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

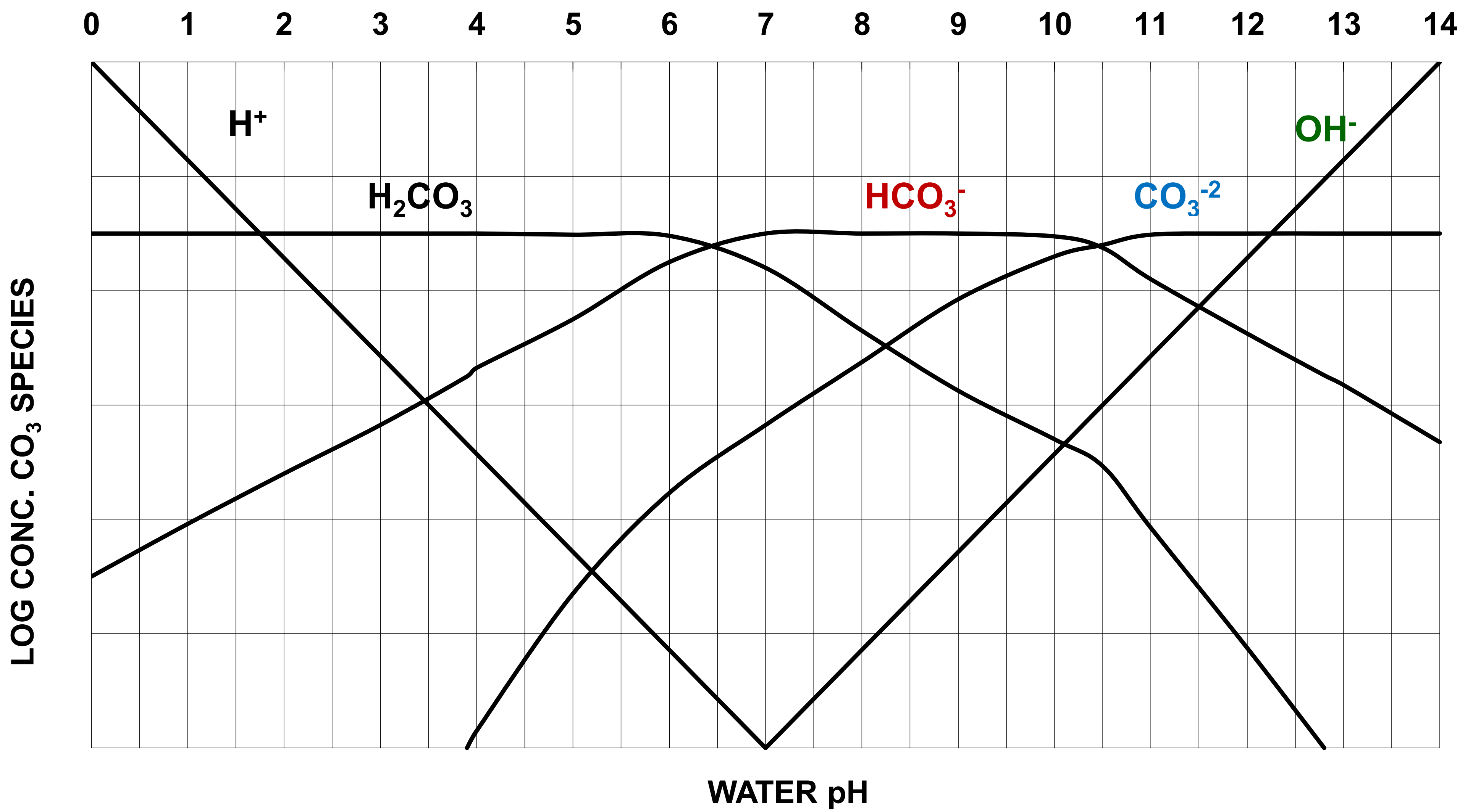
Agenda

- Magnesium Fouling Issues
- Softening Demand Curves
- CO_2 Determinations

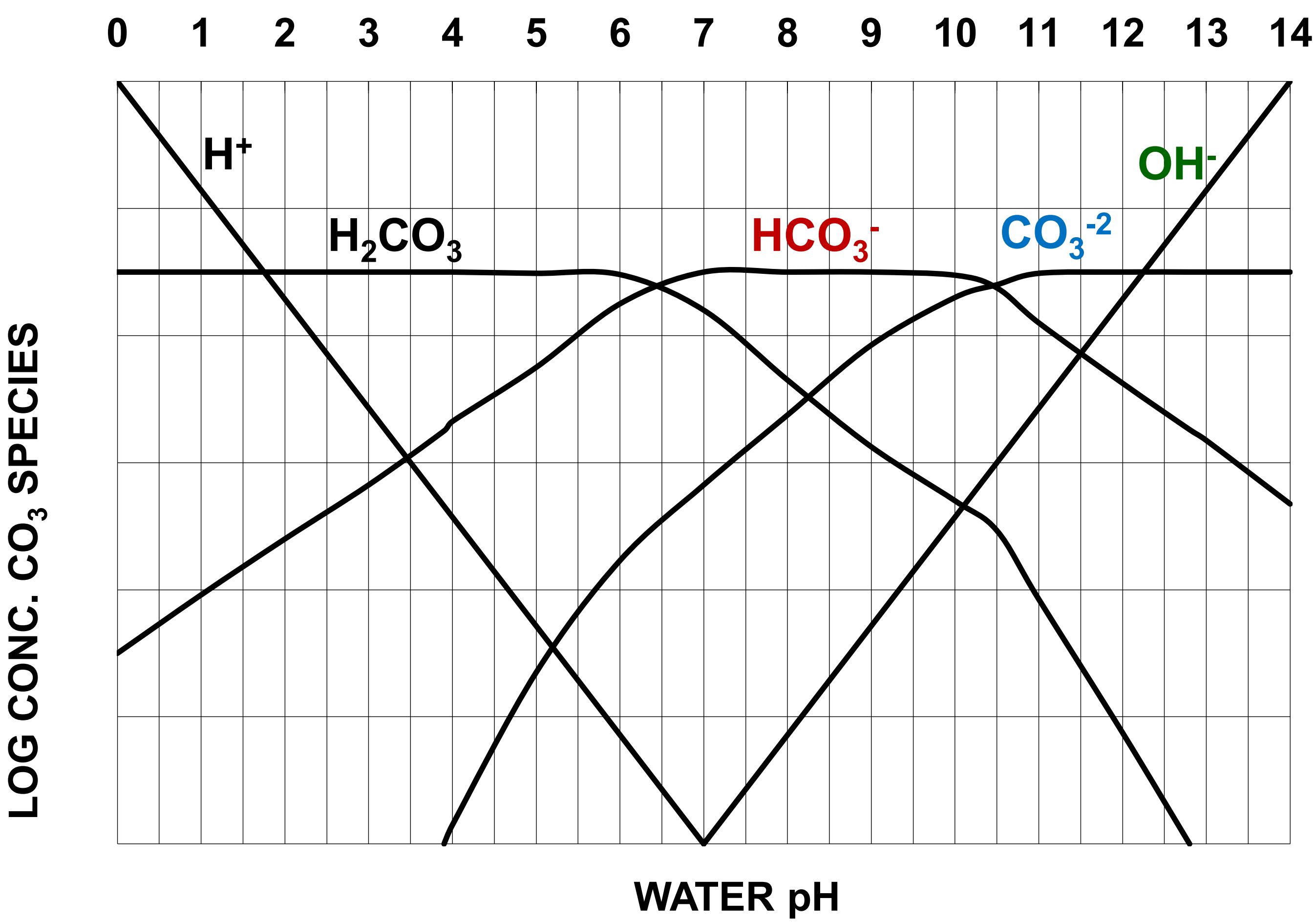
Agenda

- Coagulant Reaction Byproducts
- Recarbonation Chemistry
- CO_2 Dosage Determinations

