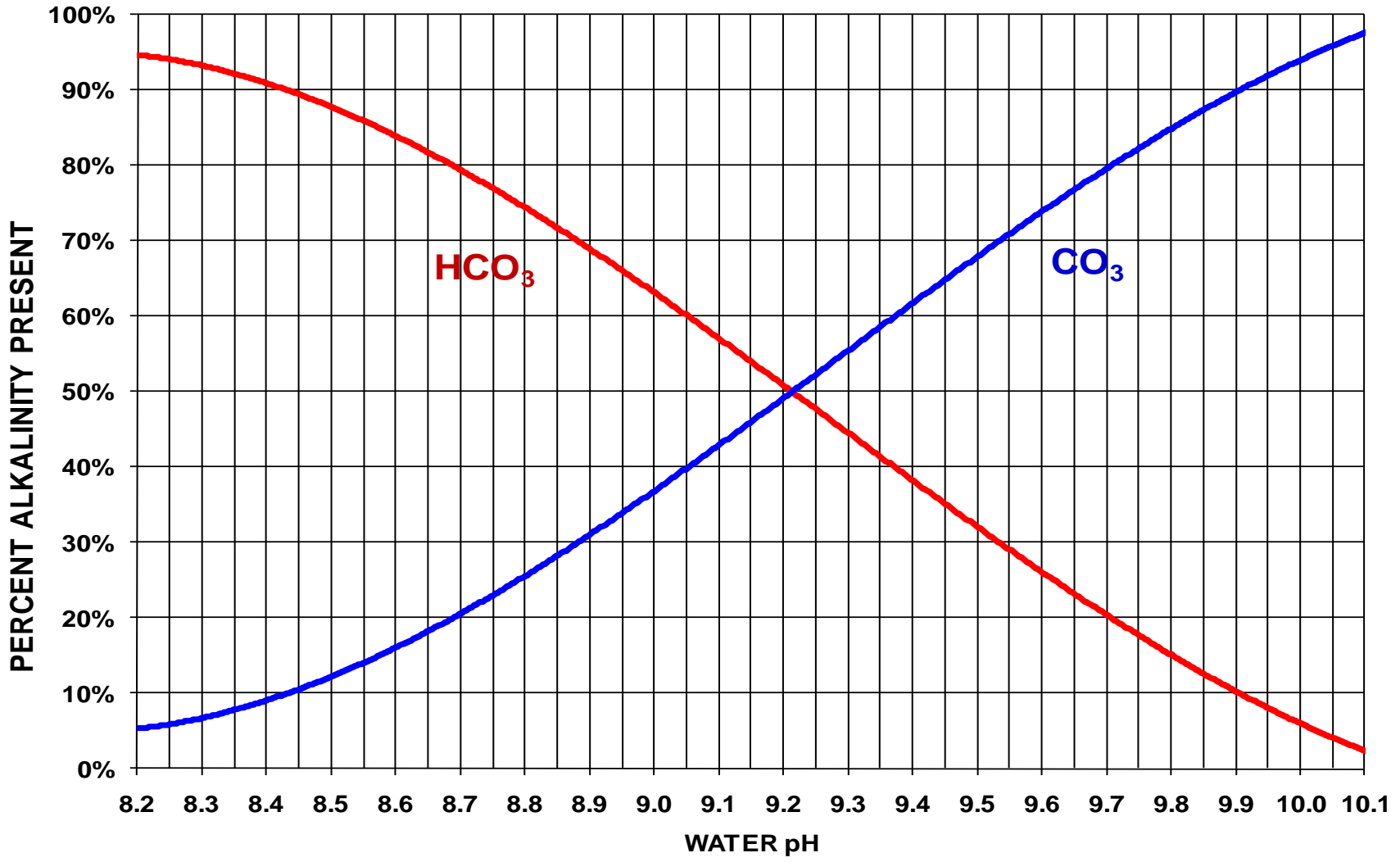
Alkalinity Distribution

- Bicarbonate Alkalinity (HCO₃⁻)
 - Low pH range
- Carbonate Alkalinity (CO₃⁻²)
 - Mid pH range
- Hydroxide Alkalinity (OH⁻)
 - High pH range
- Only two species can exist at same time
 - Restricted by equilibrium and pH

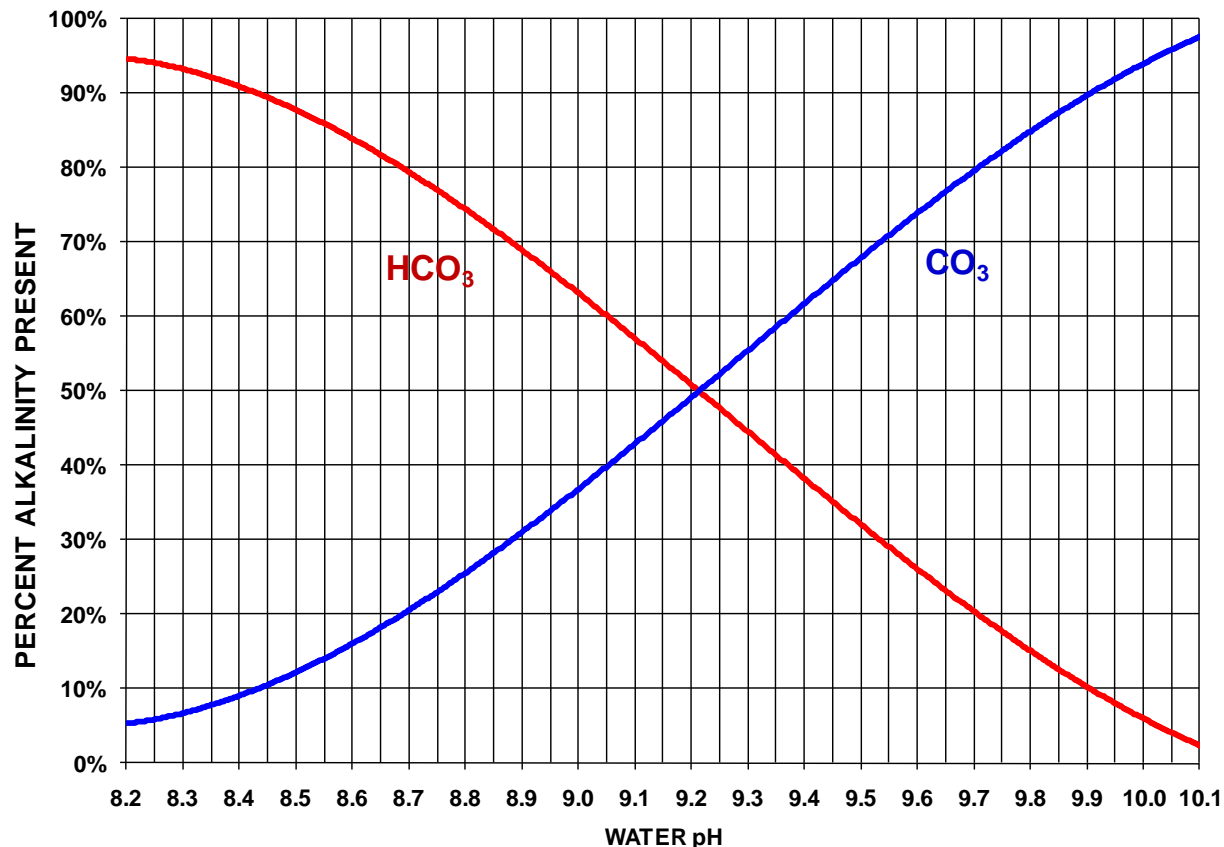
Alkalinity / pH Relationships

- Investigation of lower pH range demonstrates relationship between HCO_3^- alkalinity and CO_3^{2-} alkalinity species
- Defines percentage of each species based on equilibrium pH
- Mirror images - decrease in HCO_3^- reveals proportional increase in CO_3^{2-}

Alkalinity / pH Relationships



Alkalinity / pH Relationships



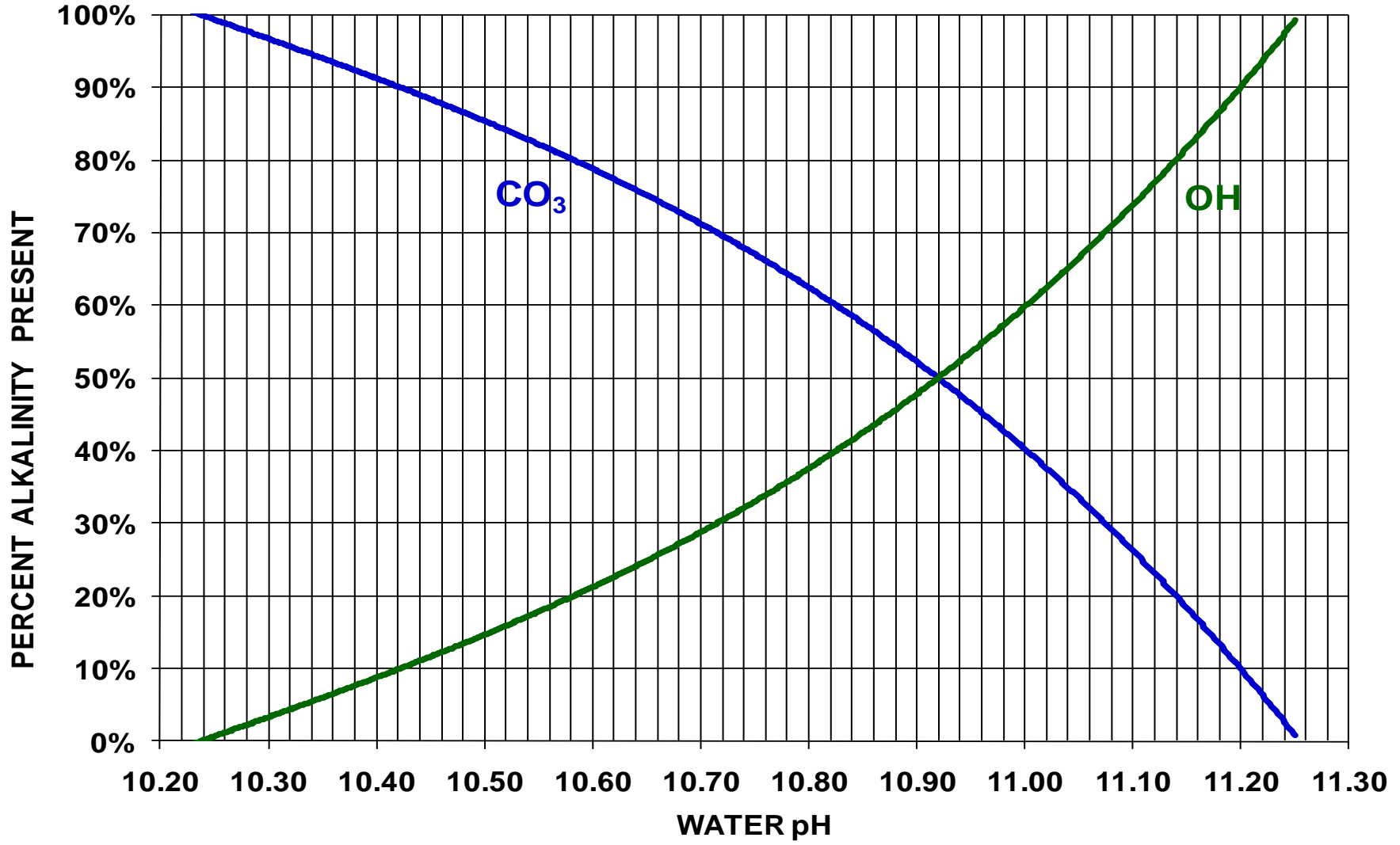
pH Relationships

- Nearly equal alkalinity species
 - At about pH 9.23
- Equilibrium pH defines percentage of species in solution
- Percentages obtained at any pH in the range of the curve

