

Process Chemistry Relationships for Precipitative Softening and Recarbonation

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Agenda

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

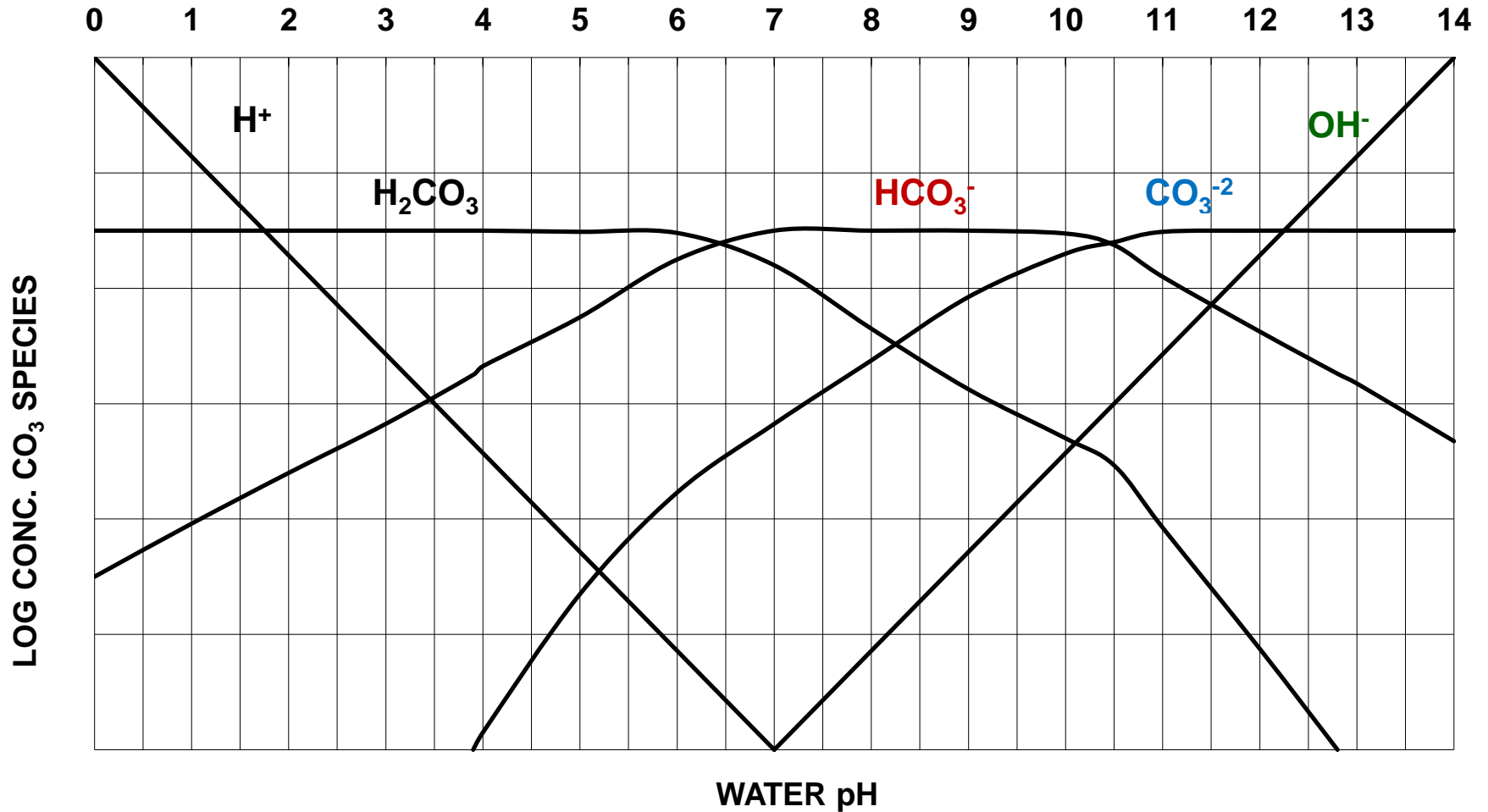
Agenda

- Magnesium Fouling Issues
- Softening Demand Curves
- CO₂ Determinations

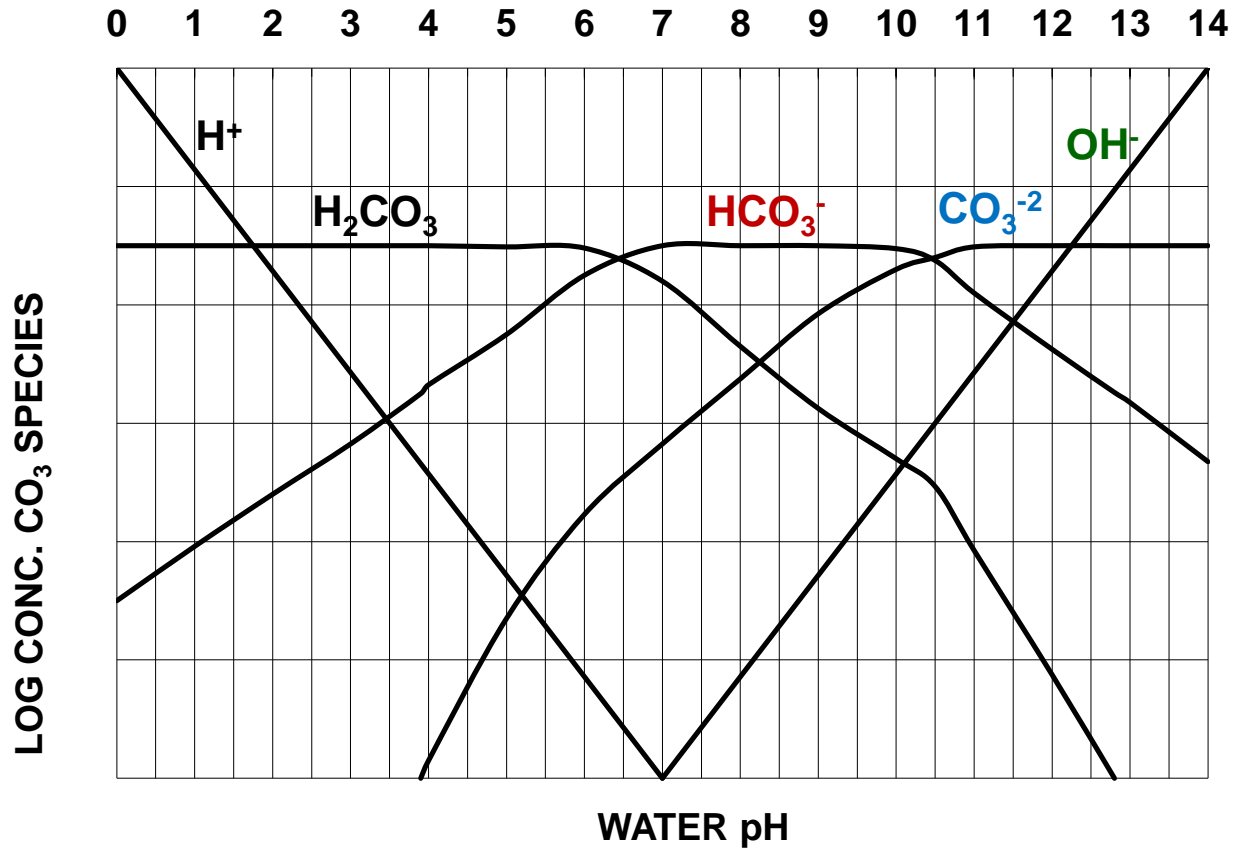
Agenda

- Coagulant Reaction Byproducts
- Recarbonation Chemistry
- CO₂ Dosage Determinations

Carbonate Equilibrium Diagram



Carbonate Equilibrium Diagram



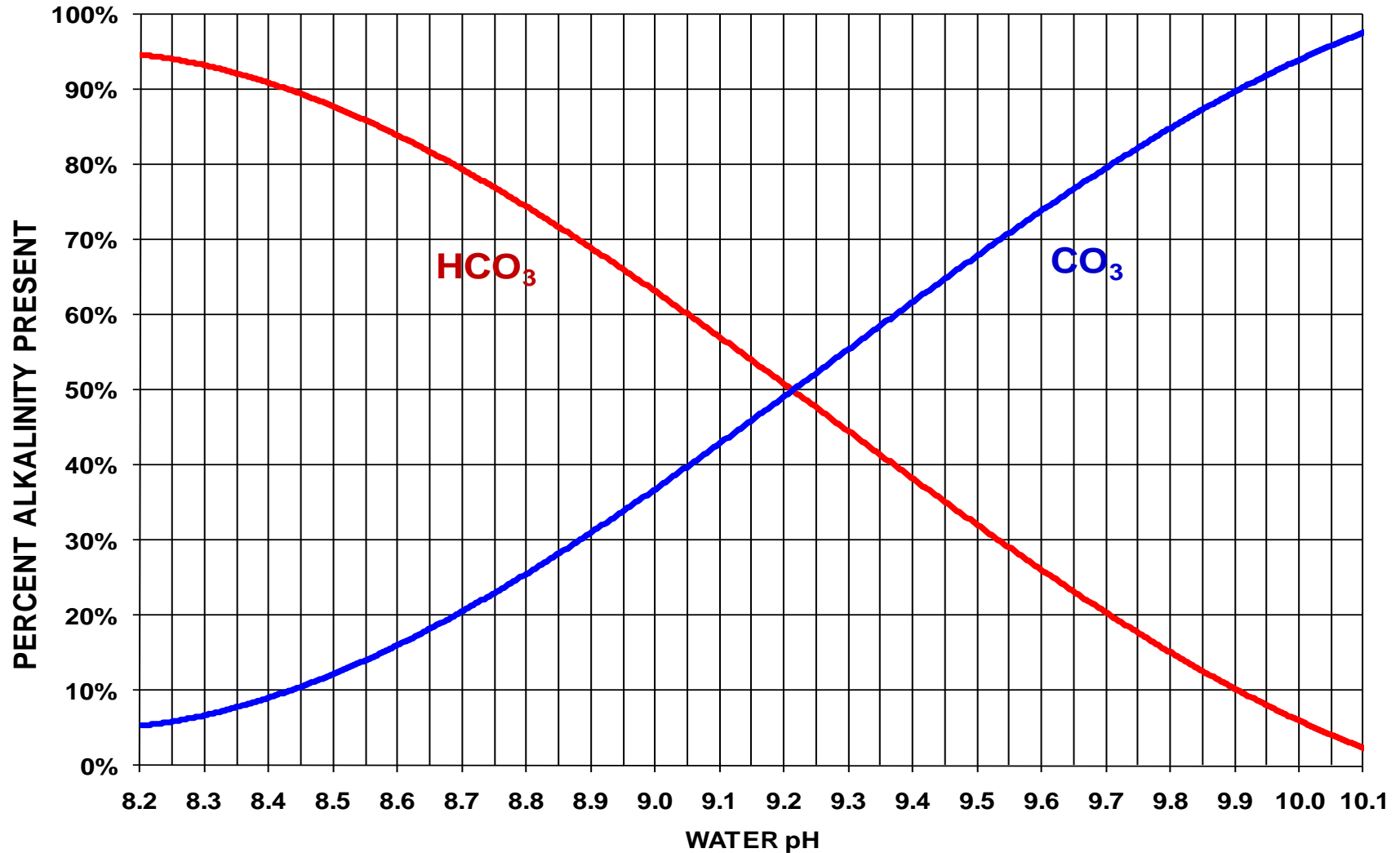
Alkalinity Distribution

- Bicarbonate Alkalinity (HCO_3^-)
 - Low pH range
- Carbonate Alkalinity (CO_3^{-2})
 - Mid pH range
- Hydroxide Alkalinity (OH^-)
 - High pH range
- Only two species can exist at same time
 - Restricted by equilibrium and pH