Carbonate Equilibrium Diagram



Carbonate Equilibrium Diagram



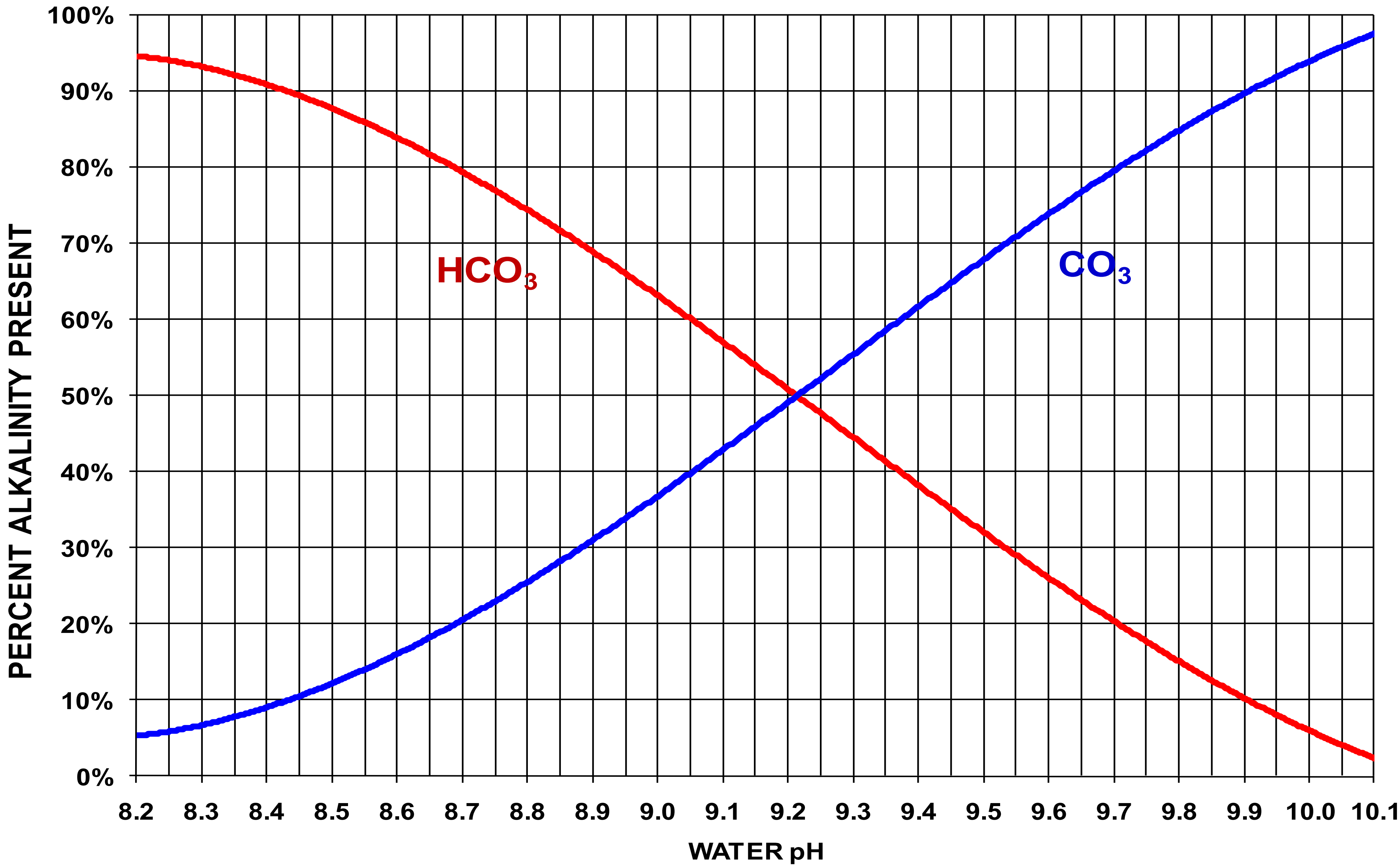
Alkalinity Distribution

- 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

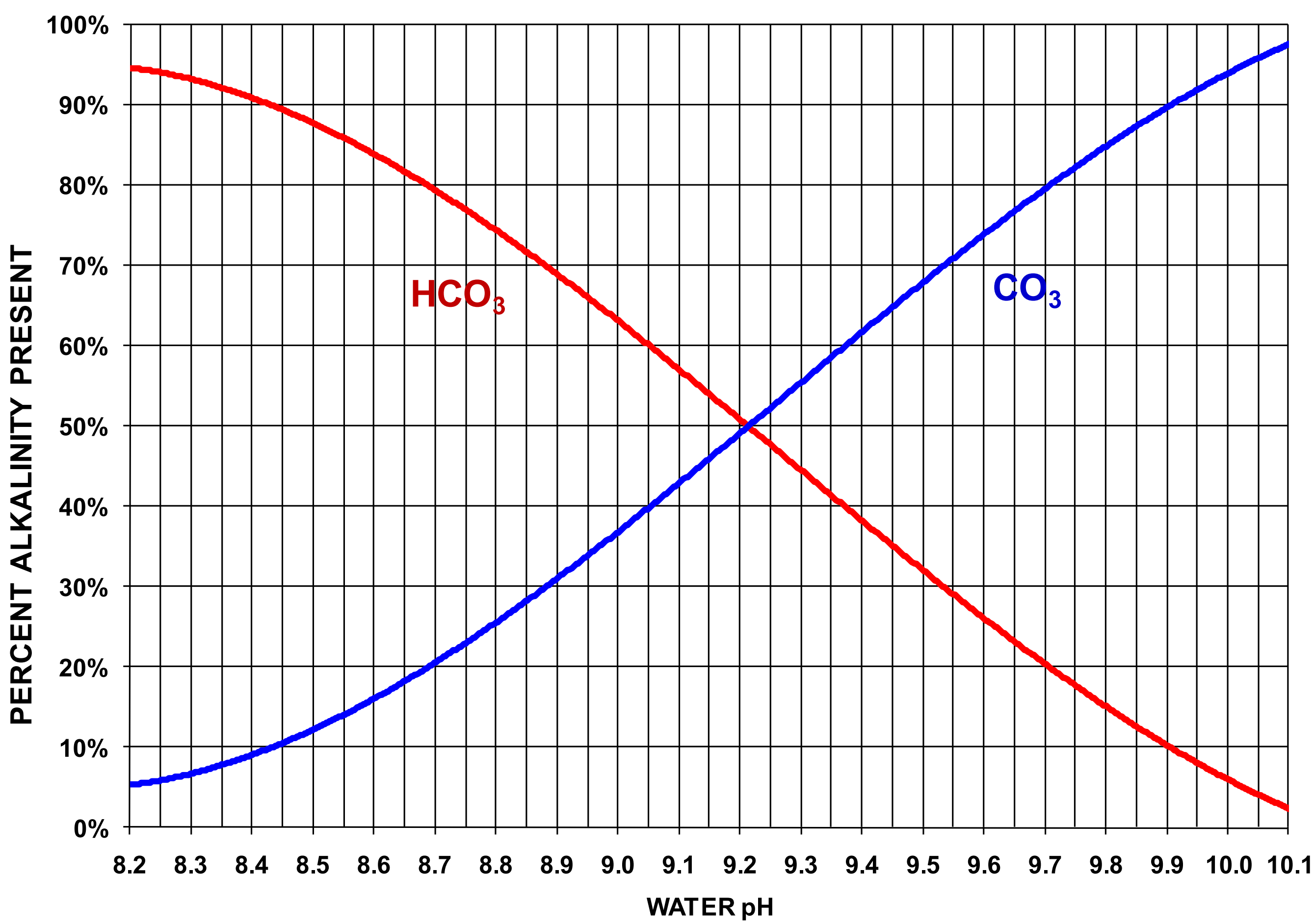
Alkalinity / pH Relationships

- 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



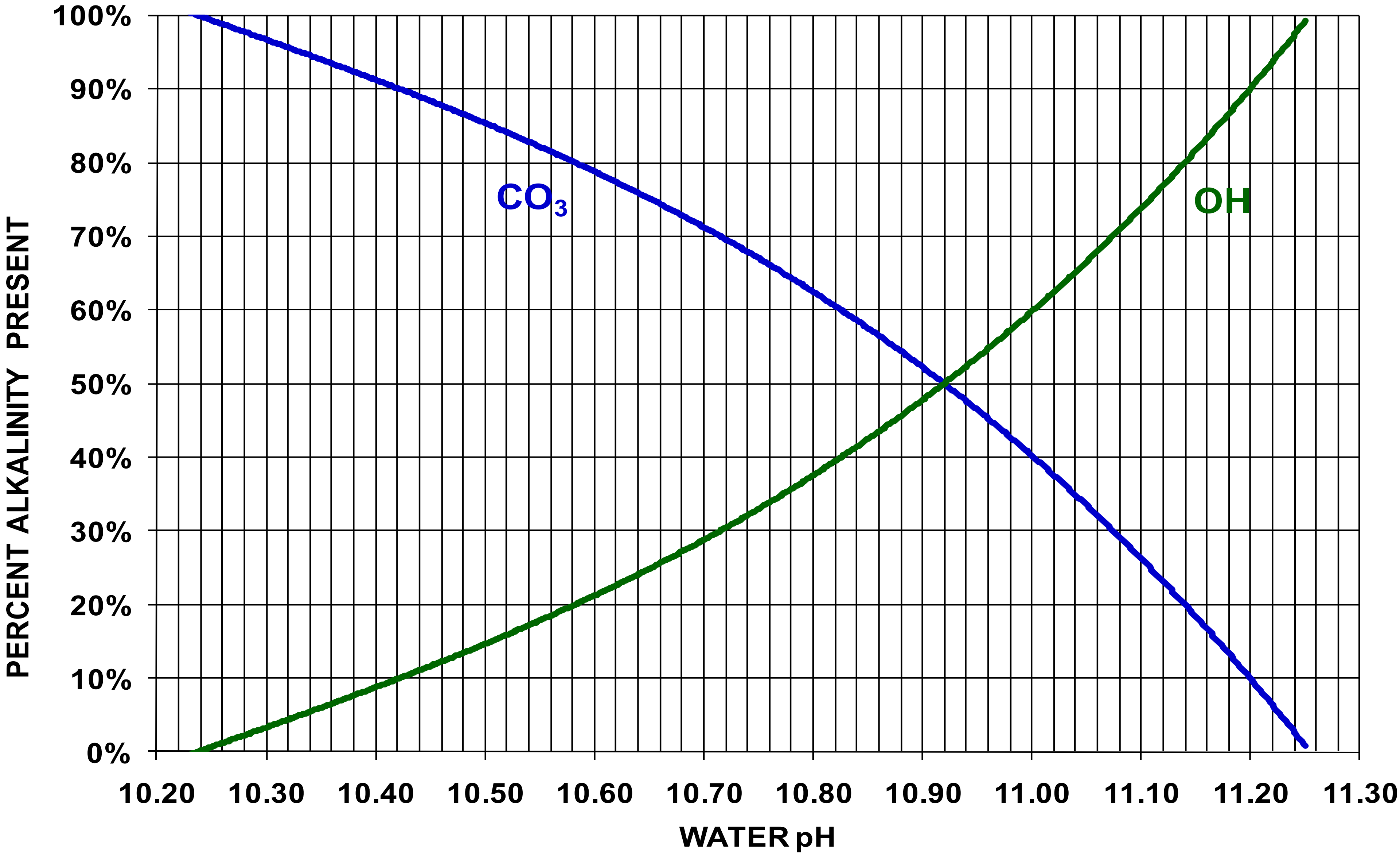