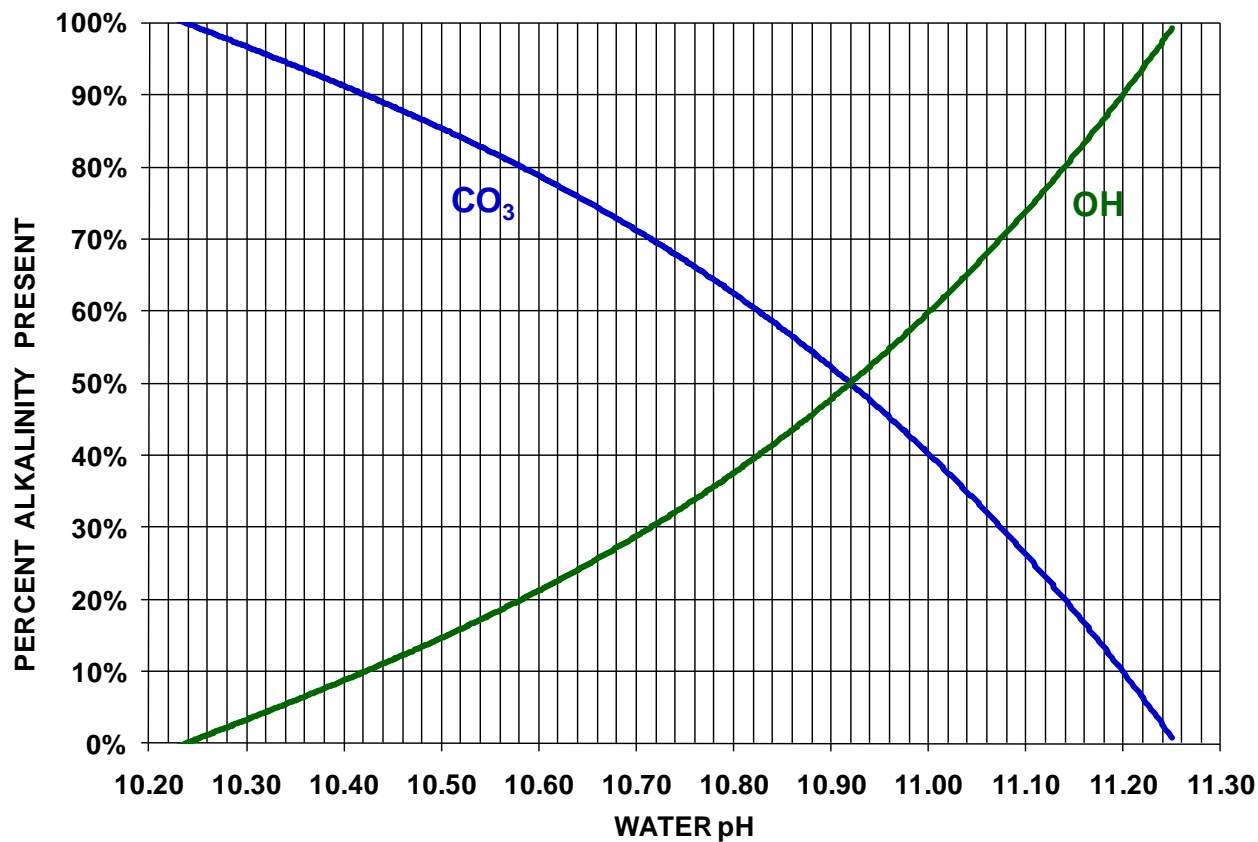
Alkalinity / pH Relationships

- Investigation of higher pH range demonstrates relationship between CO_3 alkalinity and OH alkalinity species
- Defines percentage of each species based on equilibrium pH
- Mirror images - decrease in CO_3 reveals proportional increase in OH

Alkalinity / pH Relationships



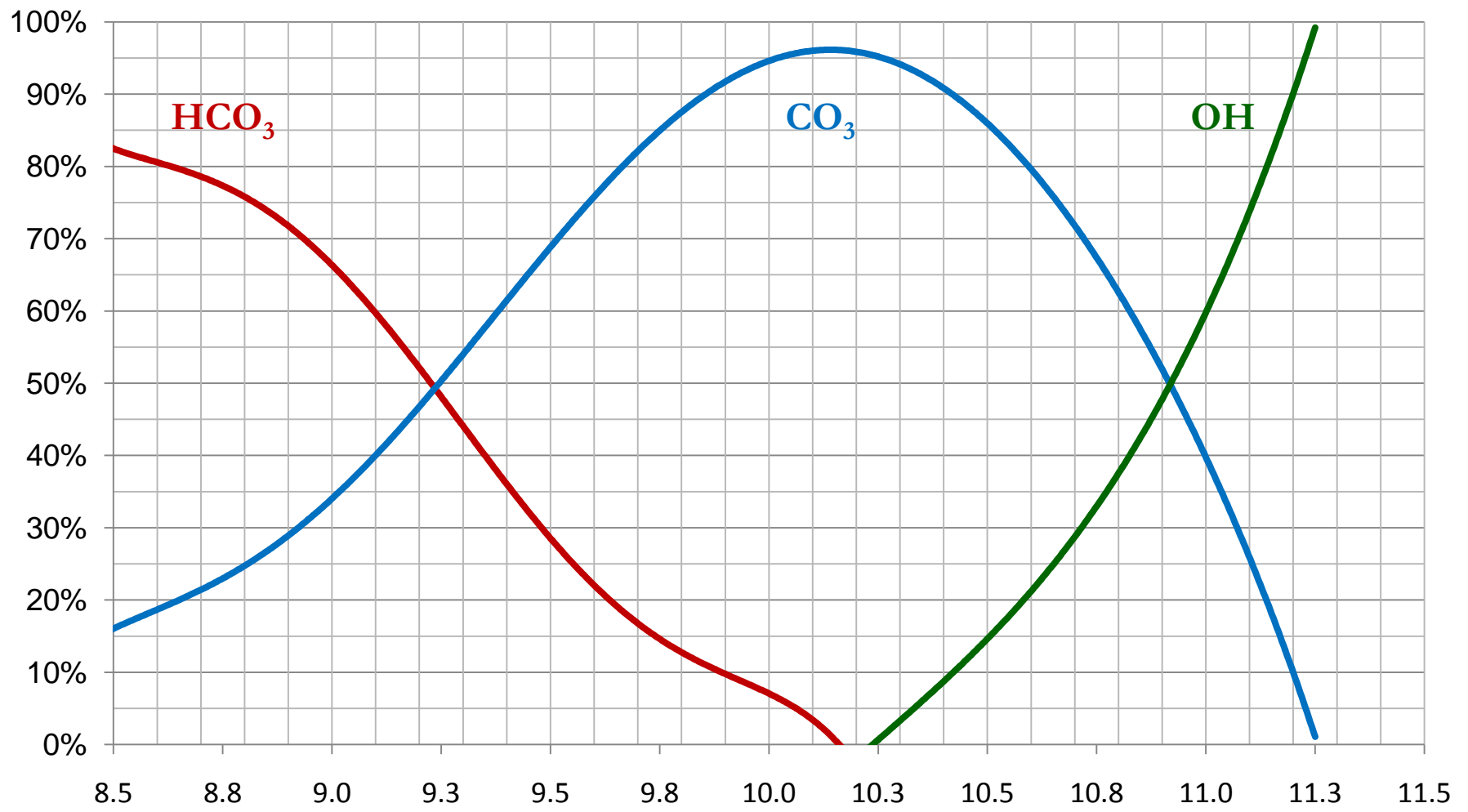
Alkalinity / pH Relationships



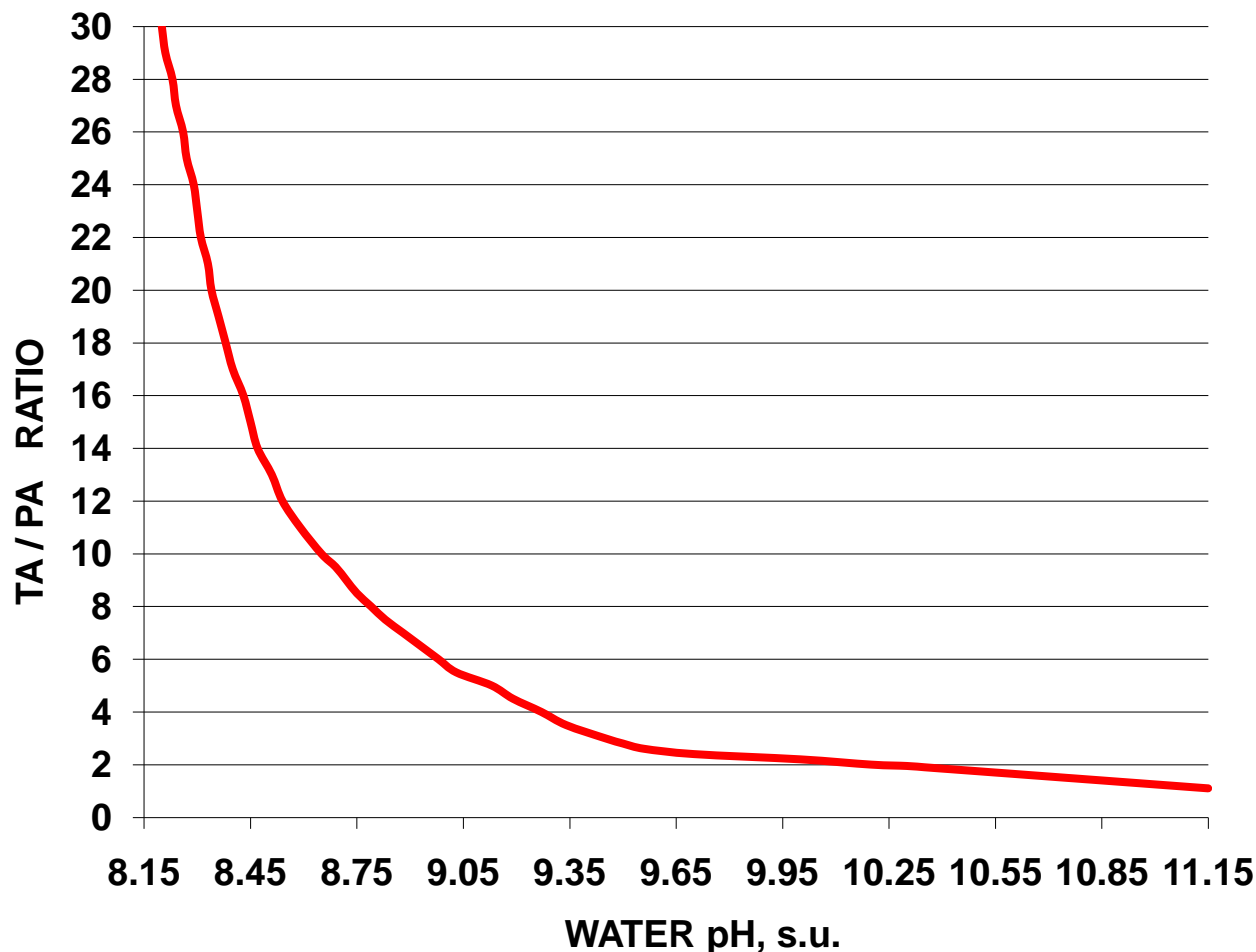
pH Relationships

- Nearly equal alkalinity species
 - At about pH 10.95
- Equilibrium pH defines percentage of species in solution
- Percentages obtained at any pH in the range of the curve