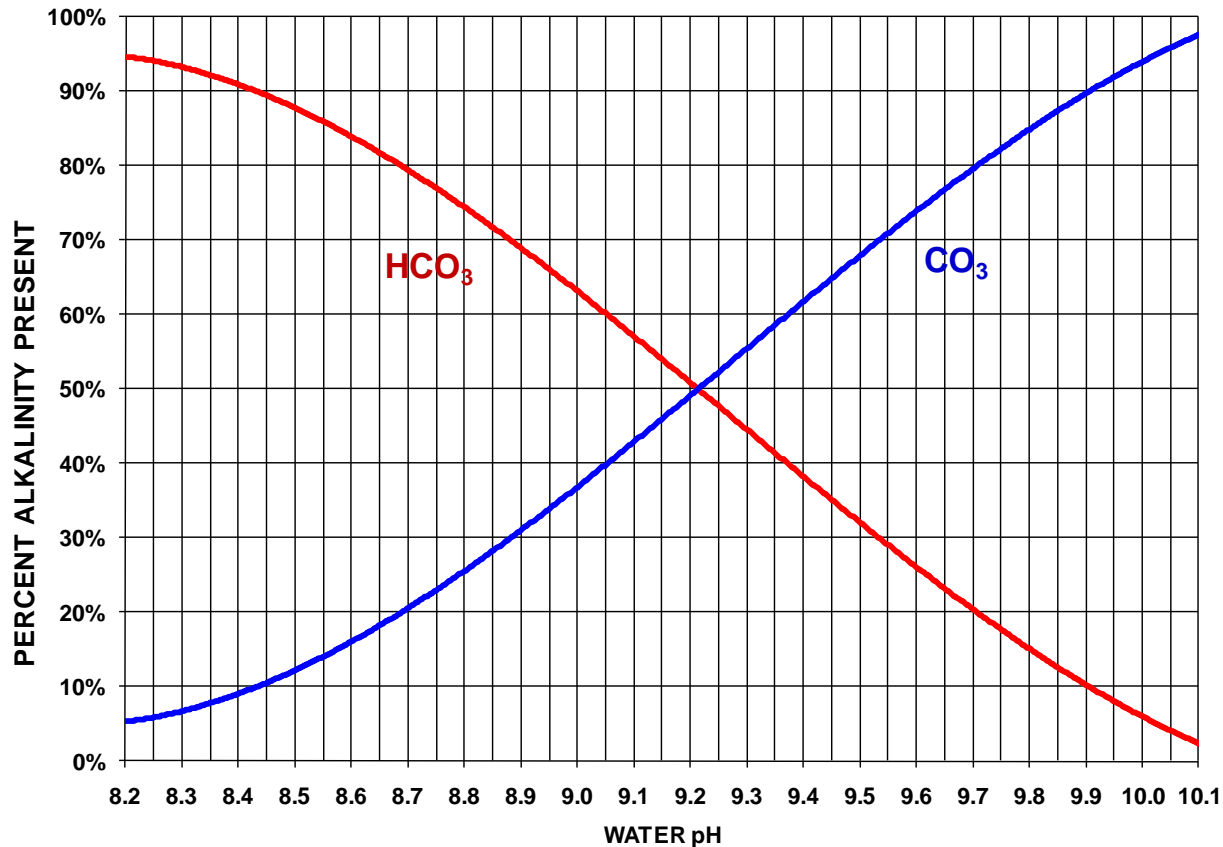
Alkalinity / pH Relationships

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

Alkalinity / pH Relationships



Alkalinity / pH Relationships



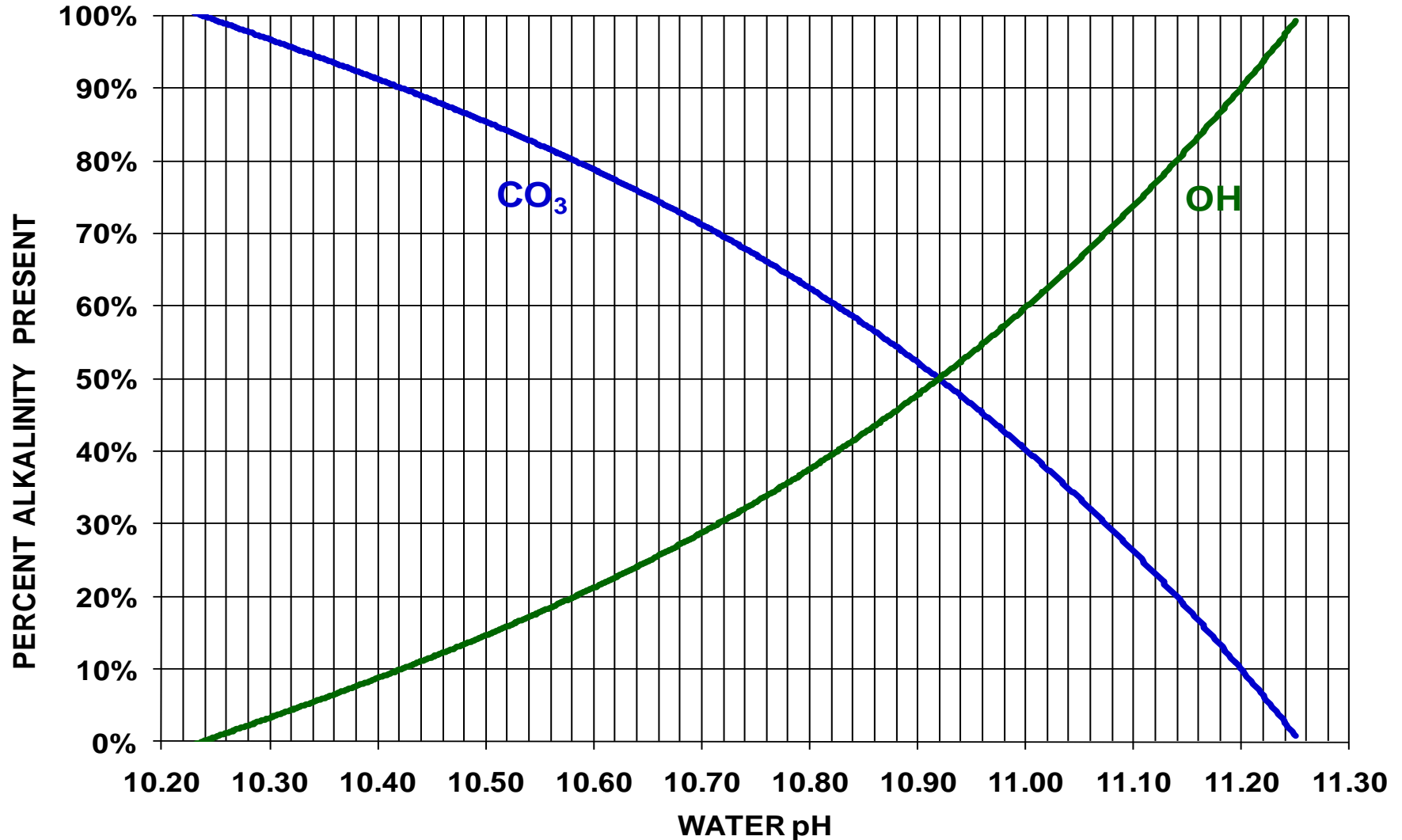
pH Relationships

- 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

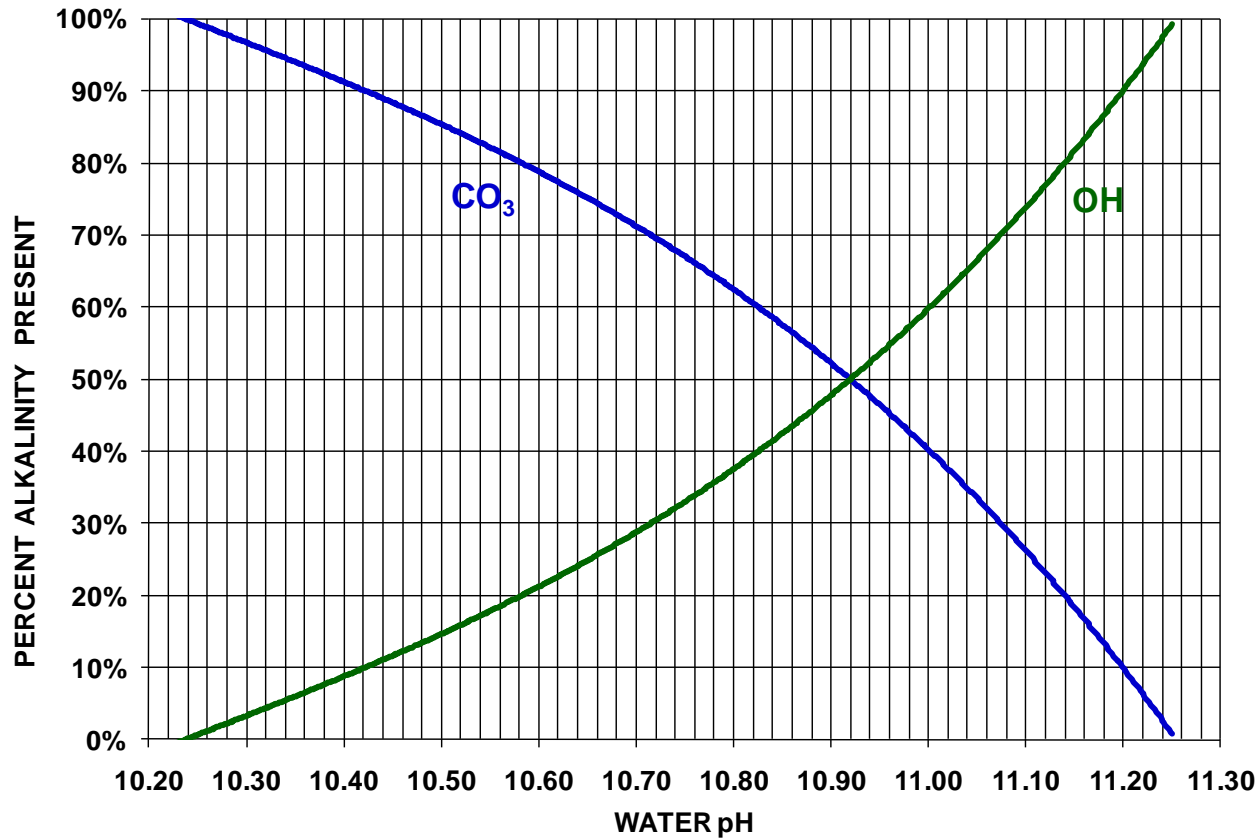
Alkalinity / pH Relationships

- 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



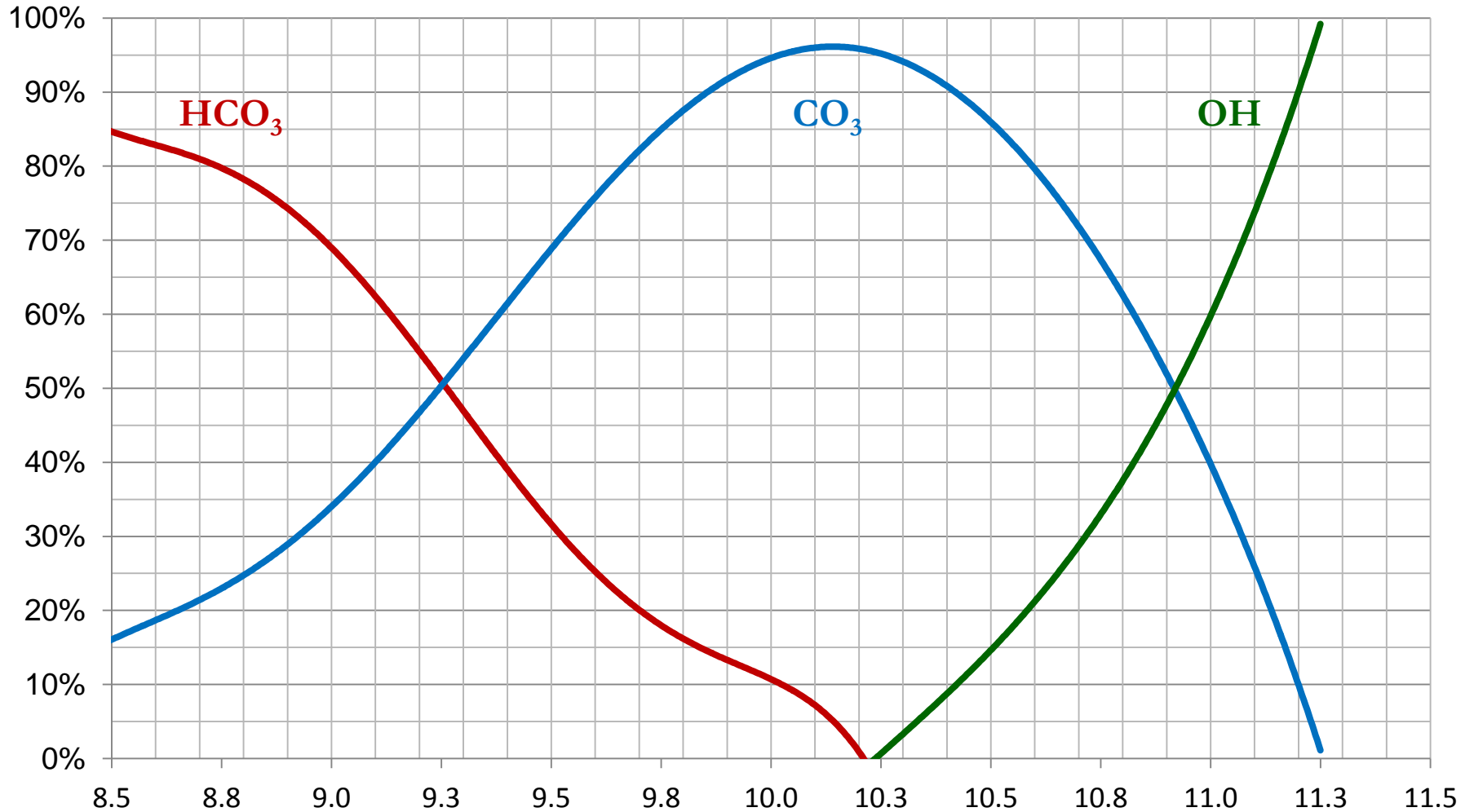
Alkalinity / pH Relationships



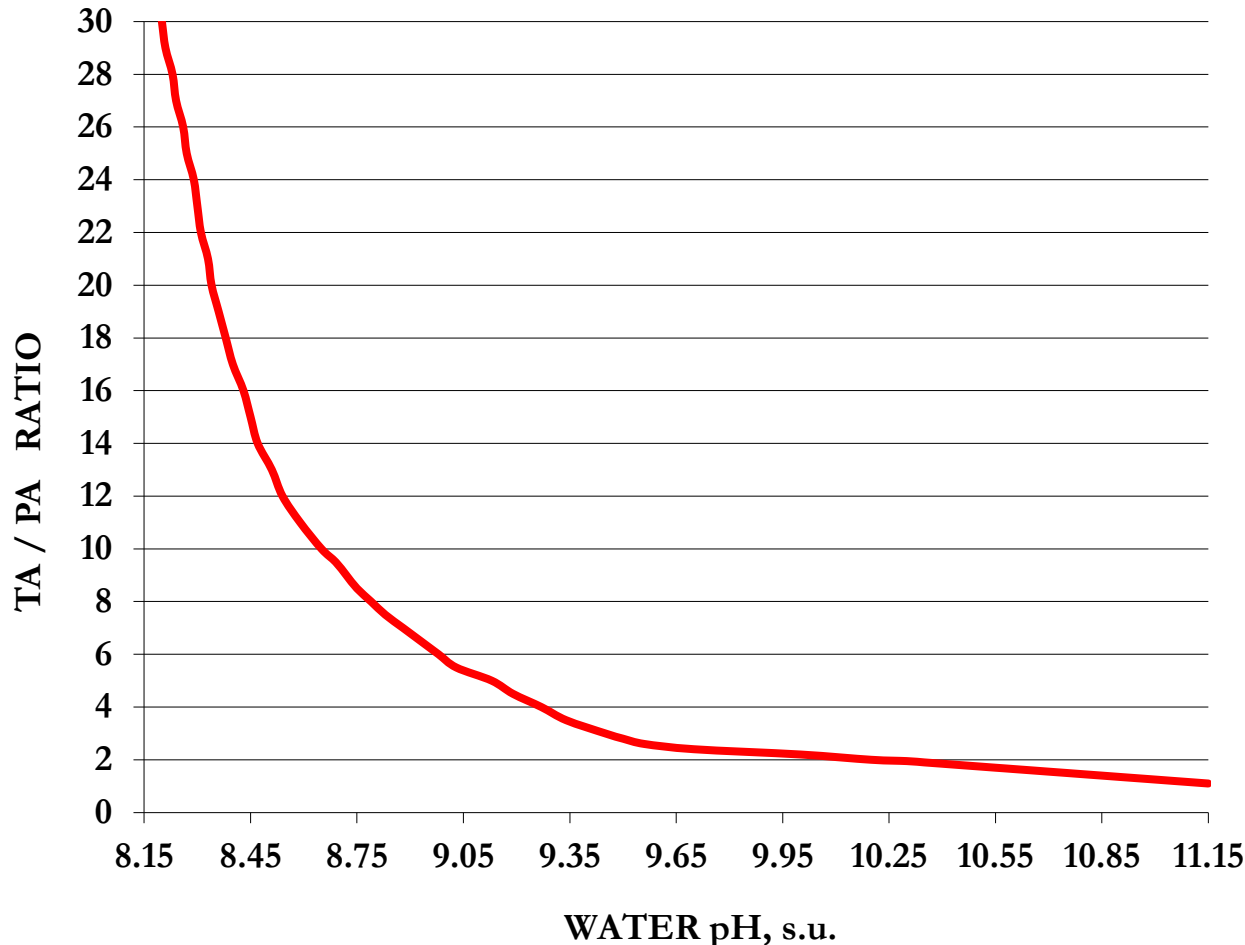
pH Relationships

- 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



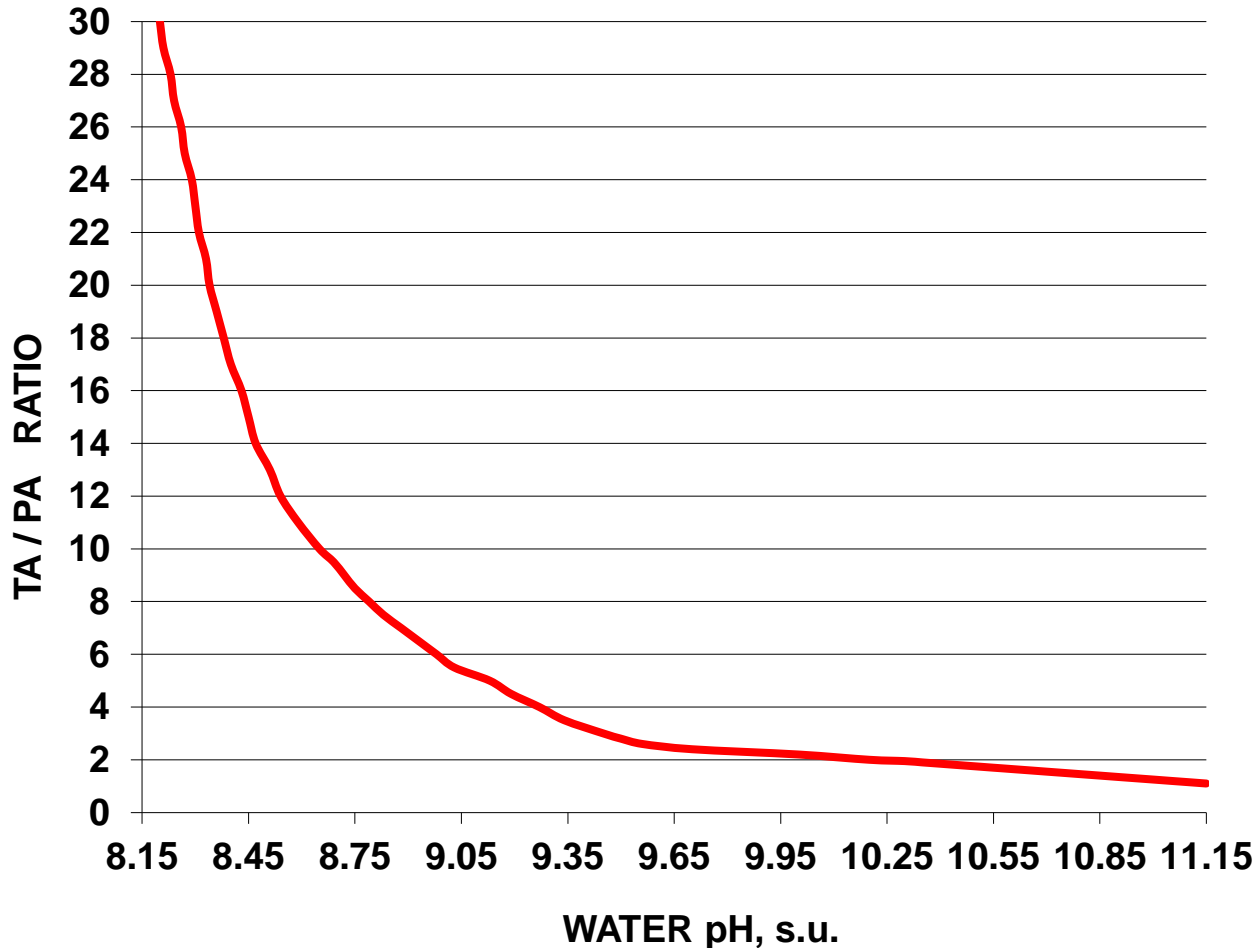
Alkalinity / pH Relationships



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