pH Relationships

- 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

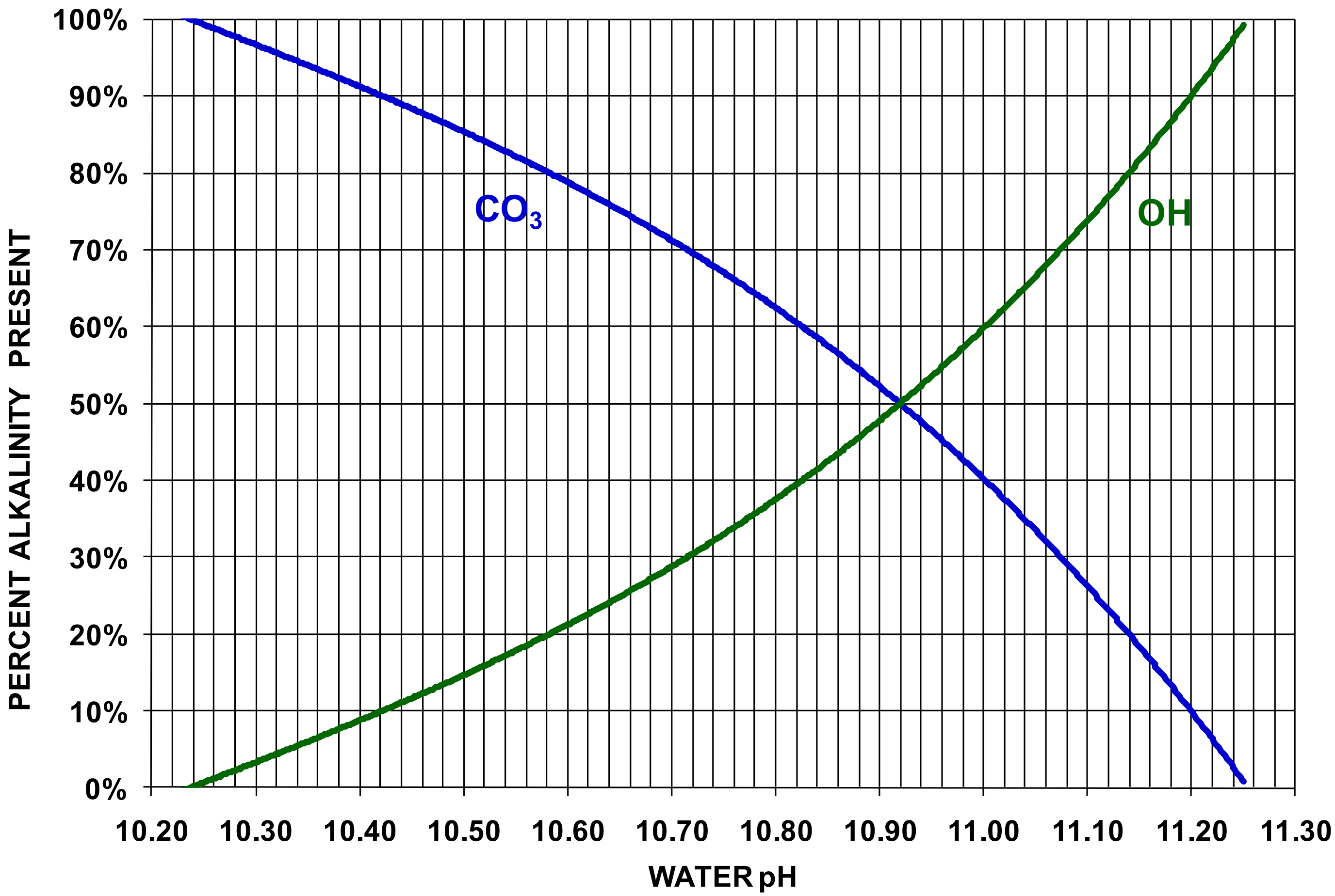
Alkalinity / pH Relationships

- 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



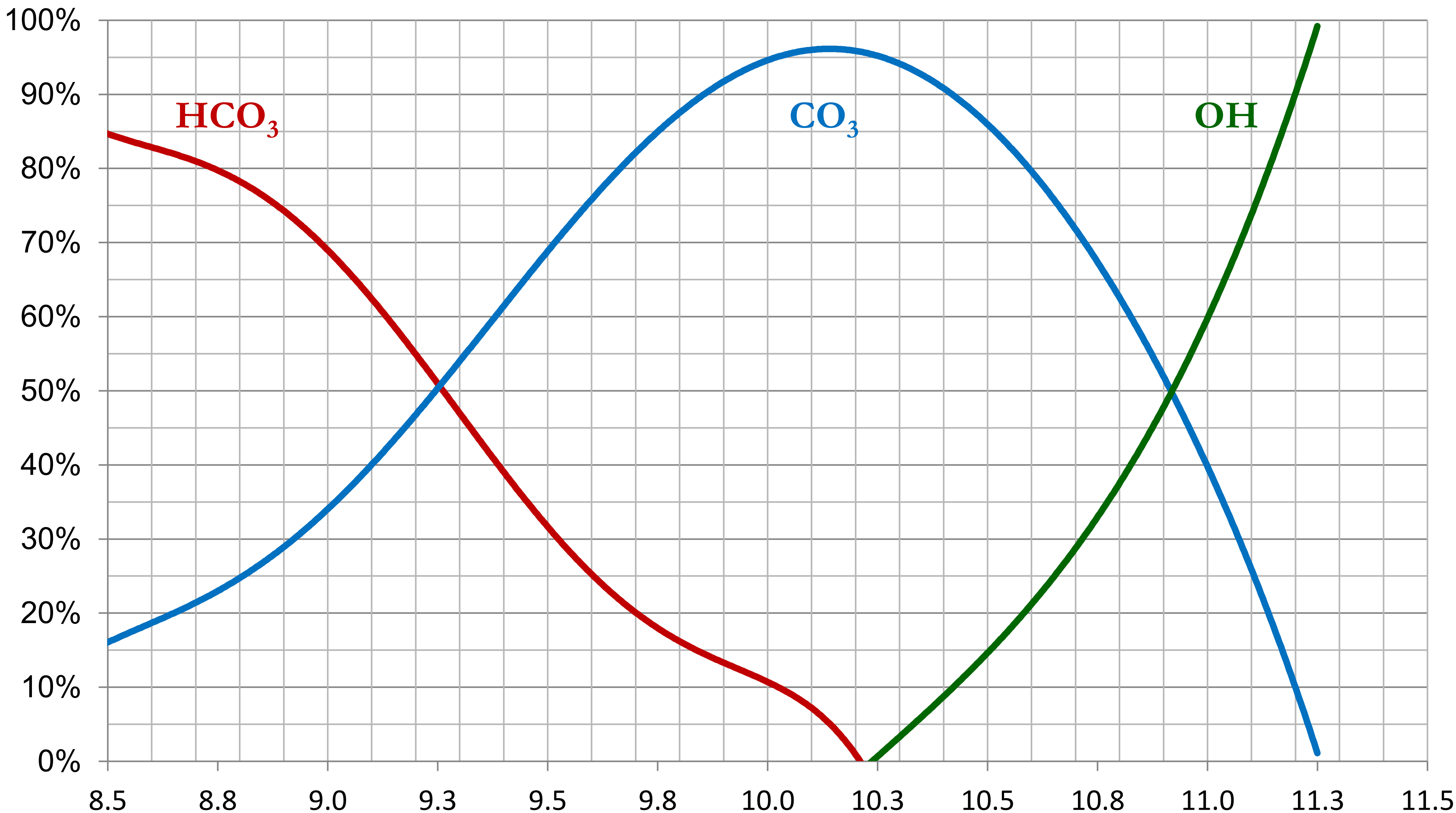
Alkalinity / pH Relationships



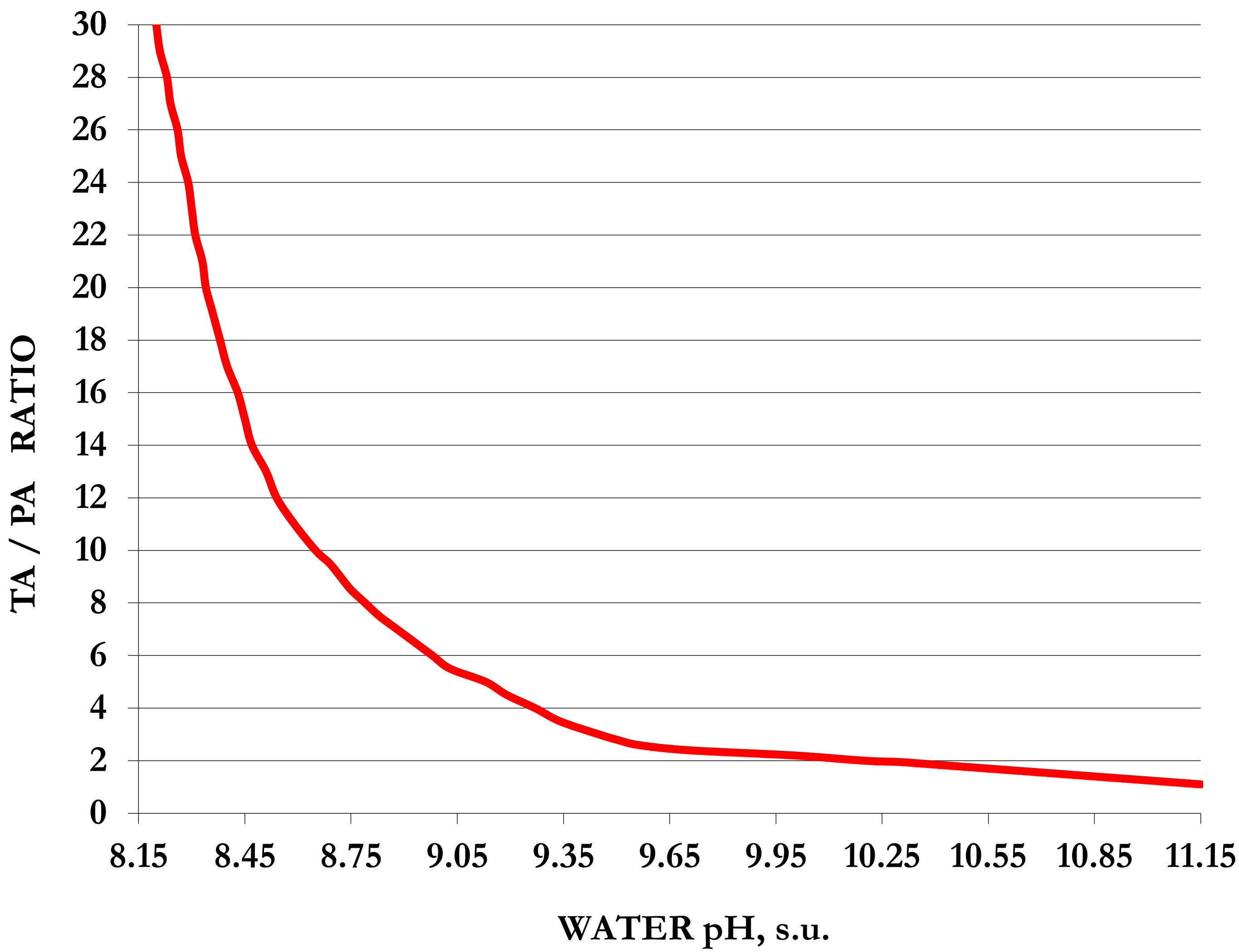
pH Relationships