Alkalinity / pH Relationships



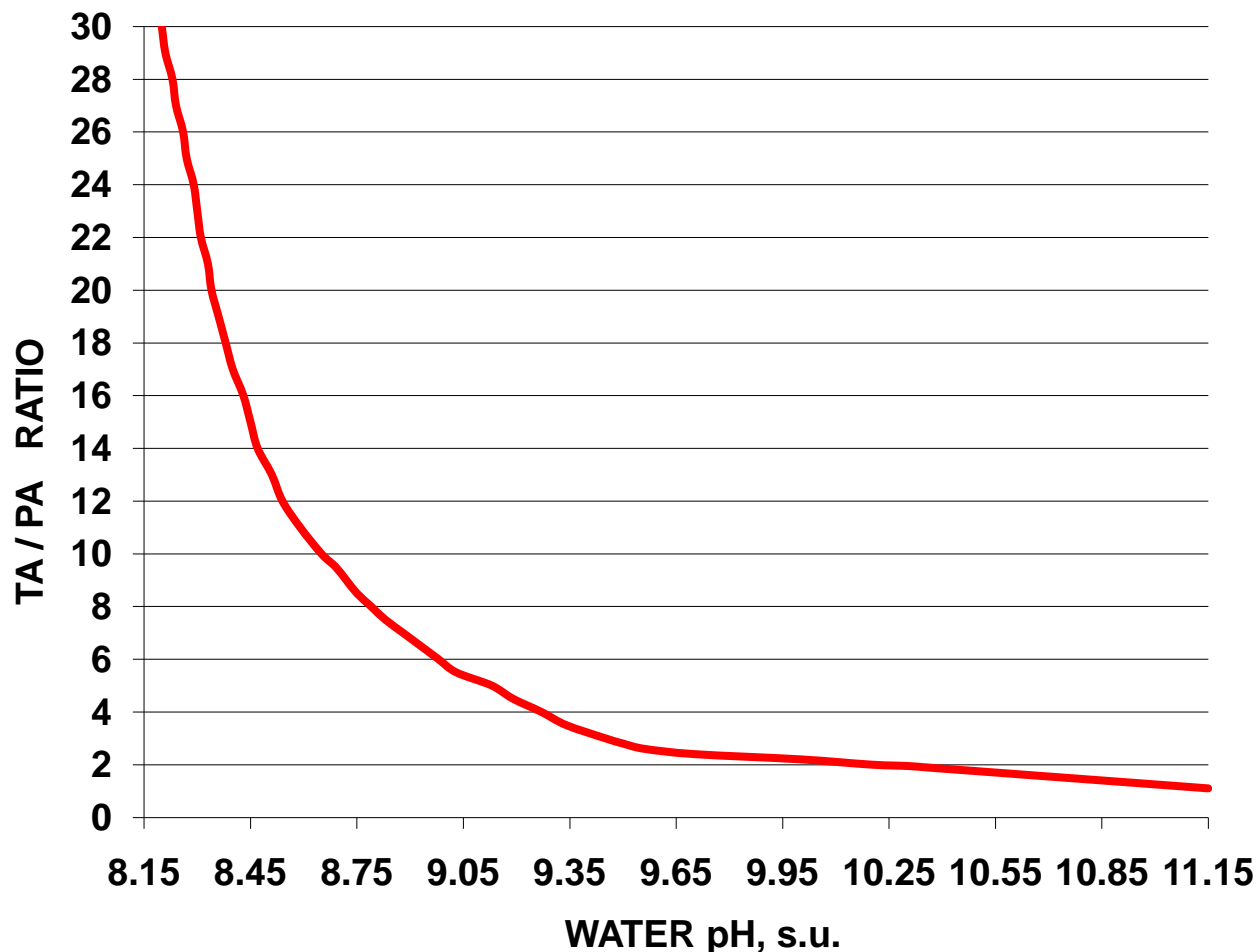
Alkalinity / pH Relationships



TA/PA Ratio Defines Equilibrium pH

- J.M. Montgomery (1954)
- Equilibrium pH established once equilibrium alkalinity concentrations occur
- TA/PA Ratio is related to specific pH values

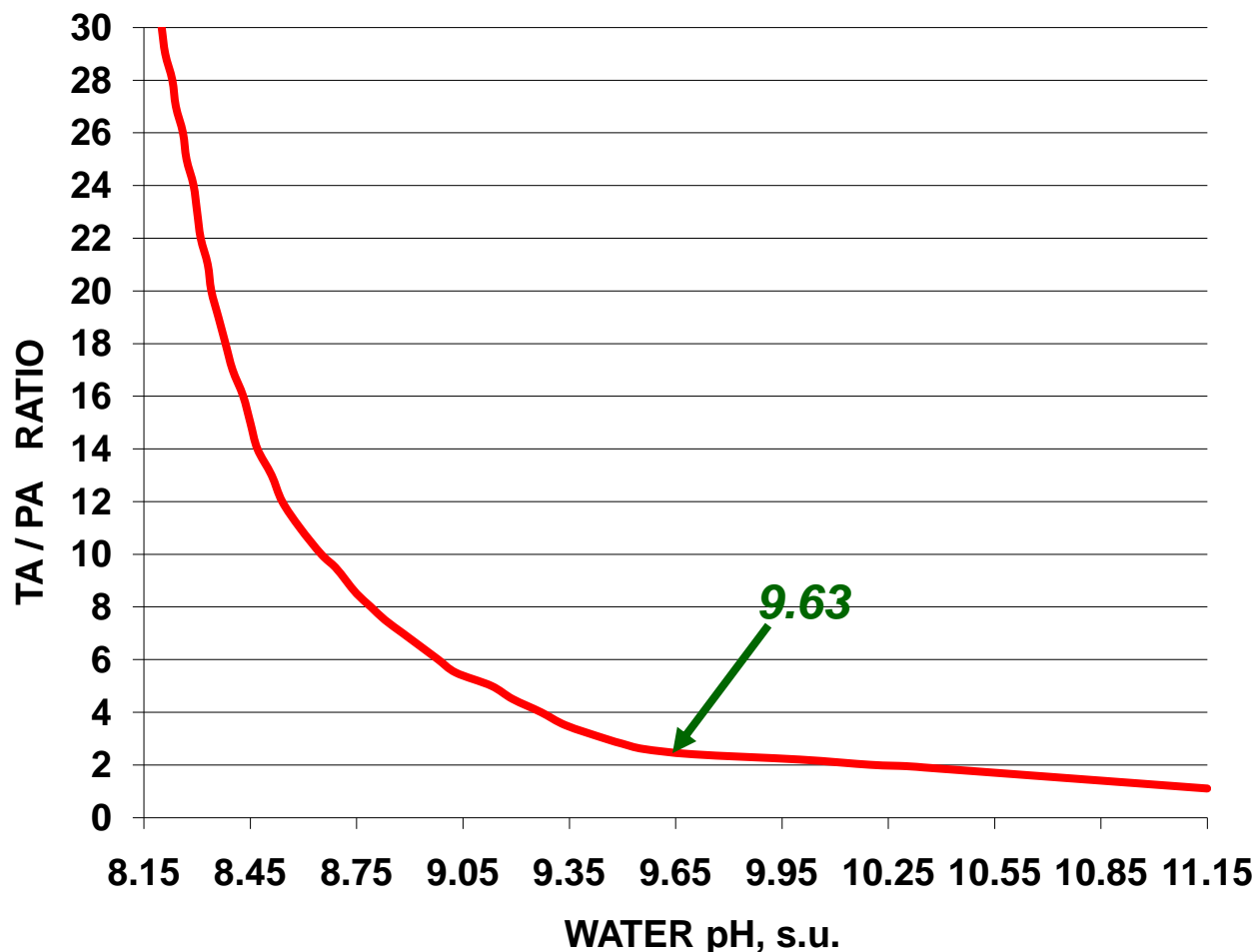
Alkalinity / pH Relationships



TA/PA Ratio Defines Equilibrium pH

- Example
 - TA - 60 mg/L
 - PA - 24 mg/L
- TA/PA Ratio is **2.50**
- Equilibrium pH is

Alkalinity / pH Relationships



TA/PA Ratio Defines Equilibrium pH

- Example
 - TA - 60 mg/L
 - PA - 24 mg/L
- TA/PA Ratio is **2.50**
- Equilibrium pH is **9.63**

Alkalinity / pH Relationships

- Montgomery's work has been placed into table format
- Knowing TA/PA Ratio, pH easily found
 - Used for predictive analyses and troubleshooting
 - Check accuracy of lab tests

Alkalinity / pH Relationships

Excerpt from Table
Relationship Between TA/PA Ratio and Equilibrium pH

| TA/PA Ratio | Water pH | TA/PA Ratio | Water pH |
|-------------|----------|-------------|----------|
| 2.54 | 9.60 | 2.44 | 9.67 |
| 2.53 | 9.61 | 2.43 | 9.68 |
| 2.51 | 9.62 | 2.41 | 9.69 |
| 2.50 | 9.63 | 2.40 | 9.70 |
| 2.49 | 9.64 | 2.39 | 9.71 |
| 2.47 | 9.65 | 2.39 | 9.72 |
| 2.46 | 9.66 | 2.38 | 9.73 |

Alkalinity Titration Equation

- Defines the distribution of alkalinity species and carbonic acid in solution
- Illustrates separation of phenol alkalinity and total alkalinity
 - Demonstrates alkalinity species and where found from titration

Alkalinity Titration Equation



Alkalinity Titration Equation



- Phenol alkalinity $PA = OH + \frac{1}{2}CO_3$
–Phenolphthalein endpoint (clear) pH 8.3±

Alkalinity Titration Equation



- Phenol alkalinity $PA = OH + \frac{1}{2}CO_3$
– Phenolphthalein endpoint (clear) pH 8.3±
- Total alkalinity $TA = PA + \frac{1}{2}CO_3 + HCO_3$
– Total alkalinity endpoint (red / orange) pH 4.5±

Alkalinity Calculations Matrix

- Titration equation helps develop calculation matrix
- Matrix equations define concentrations of CO_3 alkalinity, OH alkalinity, and HCO_3 alkalinity
- Matrix is based on TA and PA relationships

Alkalinity Calculations Matrix

| | Carbonates | Hydroxides | Bicarbonates |
|------------|--------------|-------------|--------------|
| $2PA > TA$ | $2(TA - PA)$ | $TA - CO_3$ | 0 |
| $2PA < TA$ | 2PA | 0 | $TA - CO_3$ |

- Only one or two forms of alkalinity can exist in the water, third form is zero
- Forms simply difference between total alkalinity and CO_3 species
- $2PA = TA$ all alkalinity is CO_3
- $2PA = 0$ all alkalinity is HCO_3

Solubility Relationships

- Solubility of specific compounds help define how precipitative softening works
- Calcium carbonate (CaCO_3) solubility equation shows solubility product (K_{sp}) as a function of temperature

$$K_{sp}, \text{CaCO}_3 = 10^{\left[13.870 - \left(\frac{3059}{TK} \right) - 0.04035TK \right]}$$

Solubility Relationships

- Magnesium hydroxide $[Mg(OH)_2]$ solubility equation also shows solubility product (K_{sp}) as a function of temperature

$$K_{sp}, Mg(OH)_2 = 10^{[-0.0175TC - 9.97]}$$

Solubility Relationships

- K_{sp} determines soluble limit of CaCO_3 and $\text{Mg}(\text{OH})_2$ in water (temperature dependent)
 - Concentration that will remain soluble after precipitation occurs
- pH defined as $-\log(\text{H}^+)$ concentration

Solubility Relationships

- K_{sp} determines soluble limit of CaCO_3 and $\text{Mg}(\text{OH})_2$ in water (temperature dependent)
 - Concentration that will remain soluble after precipitation occurs
- pH defined as $-\log(\text{H}^+)$ concentration
- $\text{p}K_{sp}$ is $-\log(K_{sp})$
 - Defines relative pH needed to force precipitation based on water temperature

Solubility Relationships

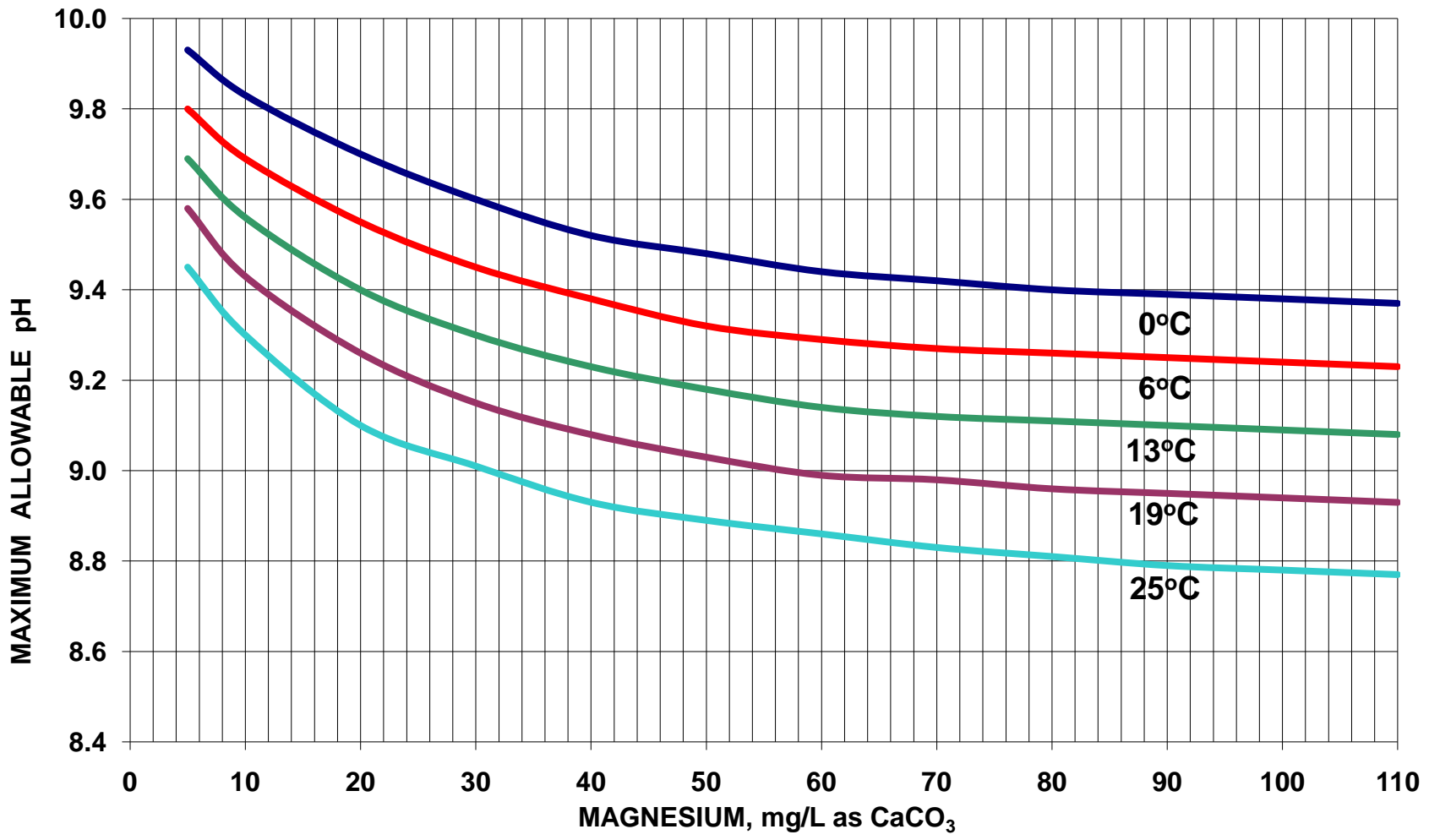
| | K_{sp} | pK_{sp} |
|-------------------|----------|-----------|
| CaCO_3 | ~24 mg/L | 8.49 |
| Mg(OH)_2 | ~12 mg/L | 10.59 |