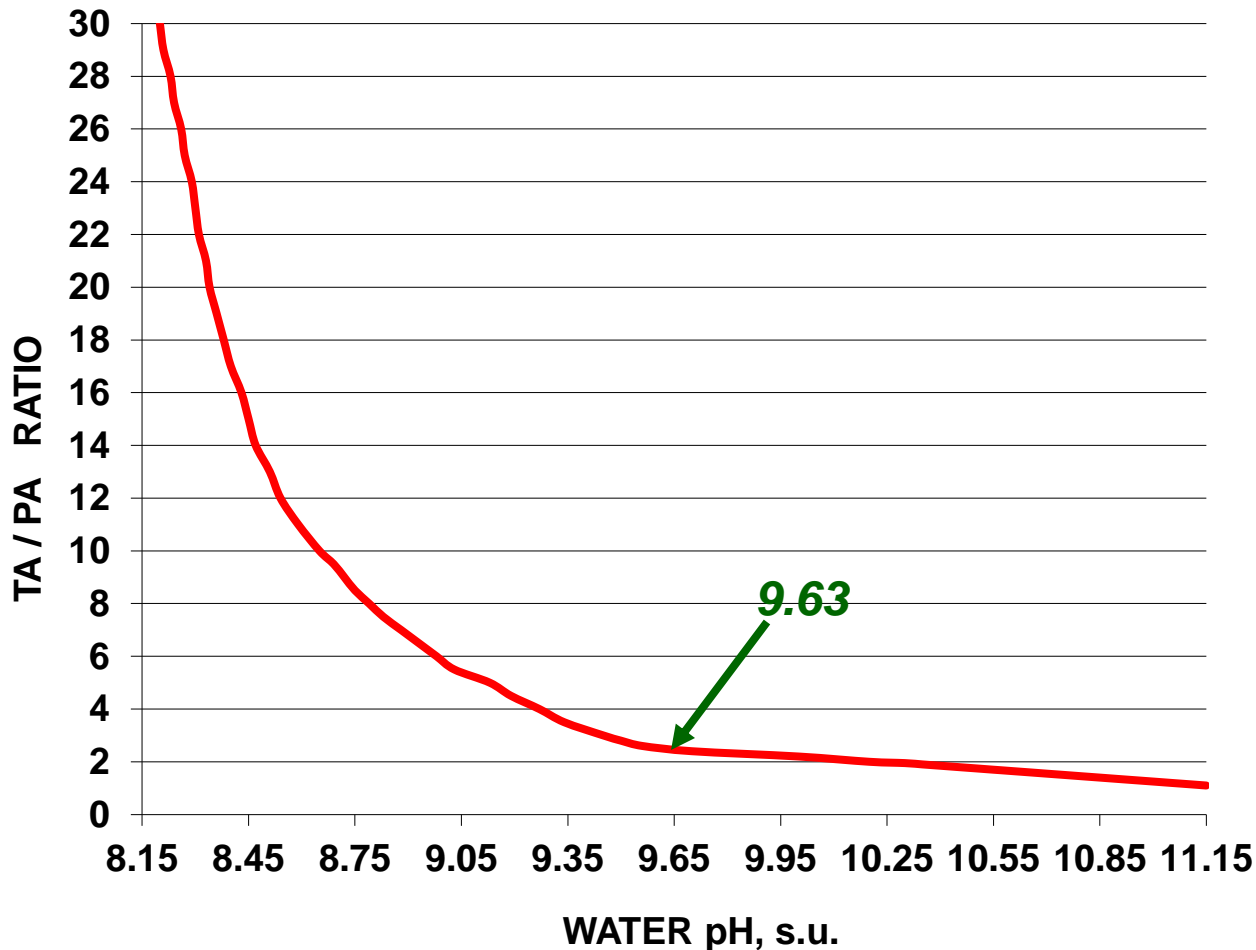
Alkalinity / pH Relationships



**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 $8.3 \pm$

Alkalinity Titration Equation



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

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

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

Solubility Relationships

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

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

Solubility Relationships

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

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- K_{sp} determines soluble limit of CaCO_3 and Mg(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