- 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



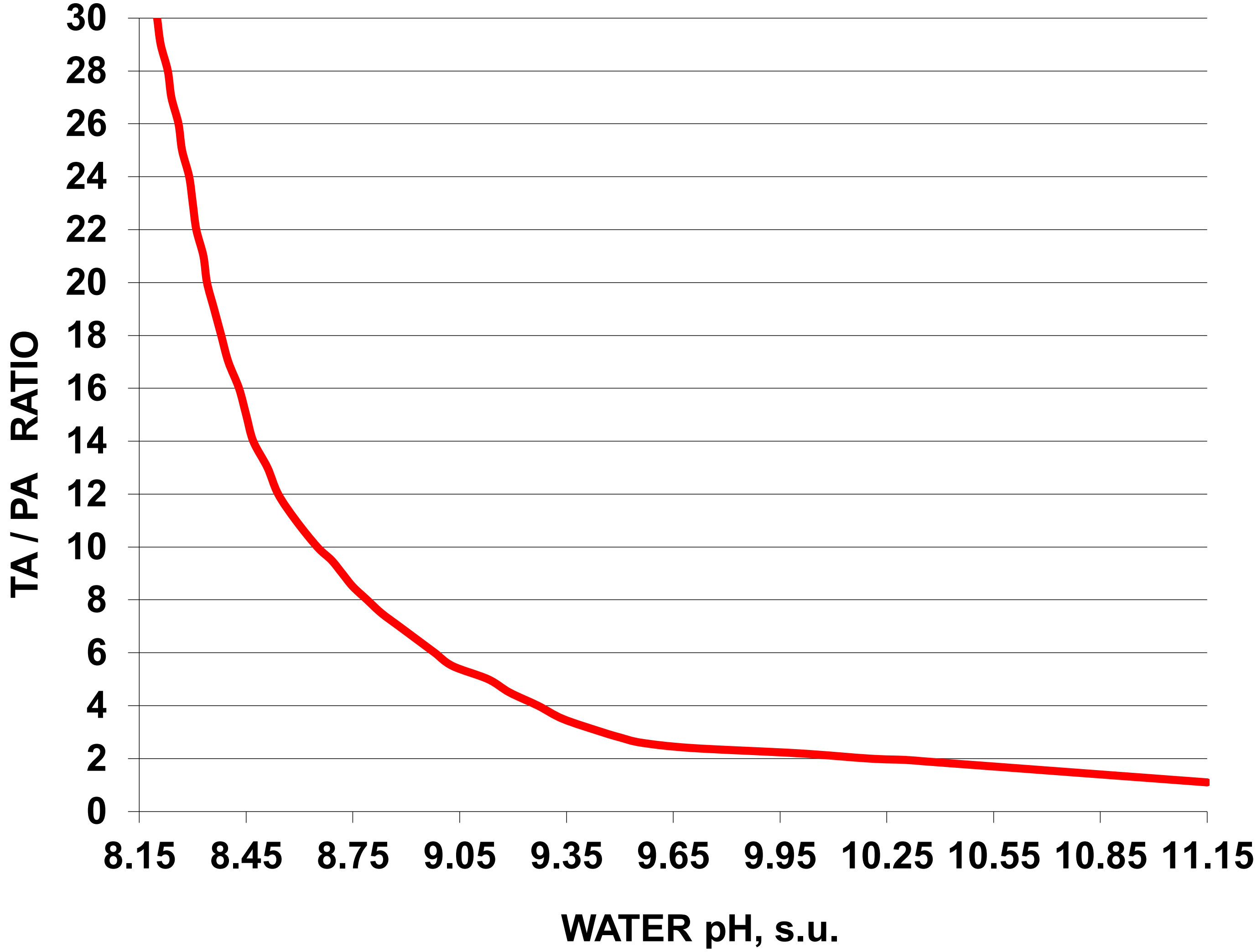
Alkalinity / pH Relationships



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

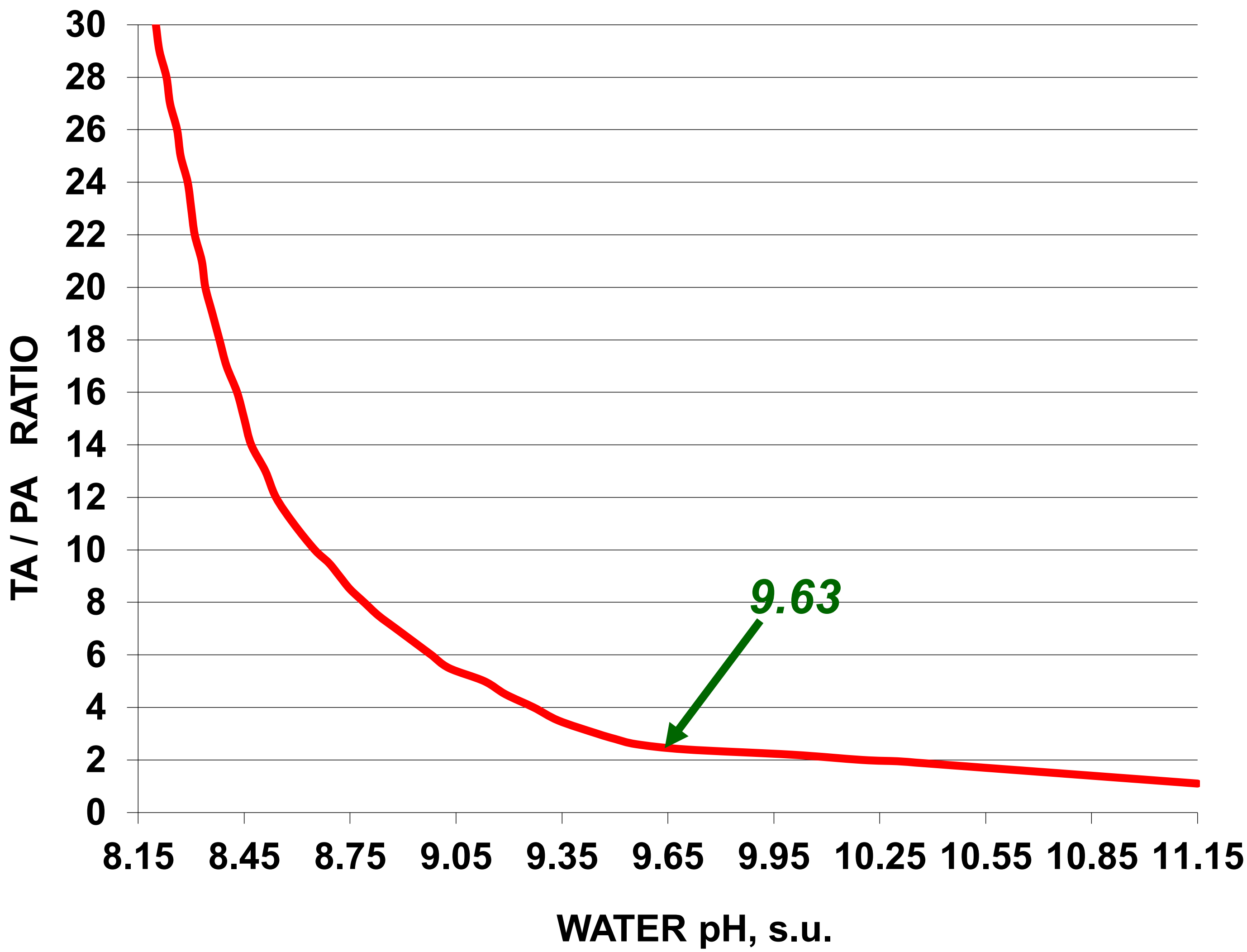
Alkalinity / pH Relationships



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

$$TA = H_2CO_3 + HCO_3^{-} + 2CO_3^{-2} + OH^{-}$$

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

Alkalinity Titration Equation

$$TA = H_2CO_3 + HCO_3^- + 2CO_3^{-2} + OH^-$$

- 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

$$K_{sp}, CaCO_3 = 10^{\left[13.870 - \left(\frac{3059}{TK}\right) - 0.04035\ TK\right]}$$

Solubility Relationships

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

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

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
- p*H* defined as -log(H+) concentration

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
- p*H* defined as -log(H+) concentration
- pK_{sp} is $-\log(K_{sp})$
  - Defines relative pH needed to force precipitation based on water temperature