- K_{sp} concentrations remain soluble in water, relative minimum hardness and alkalinity are about 36 mg/L
- pK_{sp} defines pH necessary to precipitate solids, demonstrates that Ca^{+2} is removed first and Mg^{+2} follows once calcium precipitation is completed

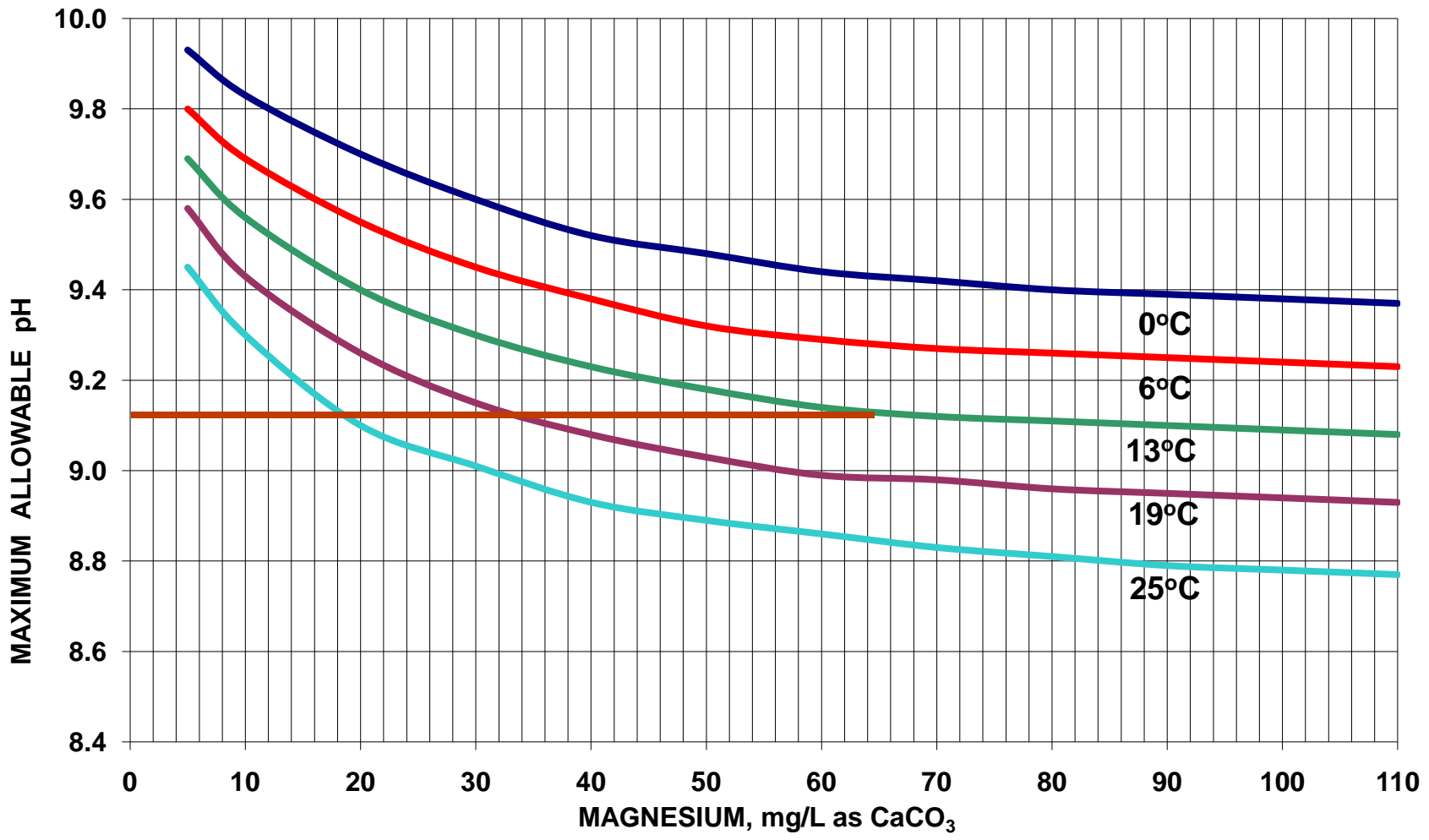
Magnesium Fouling Issues

- Magnesium hydroxide [$\text{Mg}(\text{OH})_2$] tends to foul hot water systems with scale
- Temperature and pH determine scale-forming tendencies of $\text{Mg}(\text{OH})_2$
- Helps establish how much magnesium can be in solution