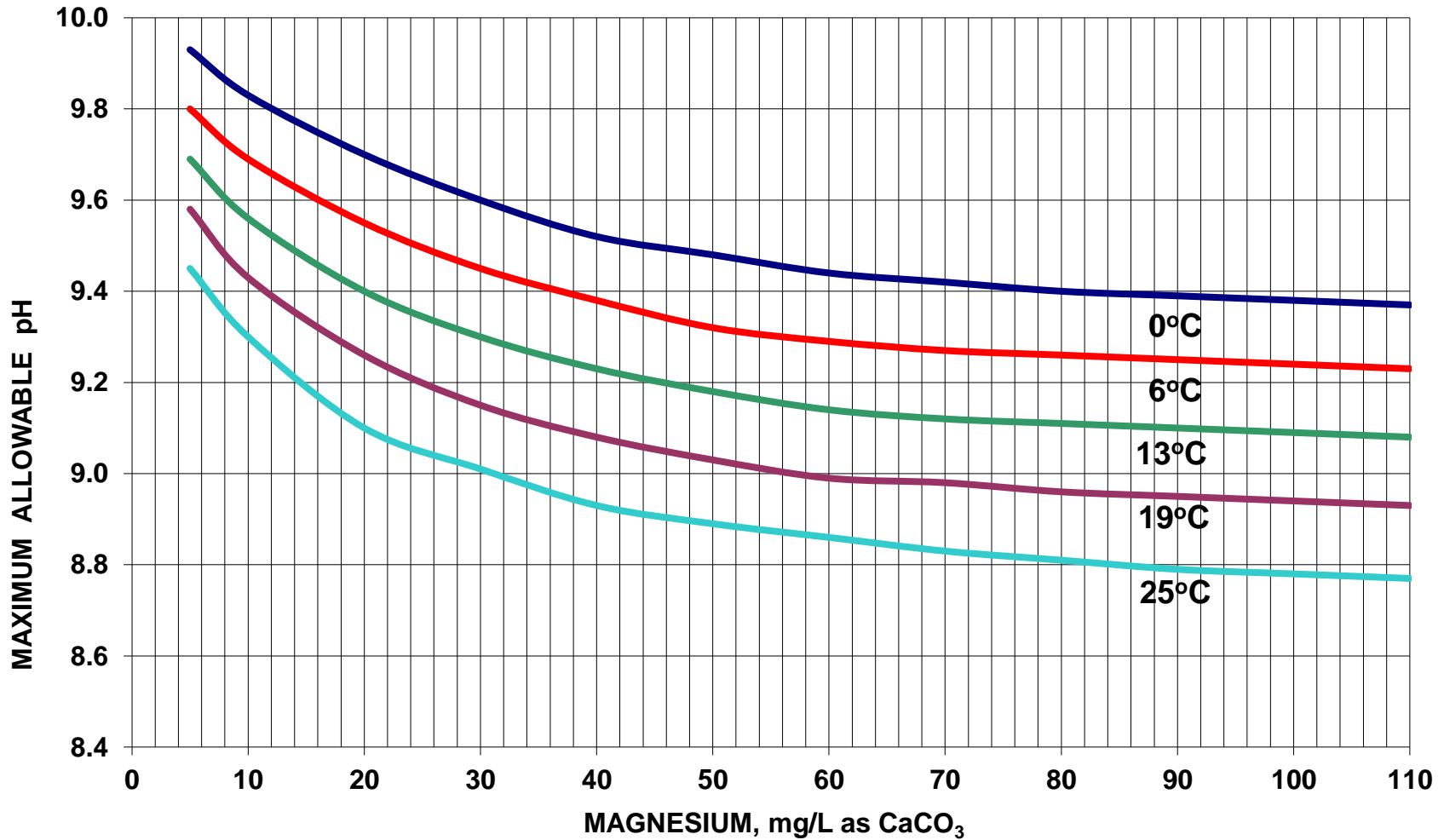
	K_{sp}	pK_{sp}
CaCO_3	~24 mg/L	8.49
Mg(OH)_2	~12 mg/L	10.59

- 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

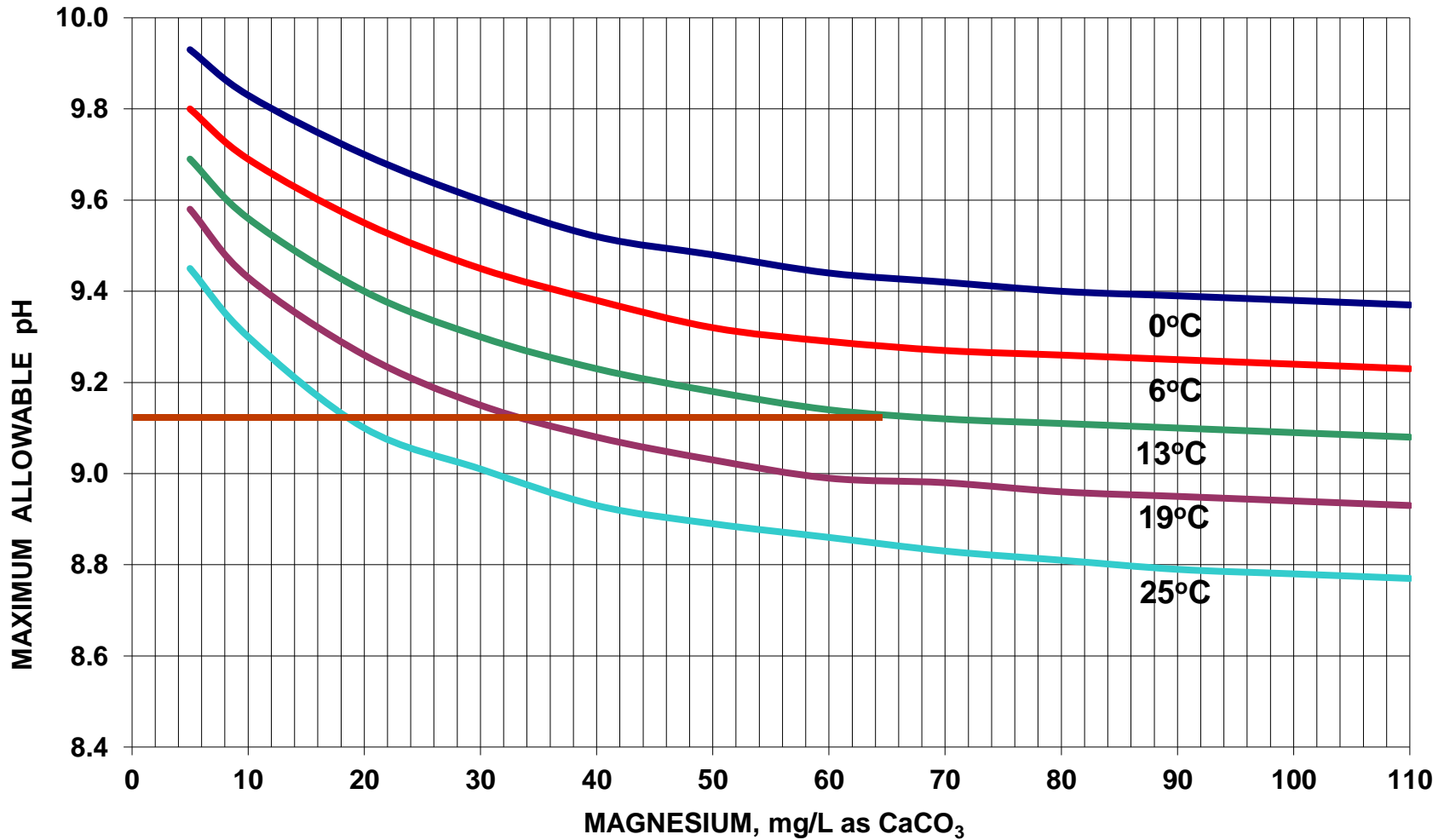
Magnesium Fouling Issues

- 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

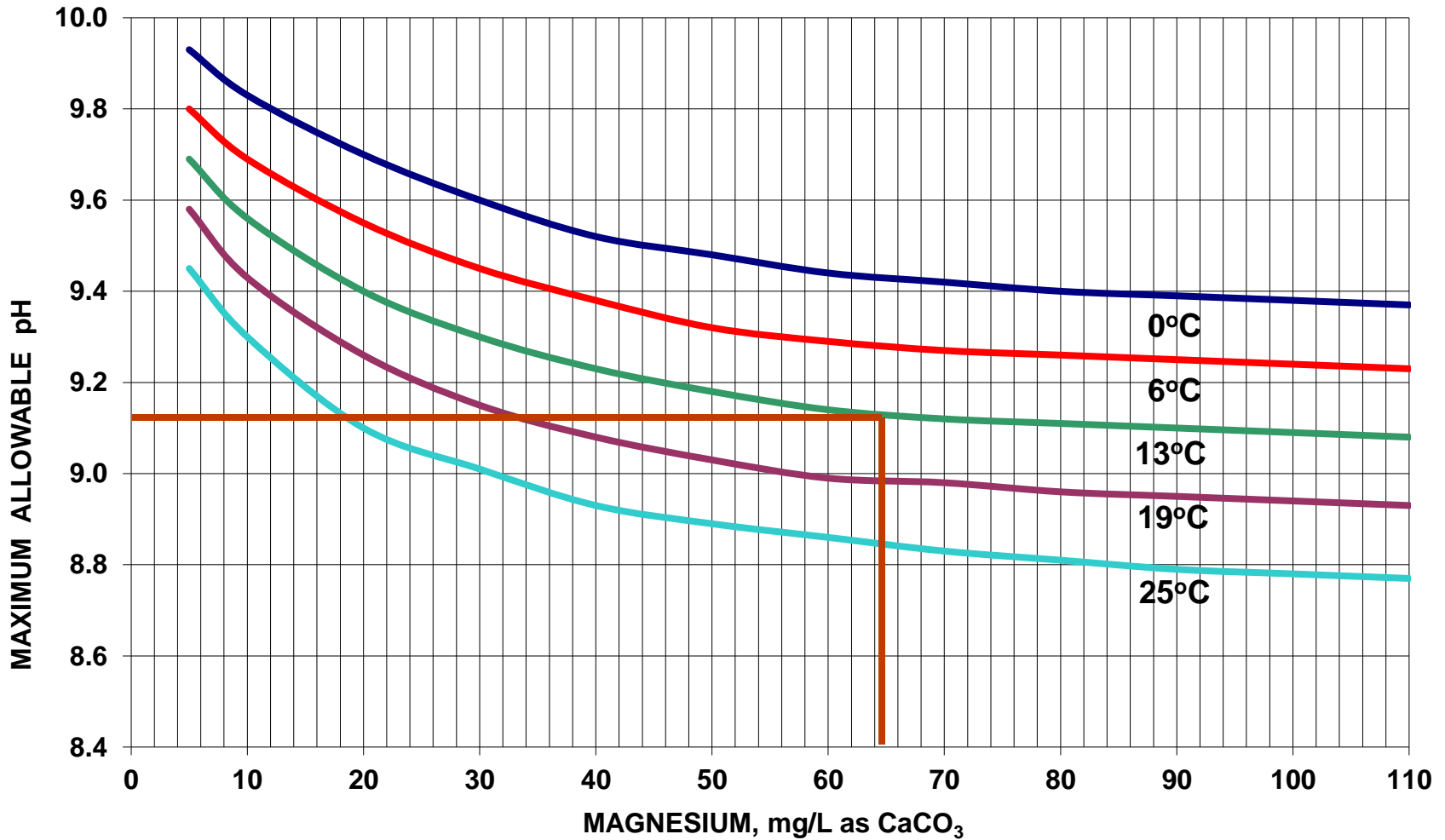
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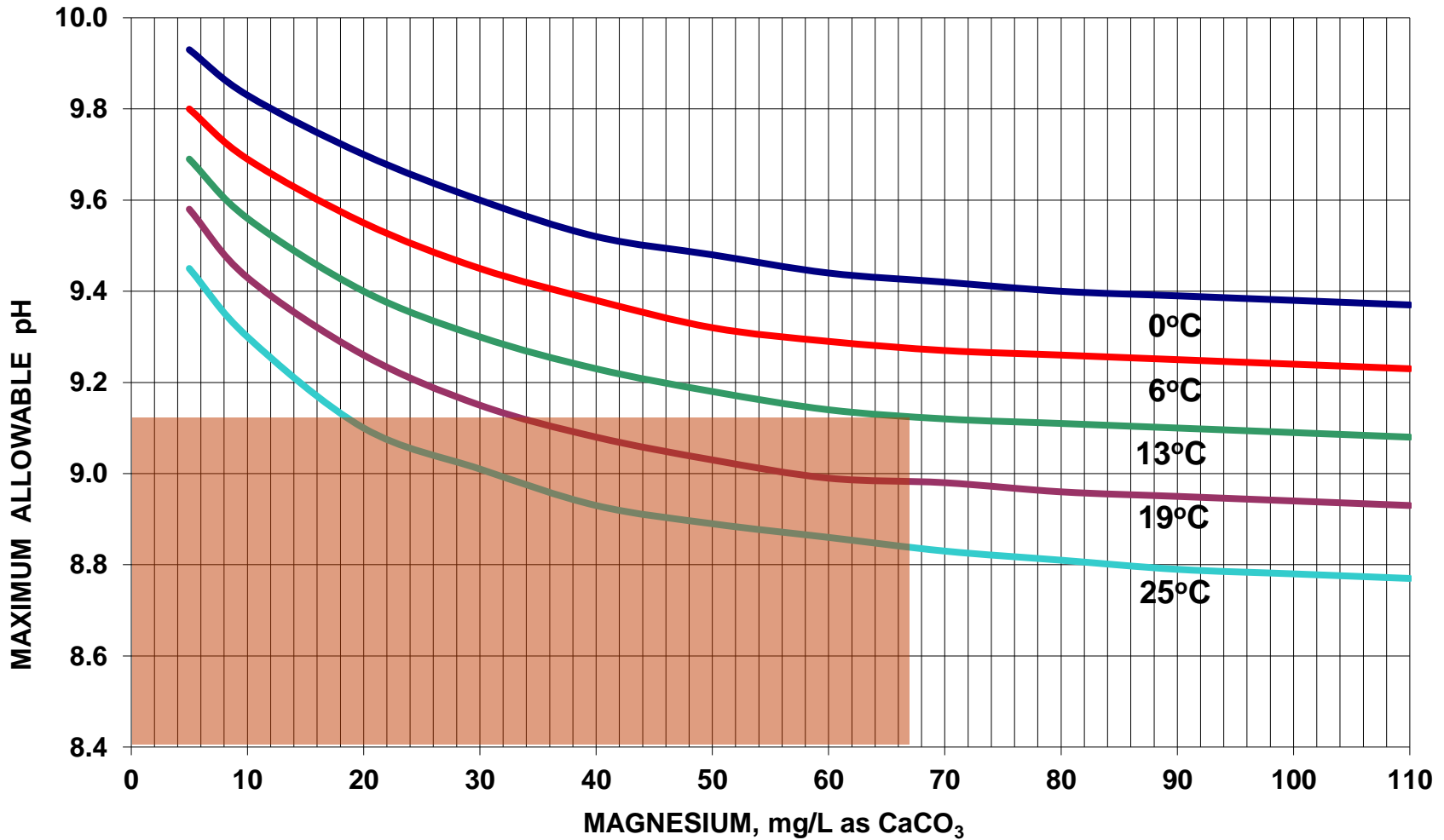
Magnesium Fouling Issues