Solubility Relationships

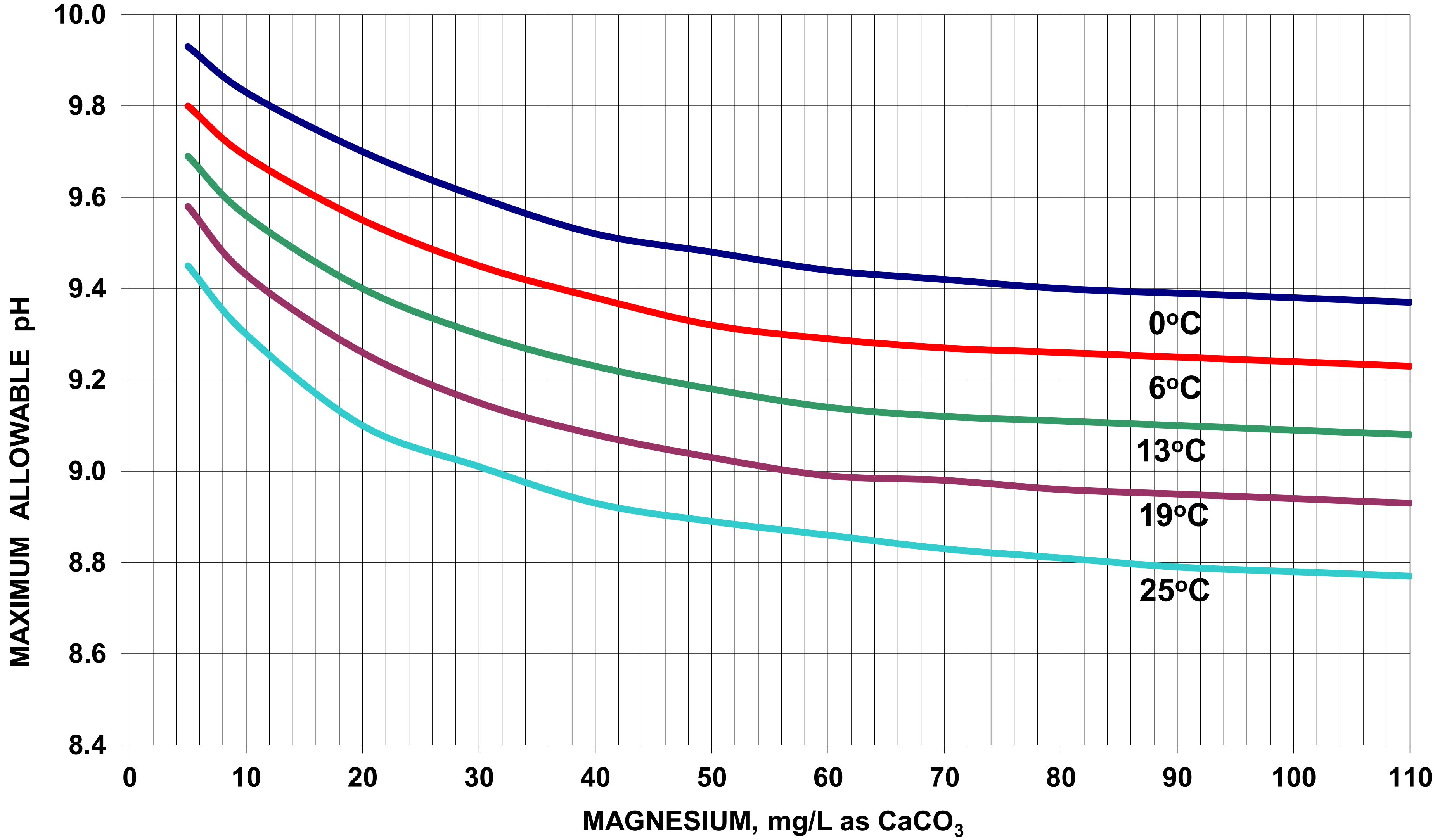
	K_{sp}	pK_{sp}
$CaCO_3$	~24 mg/L	8.49
$Mg(OH)_2$	~12 mg/L	10.59

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

Magnesium Fouling Issues



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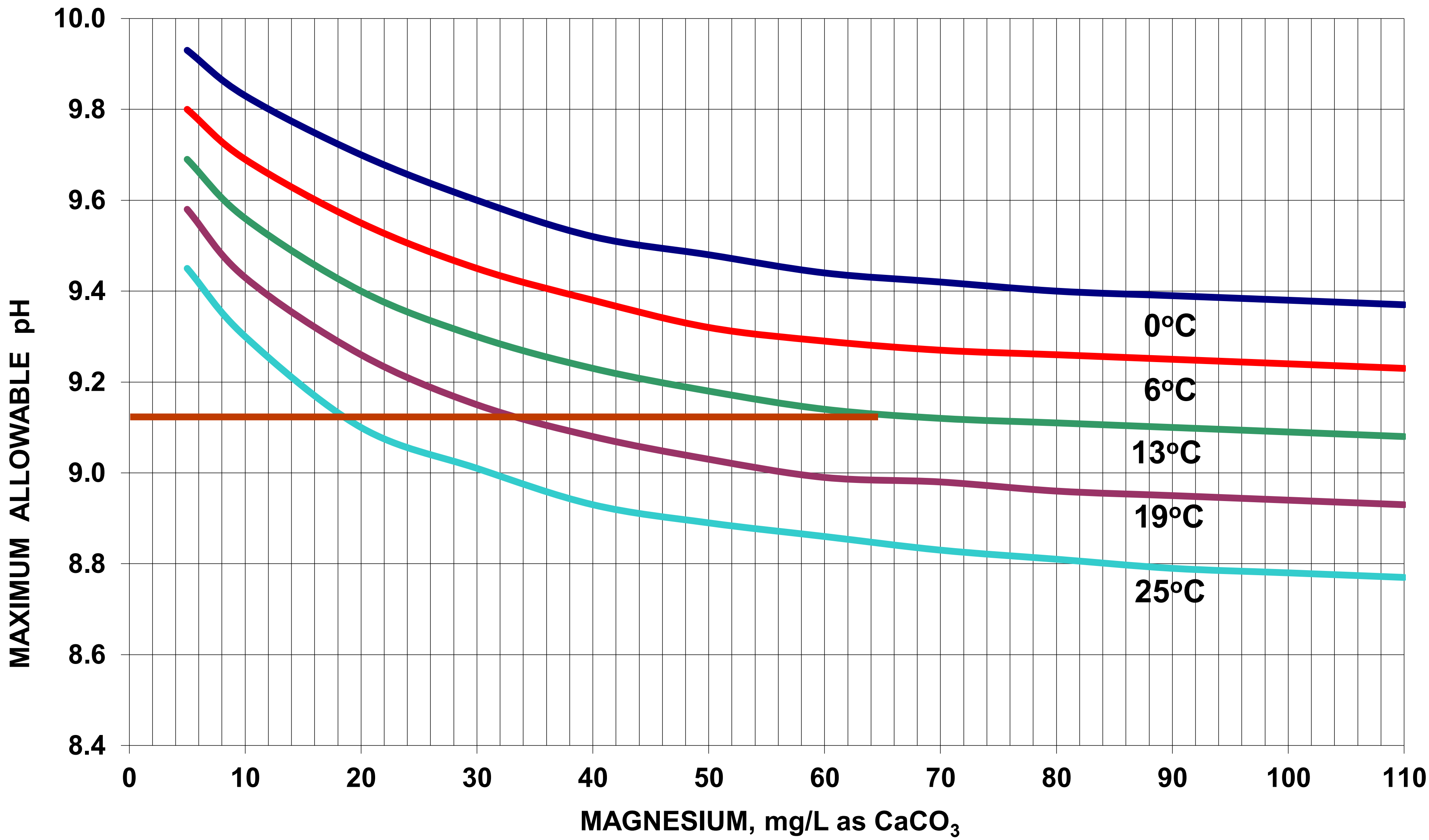