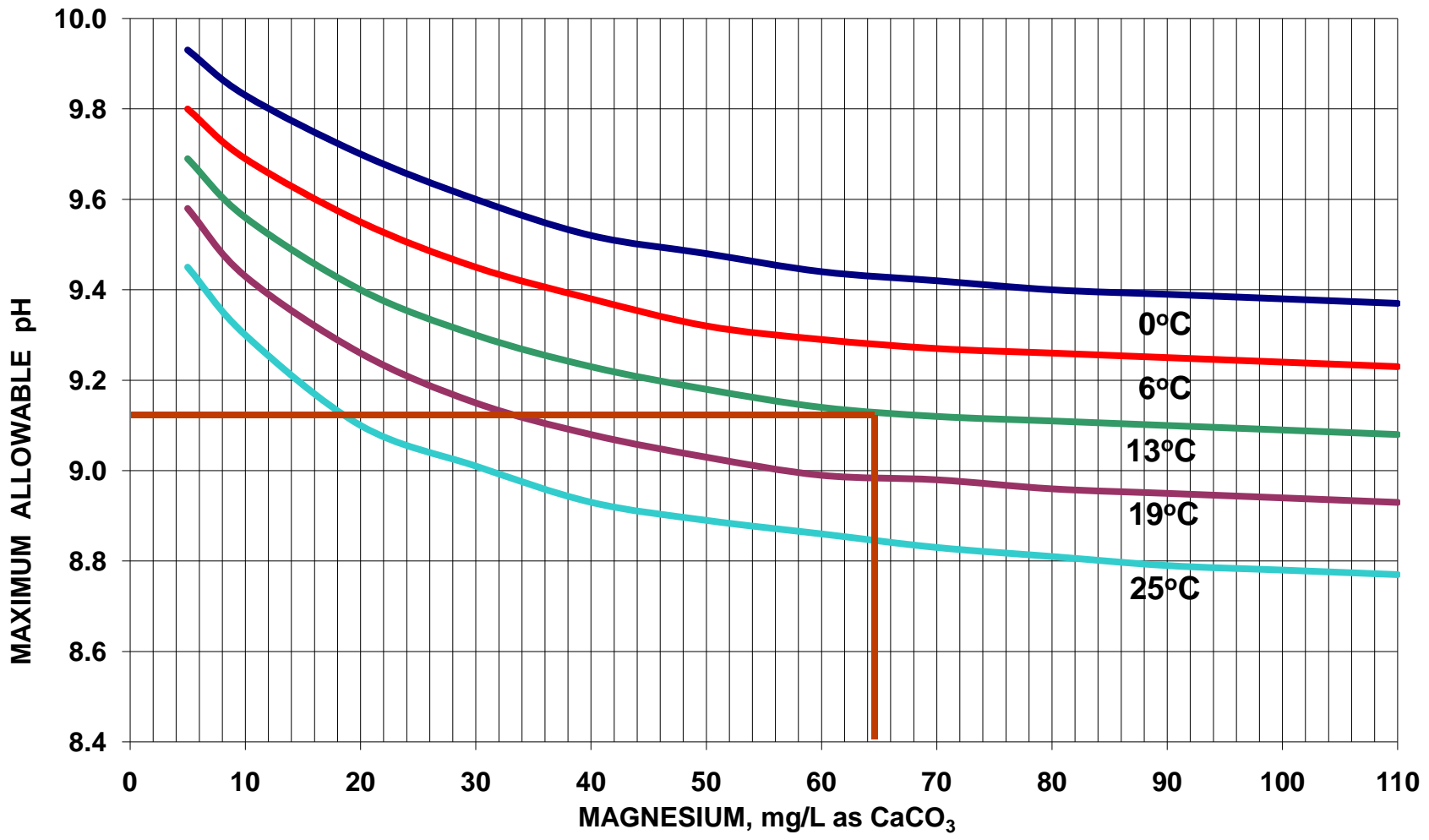
Magnesium Fouling Issues



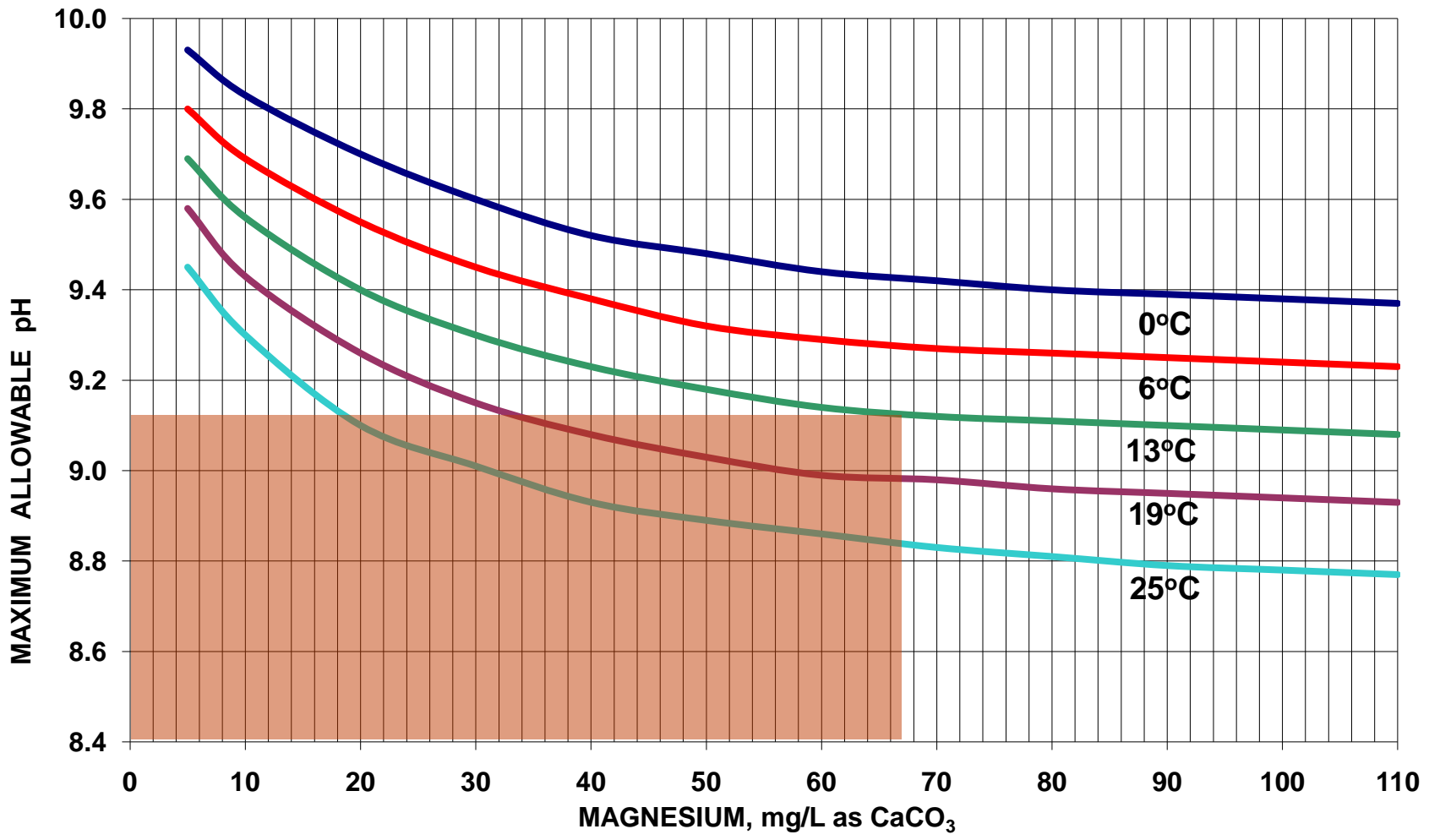
Magnesium Fouling Issues



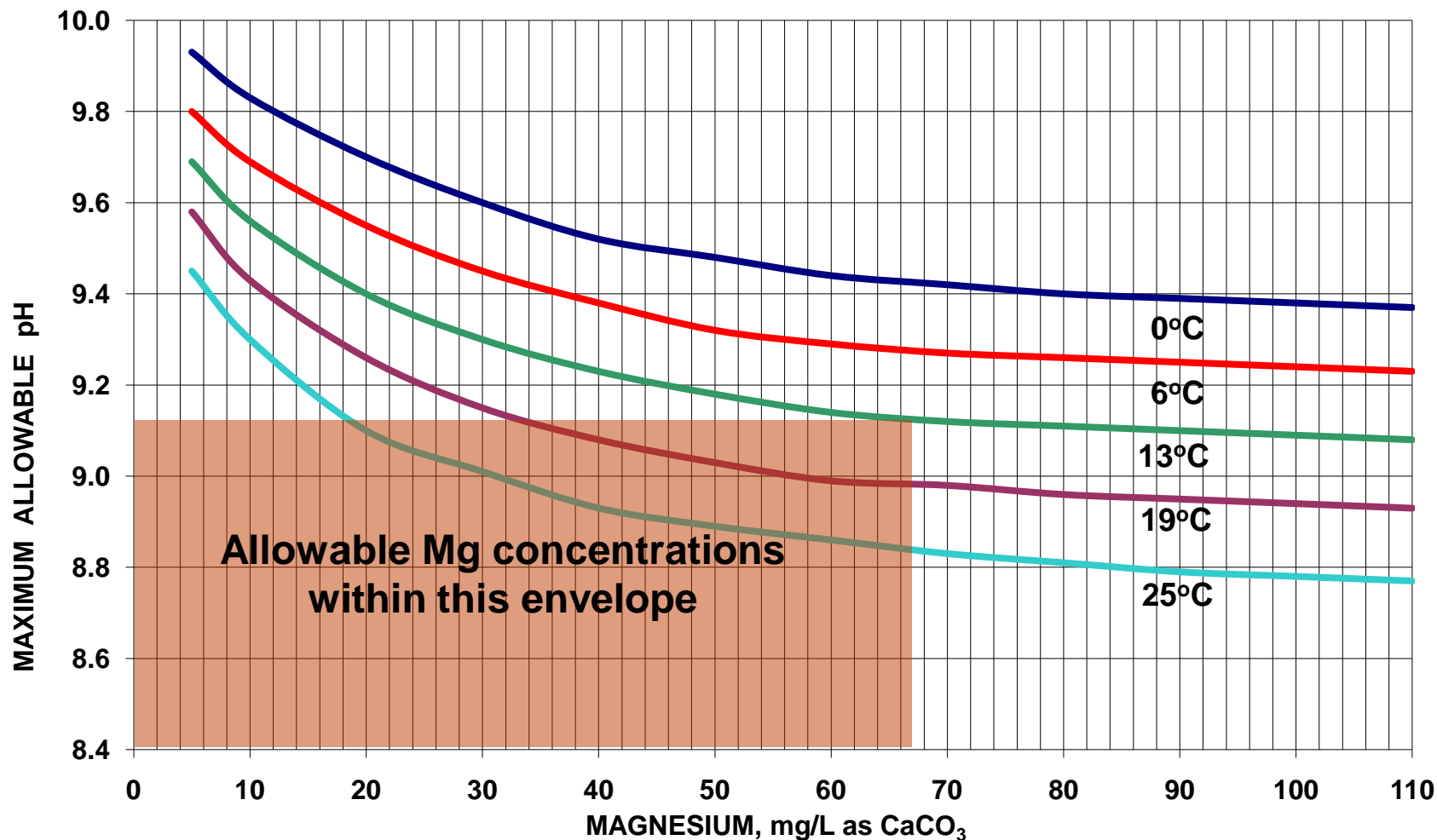
Magnesium Fouling Issues



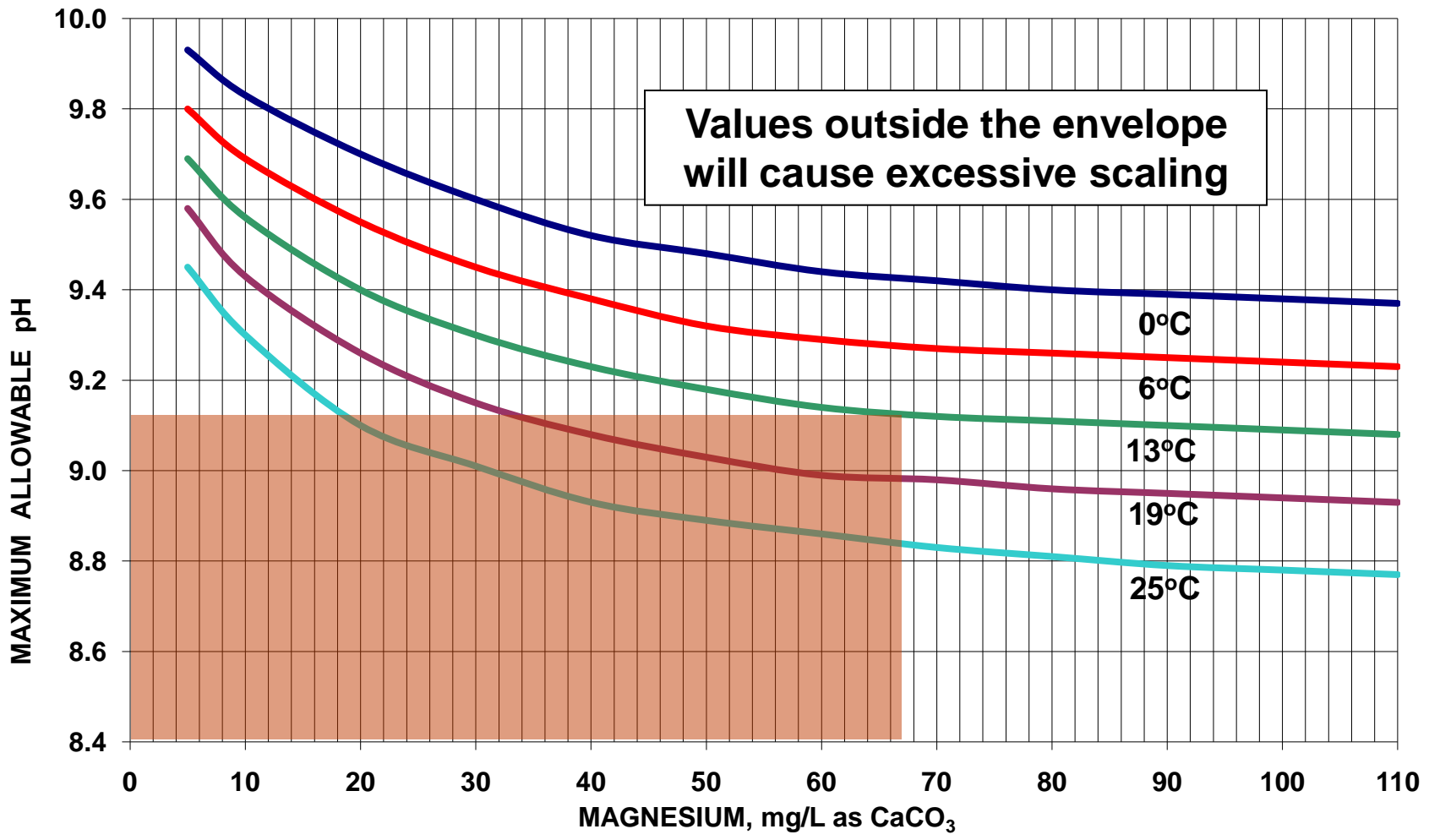
Magnesium Fouling Issues



Magnesium Fouling Issues



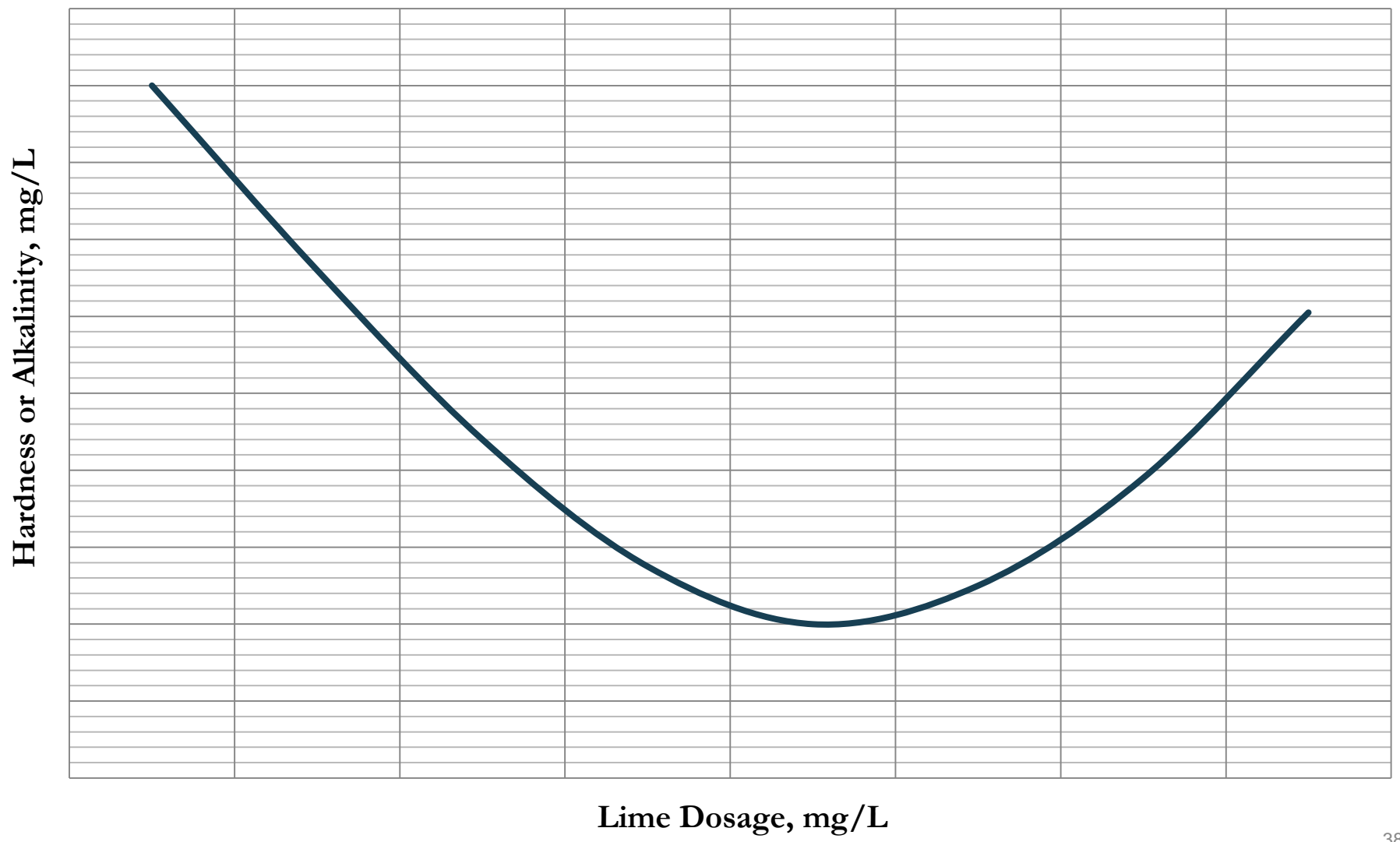