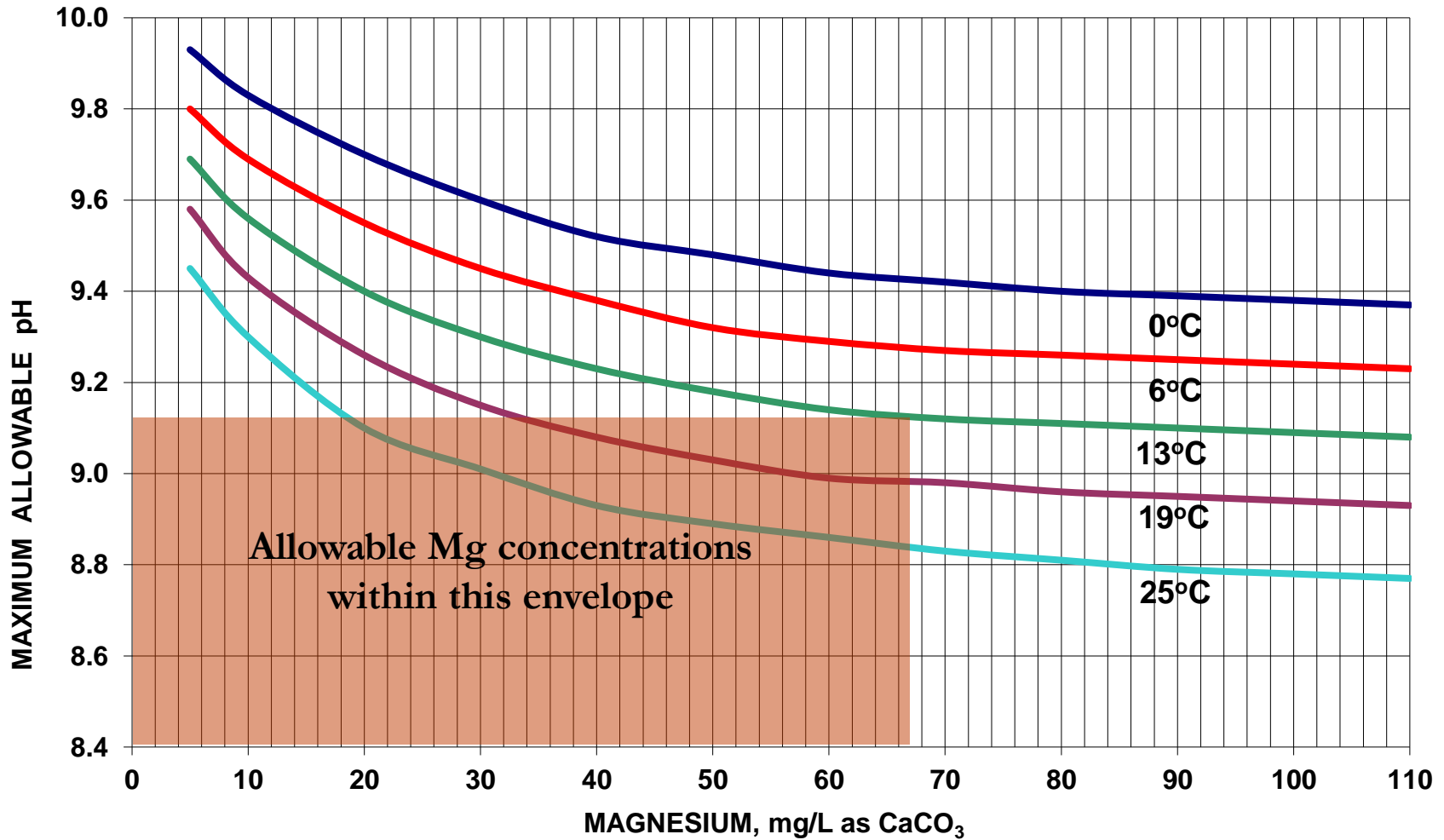
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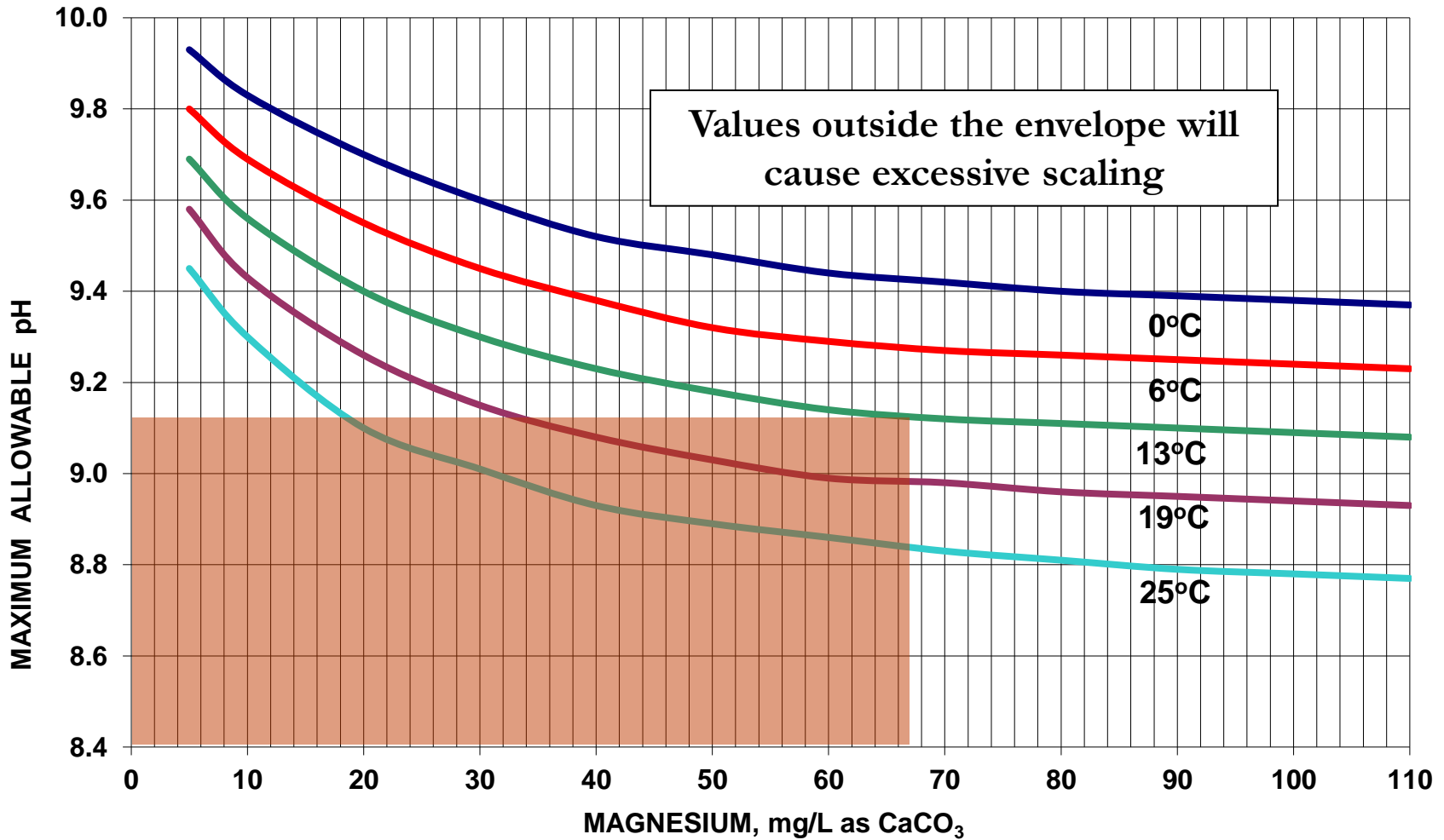
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Magnesium Fouling Issues