Magnesium Fouling Issues



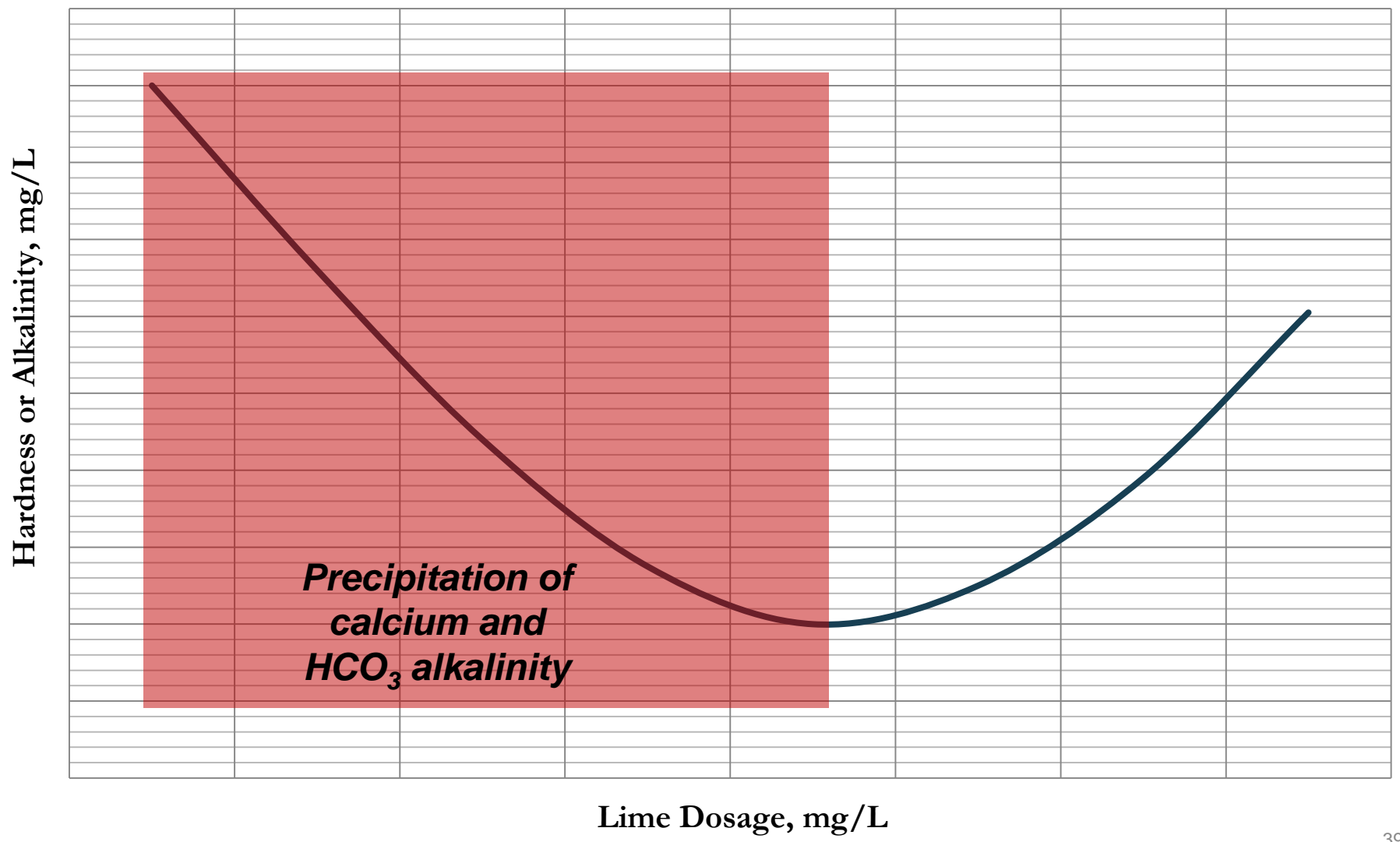
Softening Demand Curves

- Demonstrate relationships presented
- Illustrate precipitation of alkalinity and calcium
- Show magnesium precipitation occurrence as function of pH
- Depict solubility characteristics for Ca^{+2} and Mg^{+2}