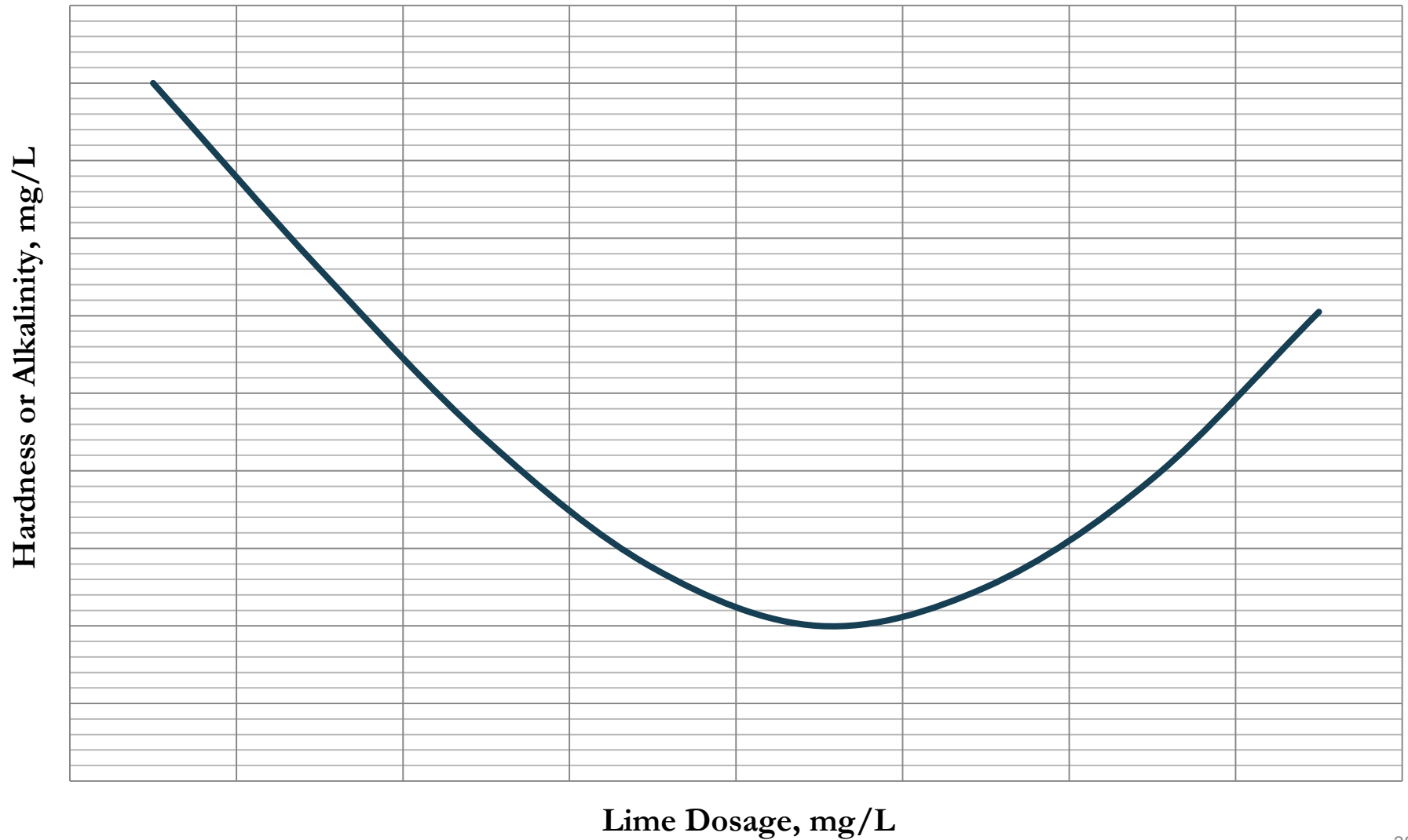
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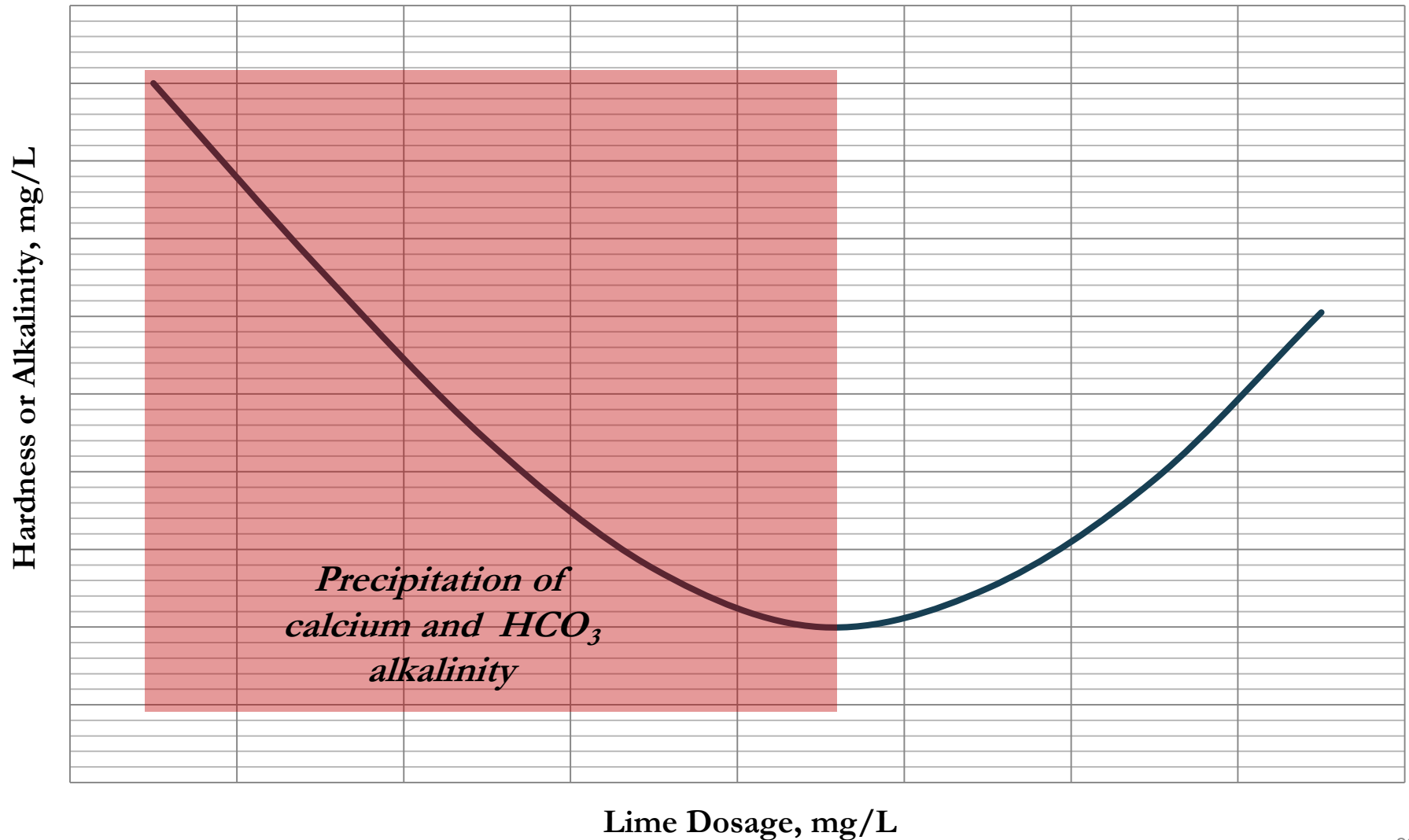
Softening Demand Curves