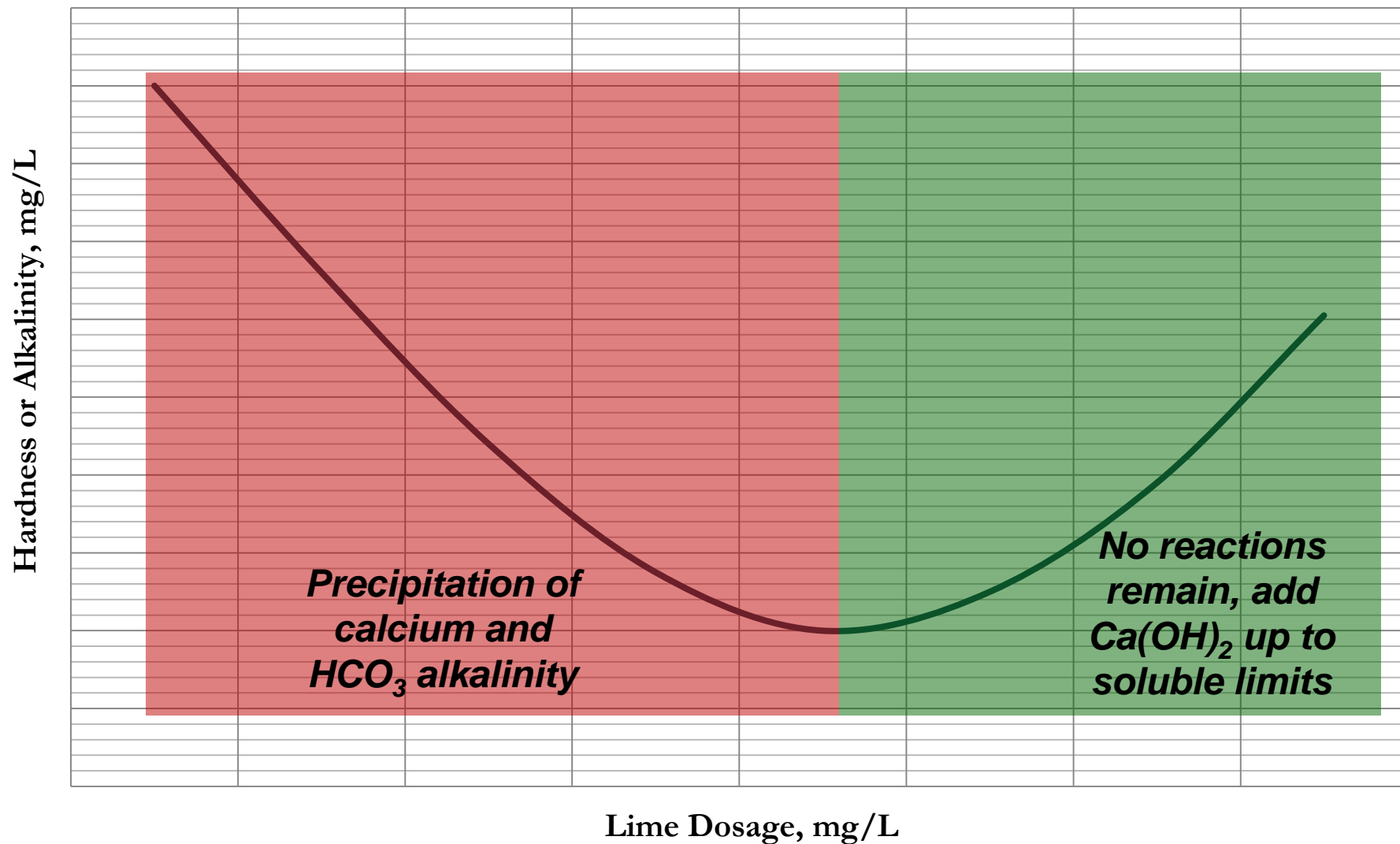
Softening Demand Curves



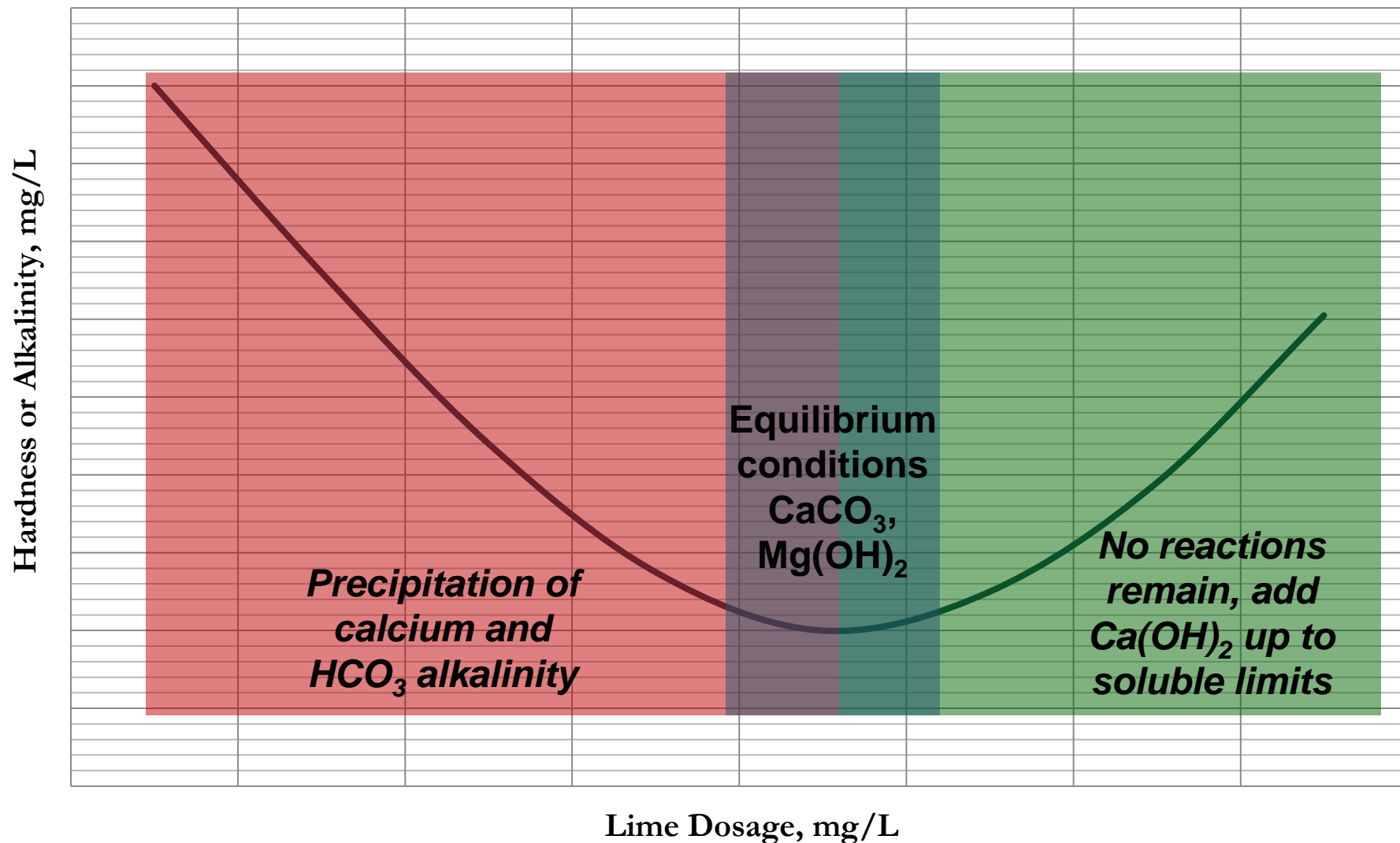
Softening Demand Curves



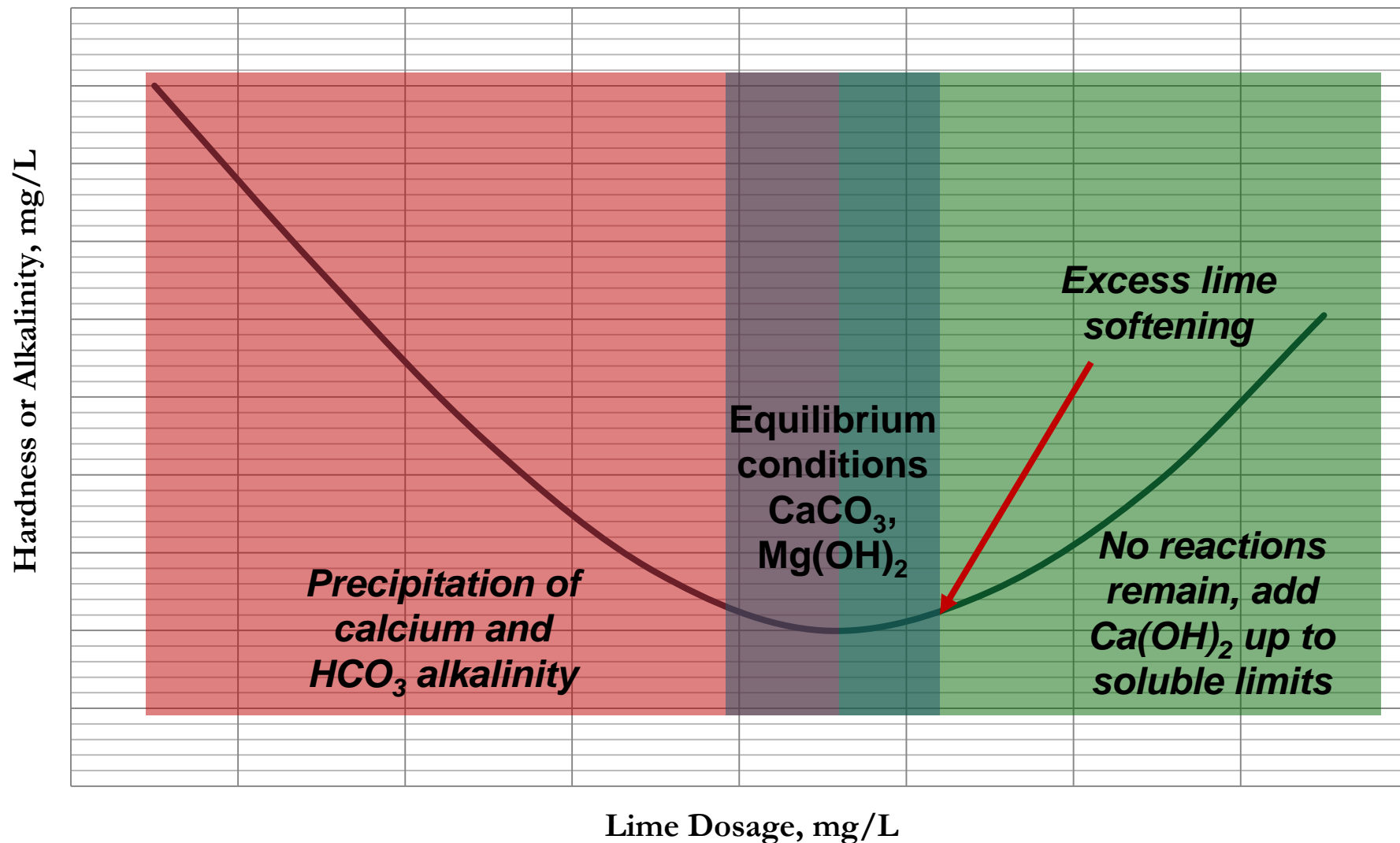
Softening Demand Curves



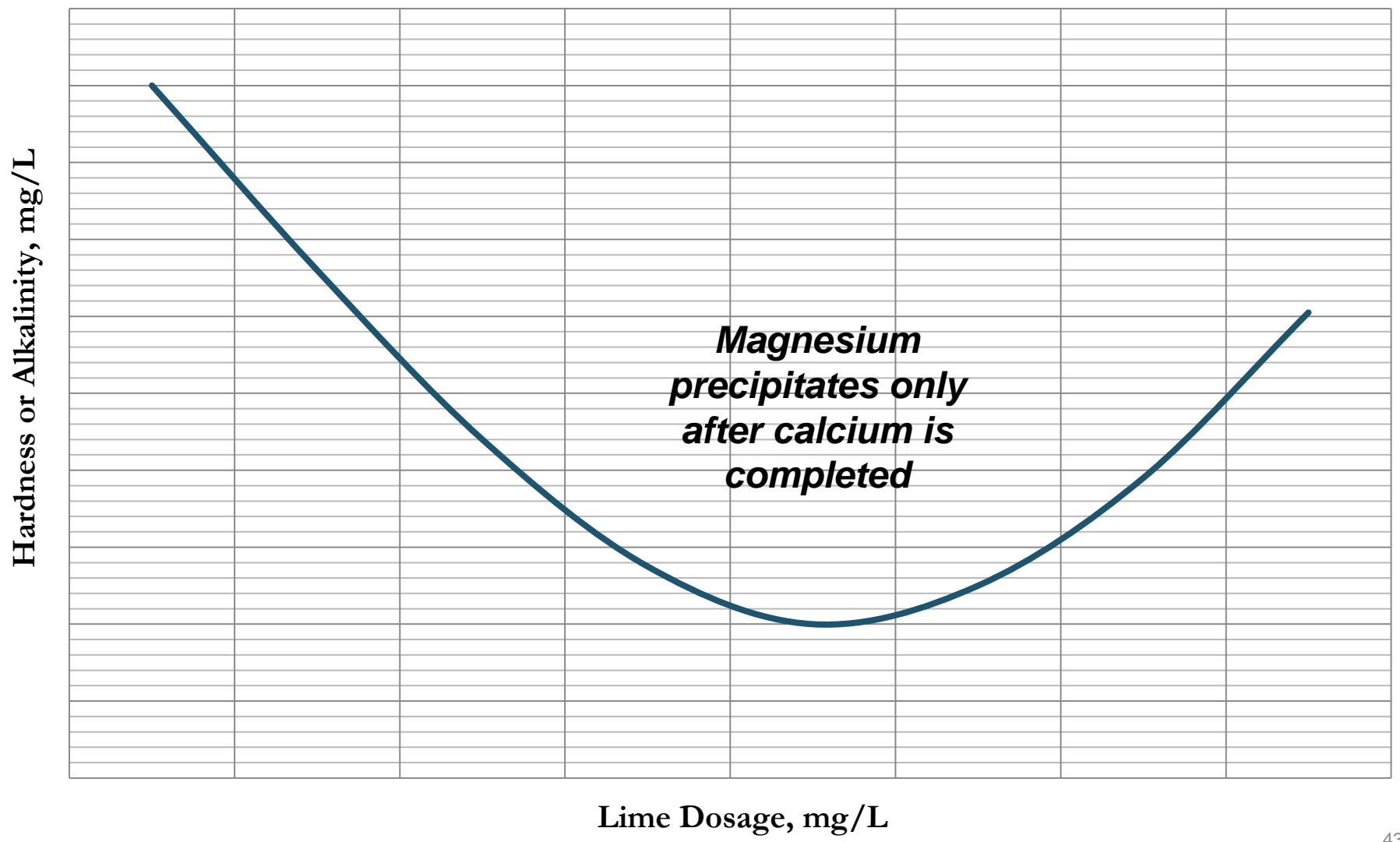
Softening Demand Curves



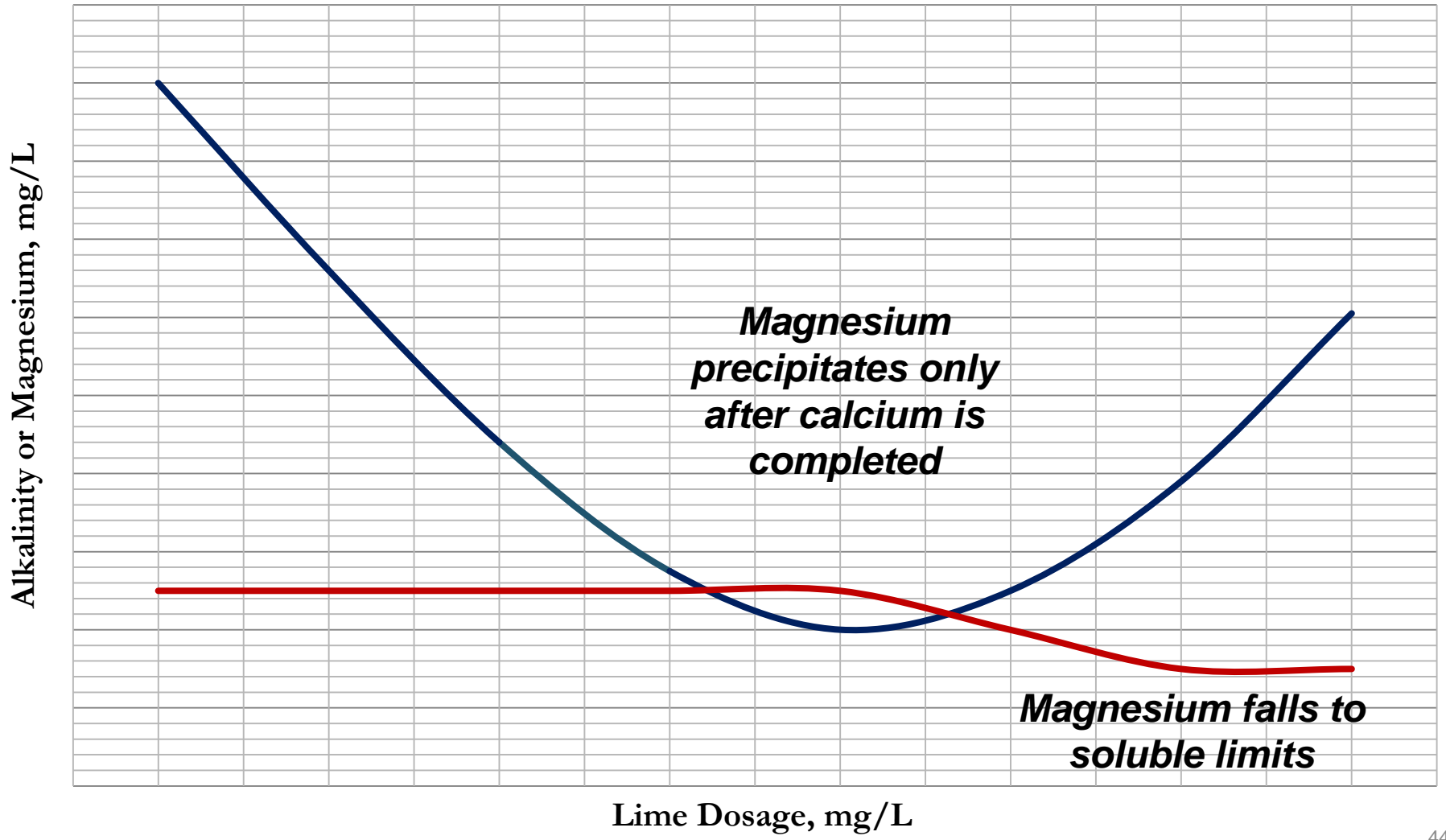
Softening Demand Curves



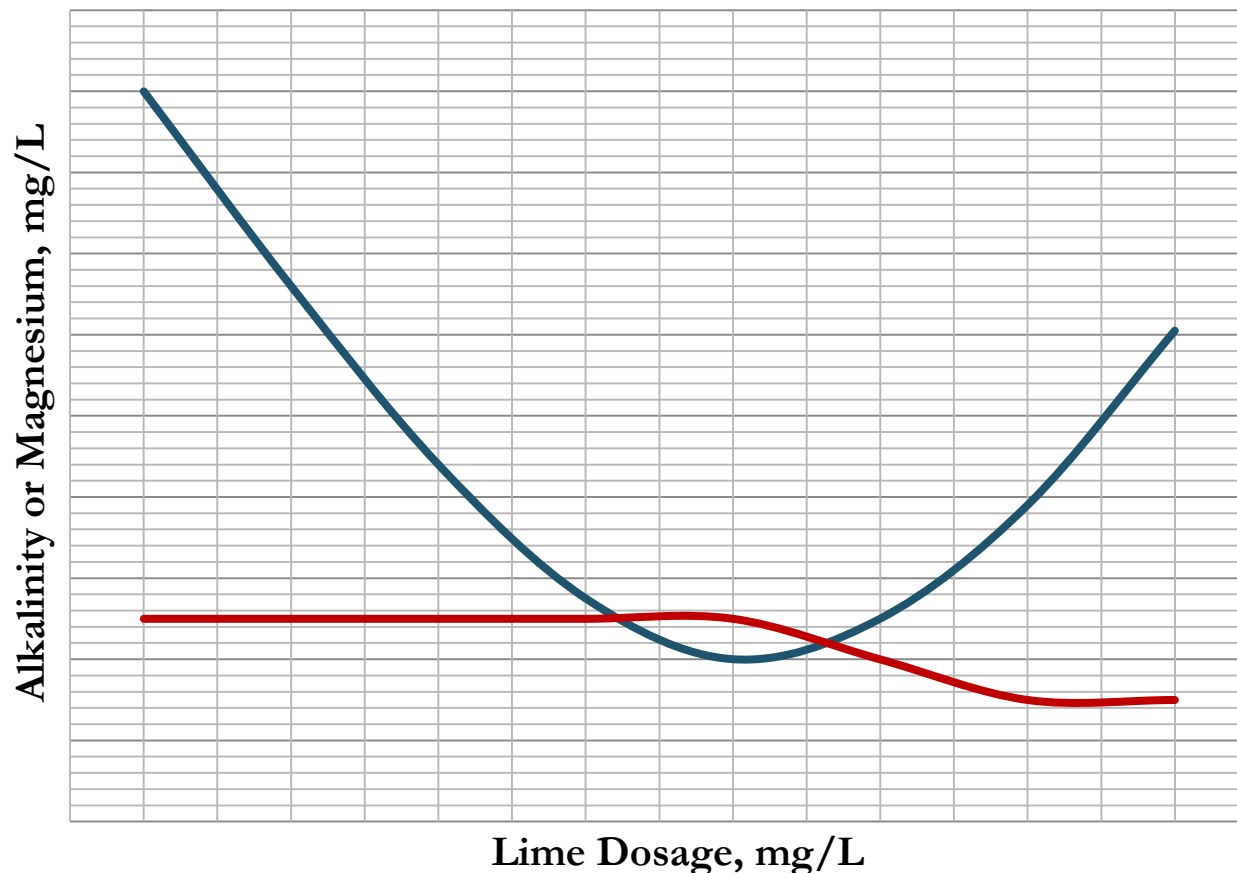
Softening Demand Curves



Softening Demand Curves



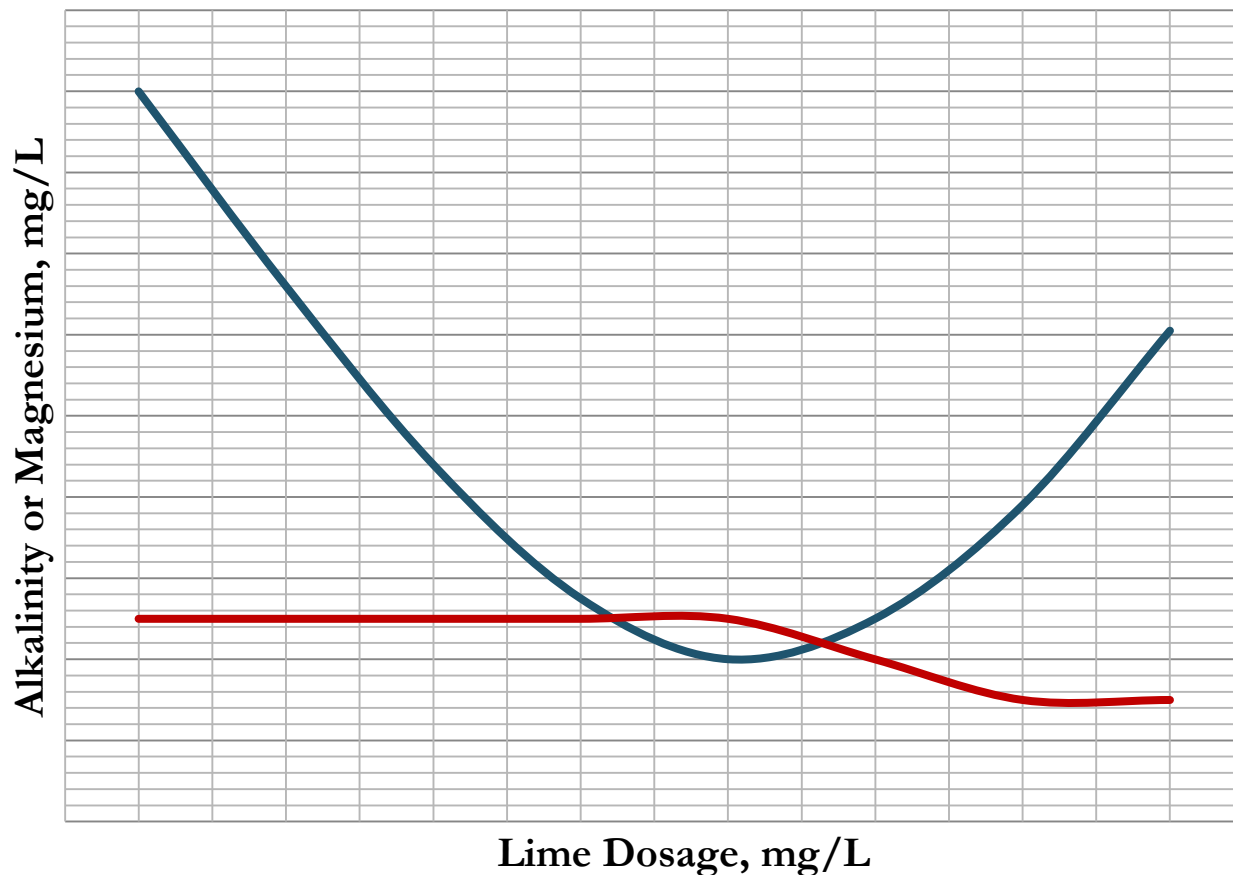
Softening Demand Curves



Demand Relationships

- Calcium and alkalinity precipitate first
 - At $\text{pH} \geq 8.49$
- Magnesium precipitation occurs after calcium completed
 - At $\text{pH} \geq 10.59$
- Can reduce hardness/alkalinity to soluble limits

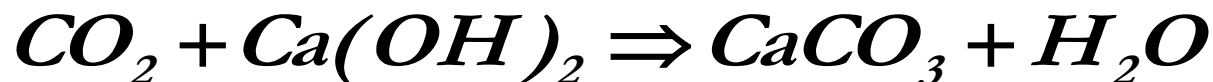
Softening Demand Curves



Demand Relationships

- Beyond minimum point - hardness, alkalinity, calcium increase
 - Soluble limit ranges from 800 mg/L to 1,600 mg/L
- Minimum turbidity often occurs near bottom of curve
 - Soluble limits for calcium
- Magnesium reduced to soluble limits only

CO₂ Determinations



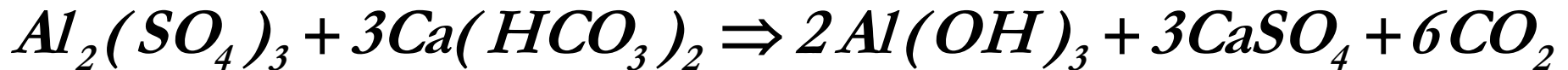
- CO₂ creates demand for lime
- High CO₂ should be removed with aeration
—>10 mg/L CO₂ aeration more cost effective

- Calculation in Standard Methods

$$CO_2, mg / L = 2HCO_3 * 10^{(6-pH)}$$

- Nomograph method also available

Coagulant Reaction Byproducts



- Alkalinity consumed during coagulation reactions
- Alkalinity essentially converted to **noncarbonate** hardness, soda ash or caustic soda needed for removal
- CO₂ creates additional lime demand

Coagulant Reaction Byproducts

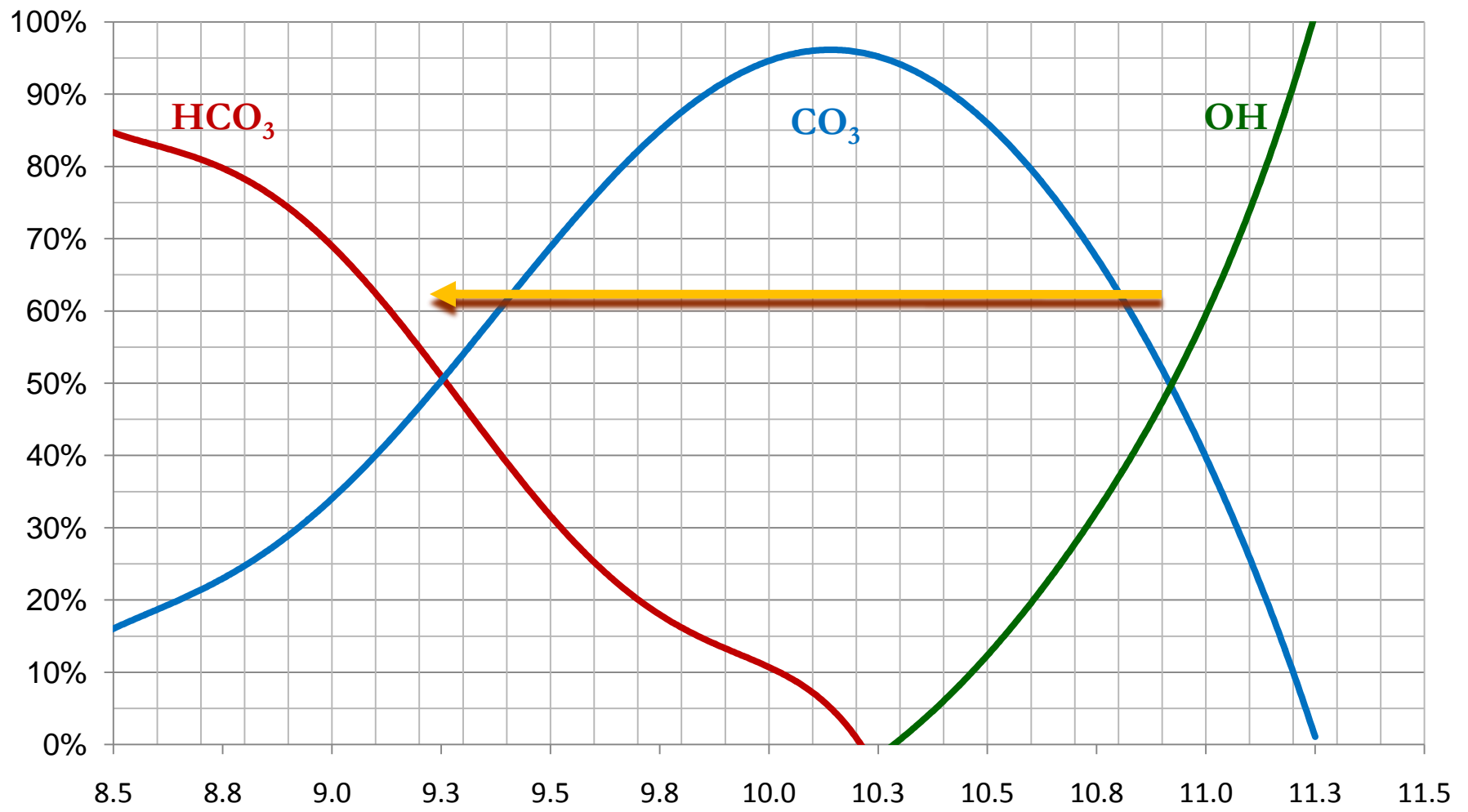
| Coagulant | Alkalinity Consumed, mg/L | Dissolved CO ₂ Formed, mg/L |
|--|---------------------------|--|
| Alum | 0.5 | 0.71 |
| Ferric Chloride | 0.92 | 0.92 |
| Ferric Sulfate | 1.28 | 0.89 |
| Aluminum Chlorohydrate and Polyaluminum Chloride | 0.25 | 0.18 |

Recarbonation Chemistry



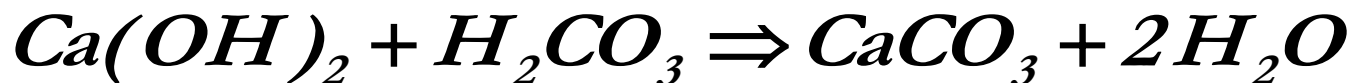
- Carbonic acid shifts alkalinity species due to chemical reactions
 - Total alkalinity often remains unchanged
 - $TA = PA + \frac{1}{2} CO_3 + HCO_3$
 - Phenol alkalinity changes due to change in alkalinity species
 - $PA = OH + \frac{1}{2} CO_3$
- Equilibrium conditions force shift in pH

Recarbonation Chemistry



Recarbonation Chemistry

- OH alkalinity reacts to form CO₃ alkalinity



- CO₃ alkalinity reacts to form HCO₃ alkalinity



Recarbonation Chemistry

- Author's equation

$$CO_2, mg / L = \left[OH + \left(\frac{CO_3 - HCO_3}{2} \right) \right] * 0.44$$

- If OH present, two iterations determines CO₂ dosage
- If OH absent, one iteration needed
- Examples in another presentation
 - *Precipitative Softening and Recarbonation Course*

Questions