- 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}

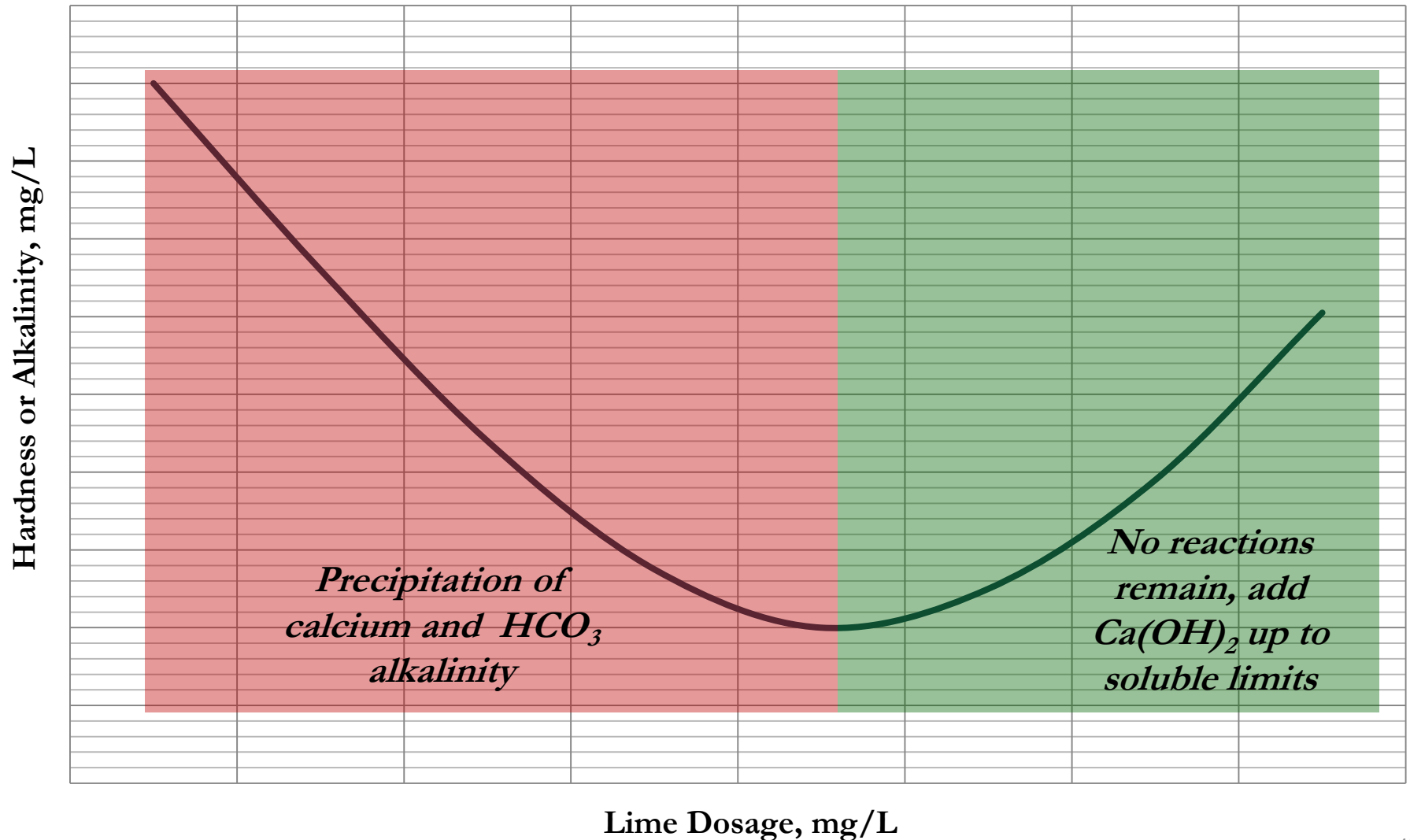
Softening Demand Curves



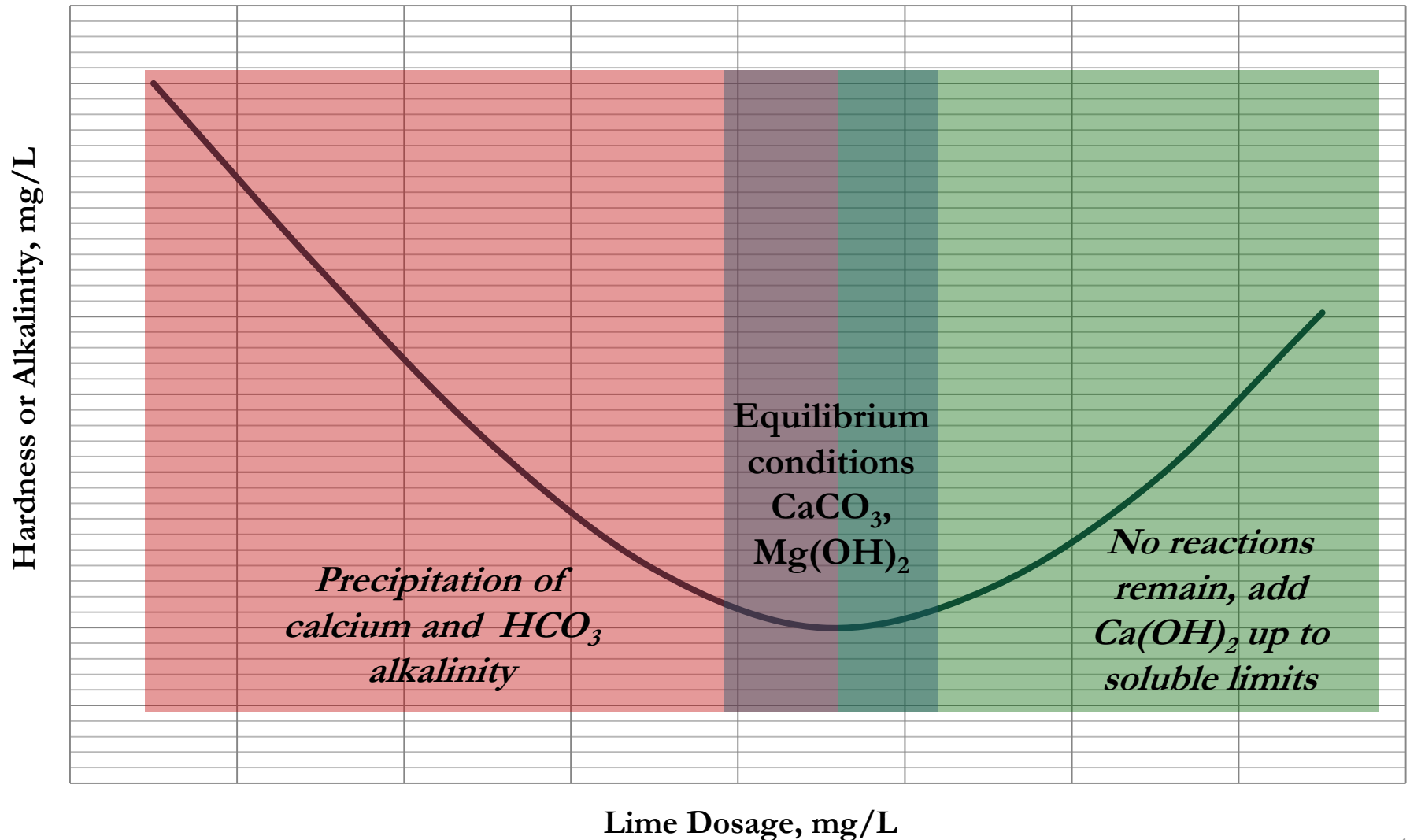
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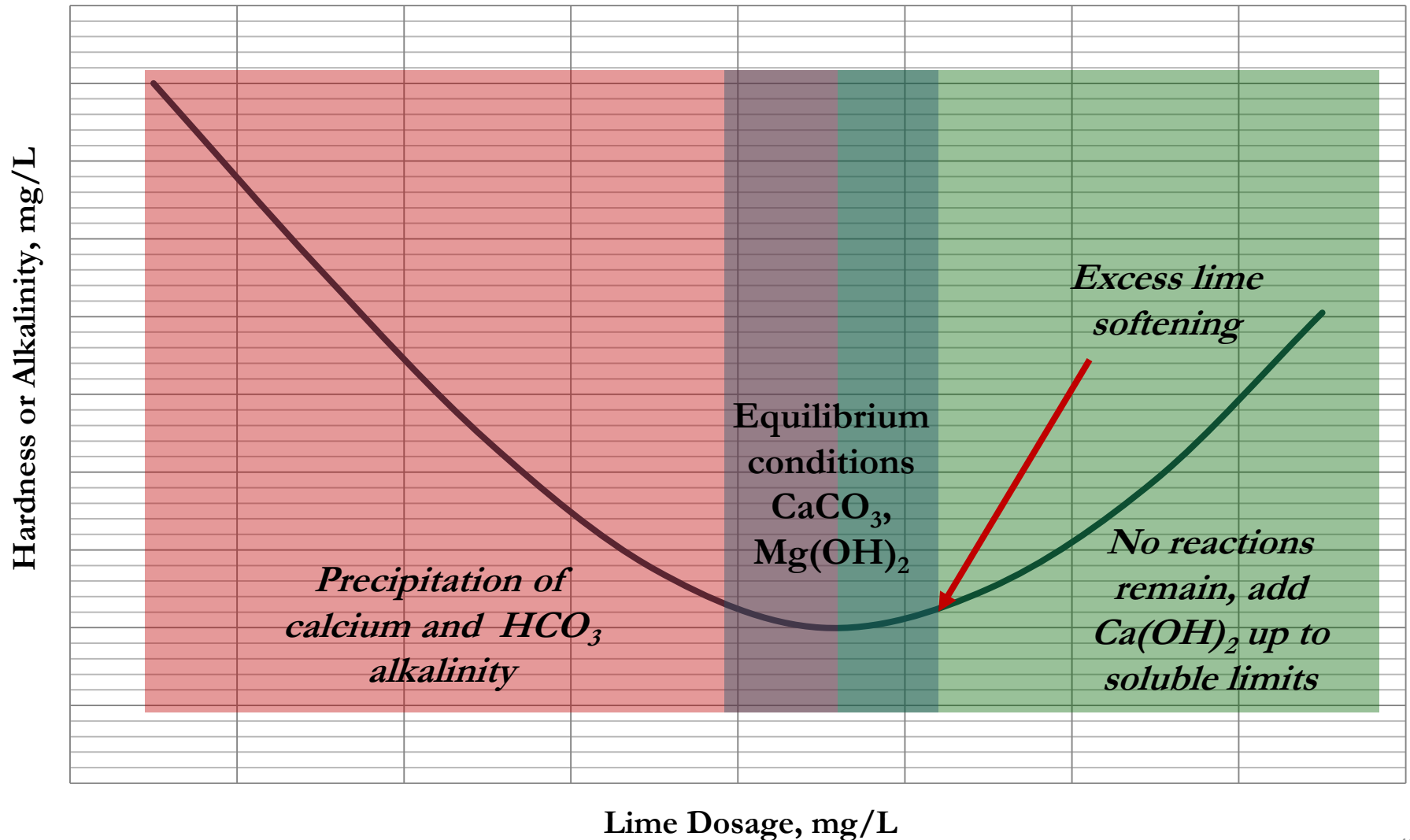
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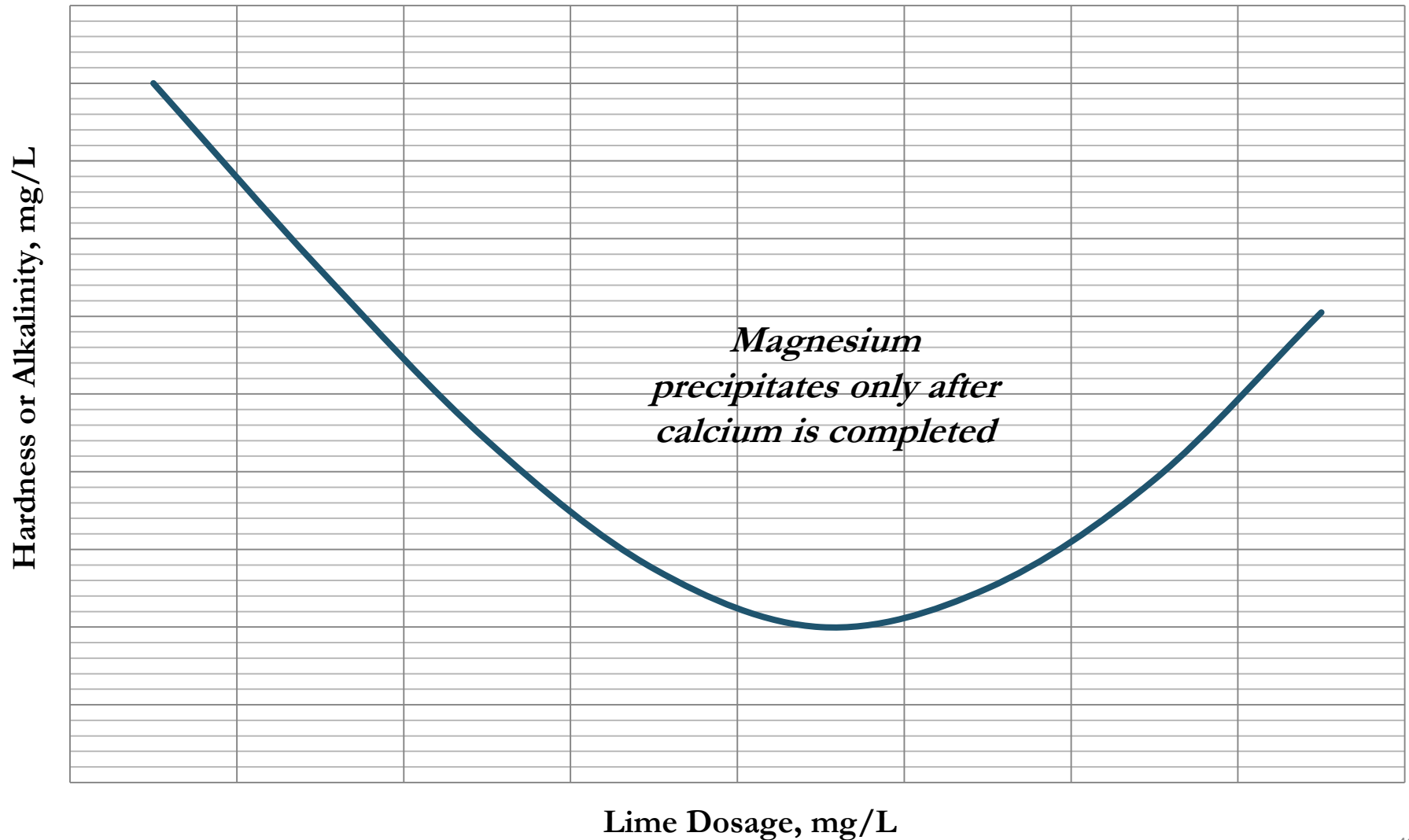
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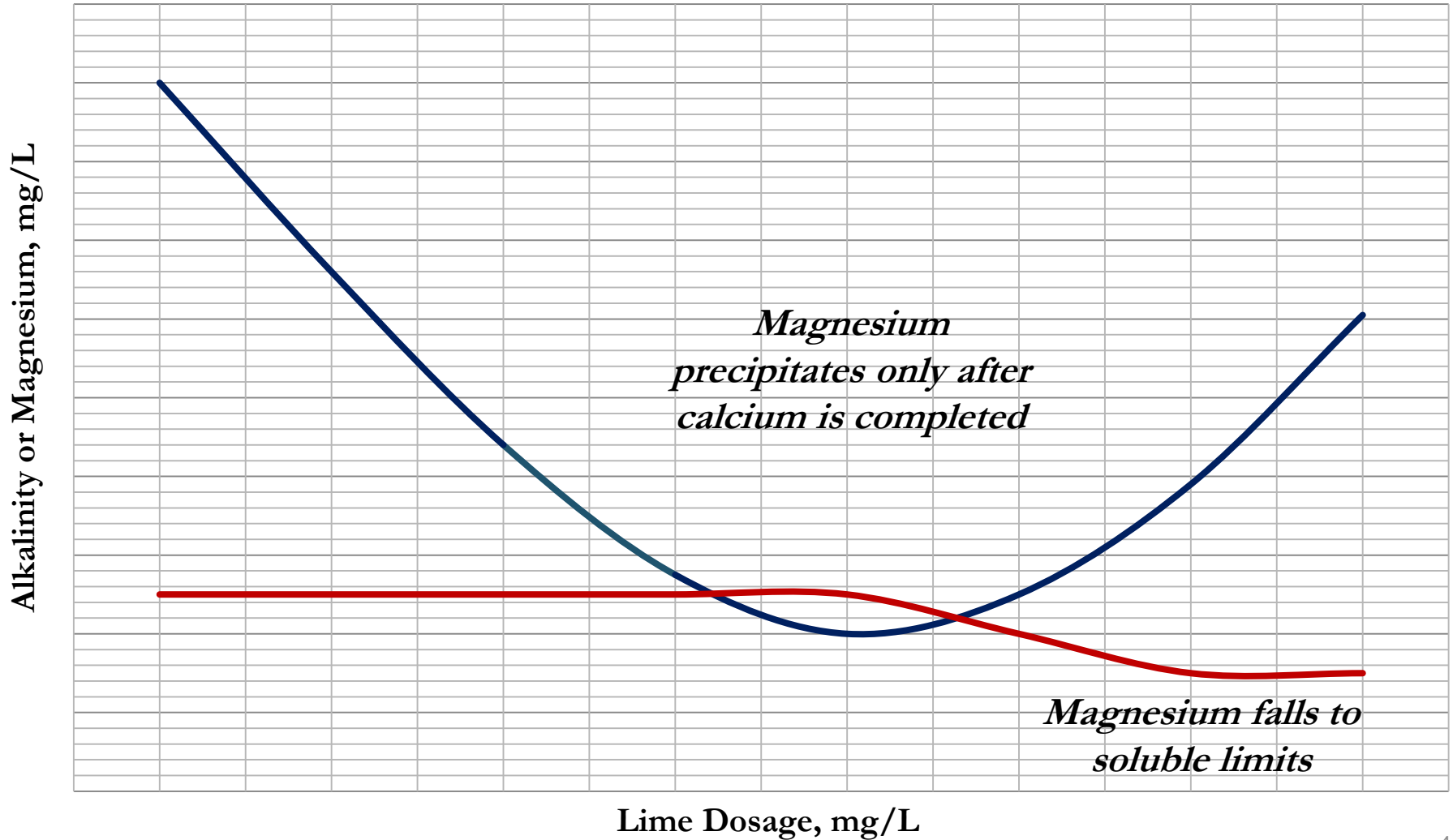
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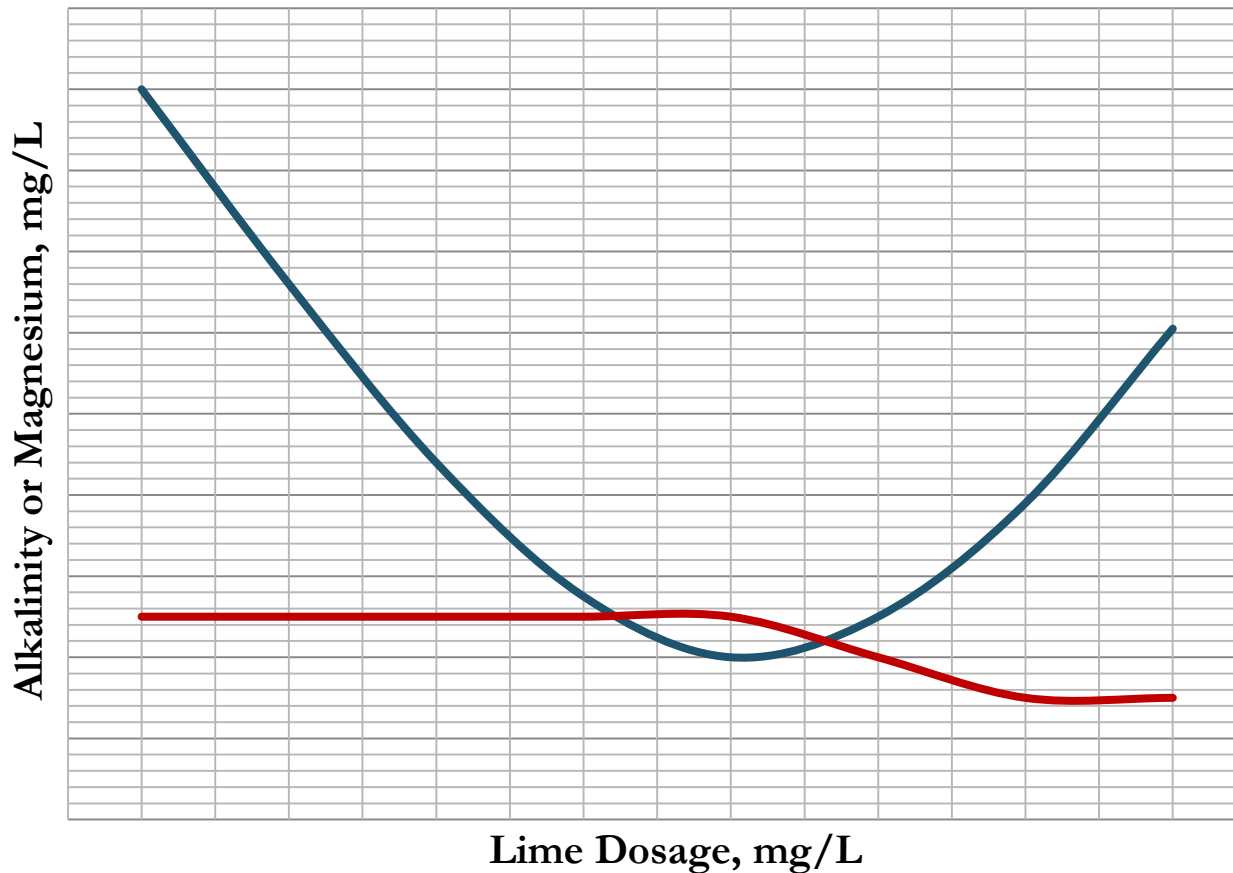
Softening Demand Curves



Softening Demand Curves



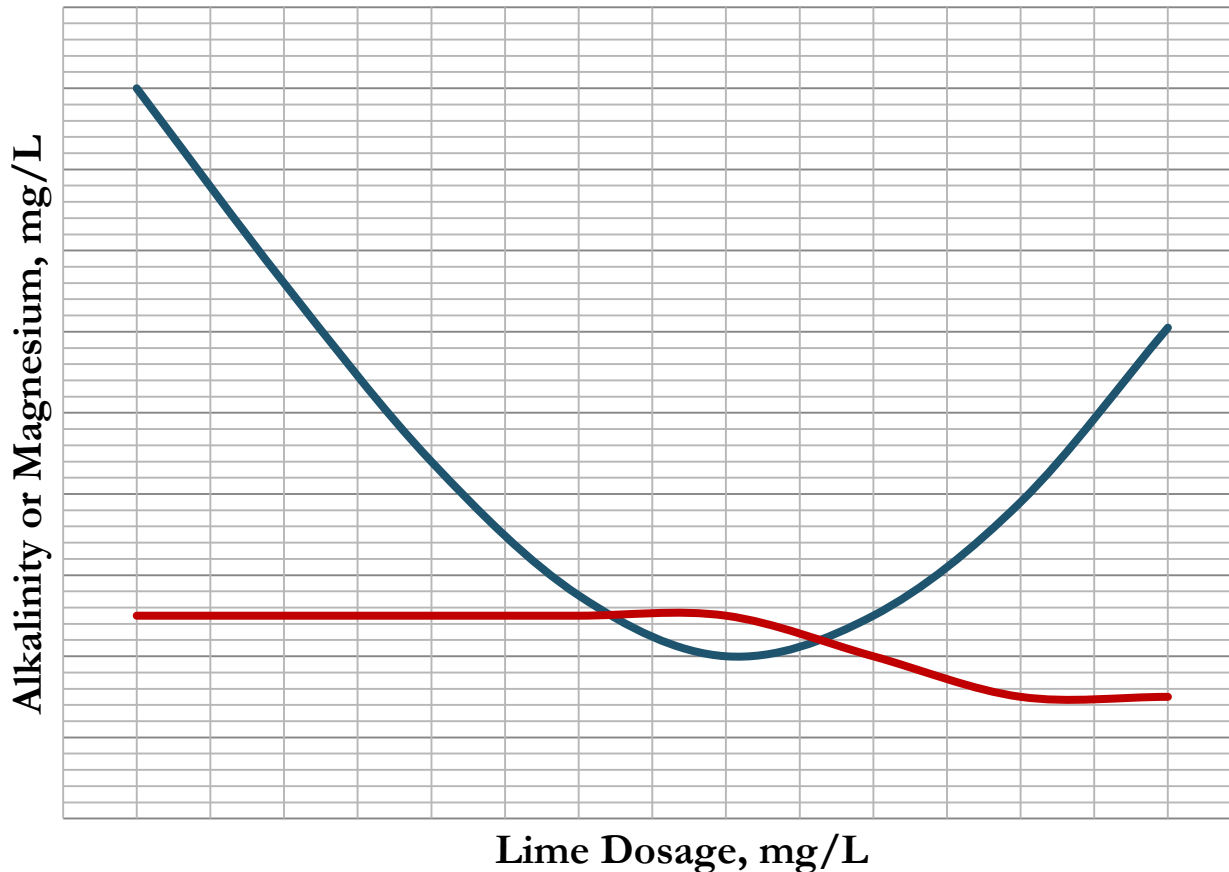
Softening Demand Curves



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

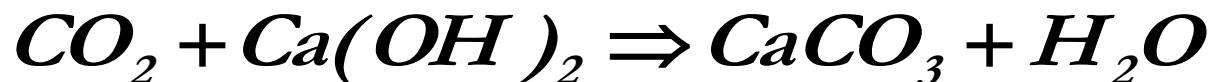
Softening Demand Curves



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



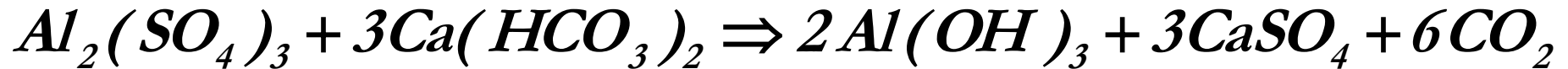
- CO₂ creates demand for lime
- High CO₂ should be removed with aeration
 - >10 mg/L CO₂ aeration more cost effective

- 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

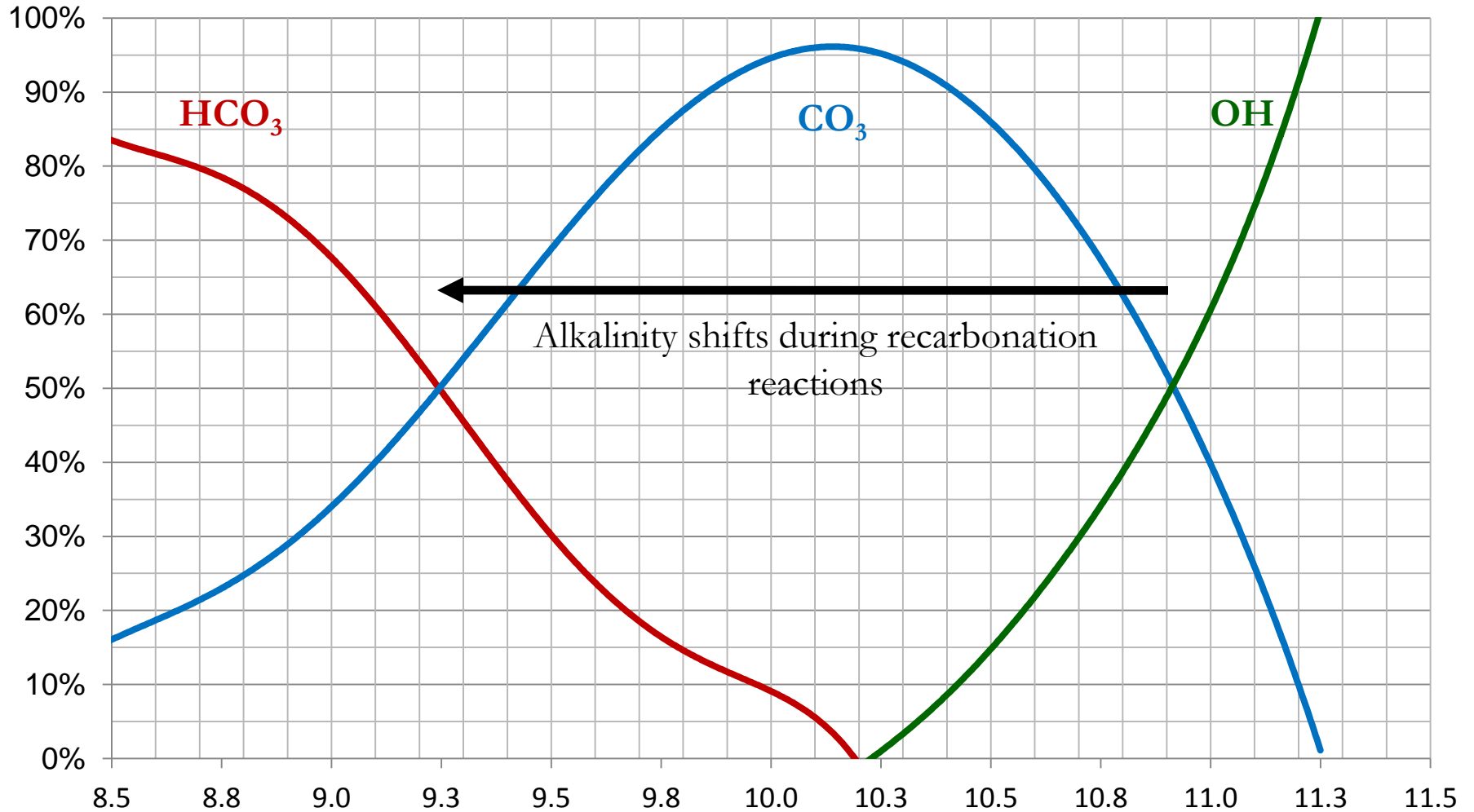
Coagulant	Alkalinity Consumed, mg/L	Dissolved CO ₂ Formed, mg/L
Alum	0.5	0.44
Ferric Chloride	0.46	0.40
Ferric Sulfate	0.53	0.23
Aluminum Chlorohydrate (ACH)	0.29	0.25
Polyaluminum Chloride (PACl)	0.71	0.62
Polyaluminum Chlorosulfate (PACS)	0.36	0.31

Recarbonation Chemistry



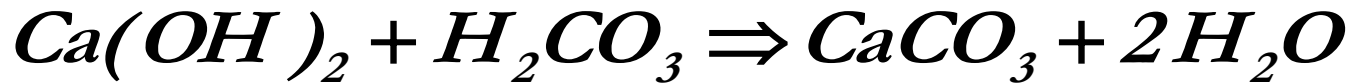
- Carbonic acid shifts alkalinity species due to chemical reactions
 - Total alkalinity often remains unchanged
 - $TA = PA + \frac{1}{2} CO_3 + HCO_3$
 - Phenol alkalinity changes due to change in alkalinity species
 - $PA = OH + \frac{1}{2} CO_3$
- Equilibrium conditions force shift in pH

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

Questions

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