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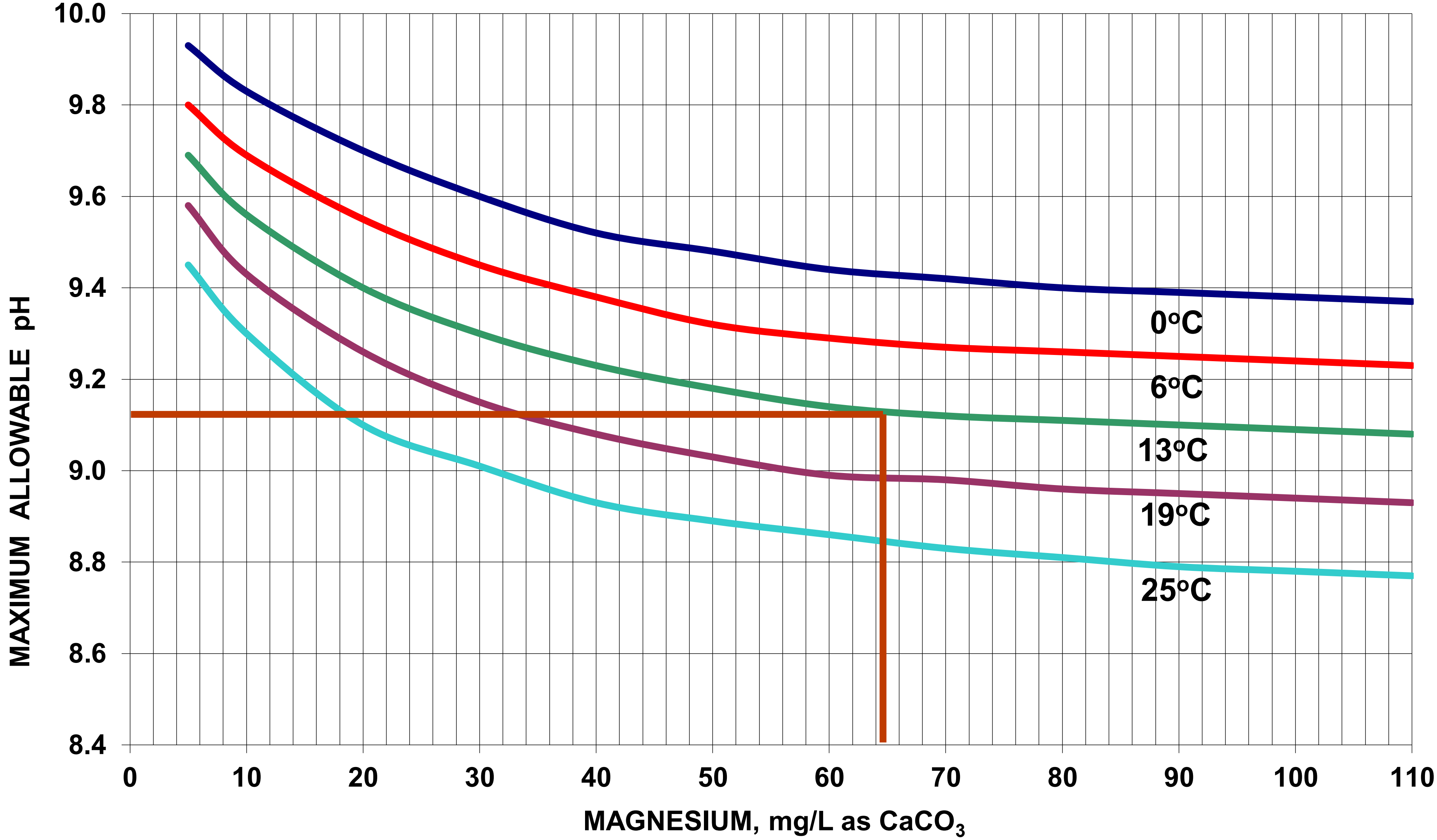

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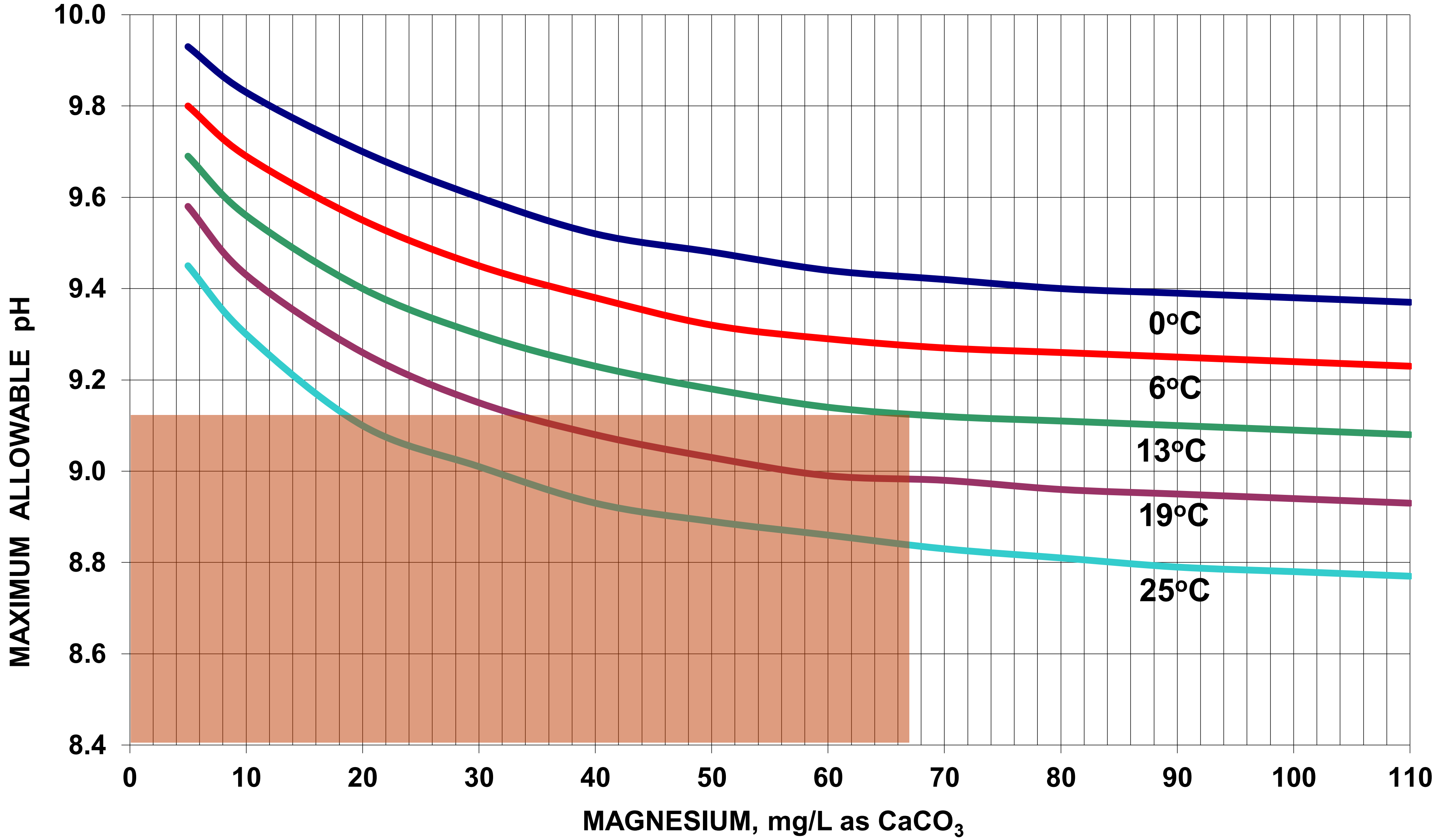

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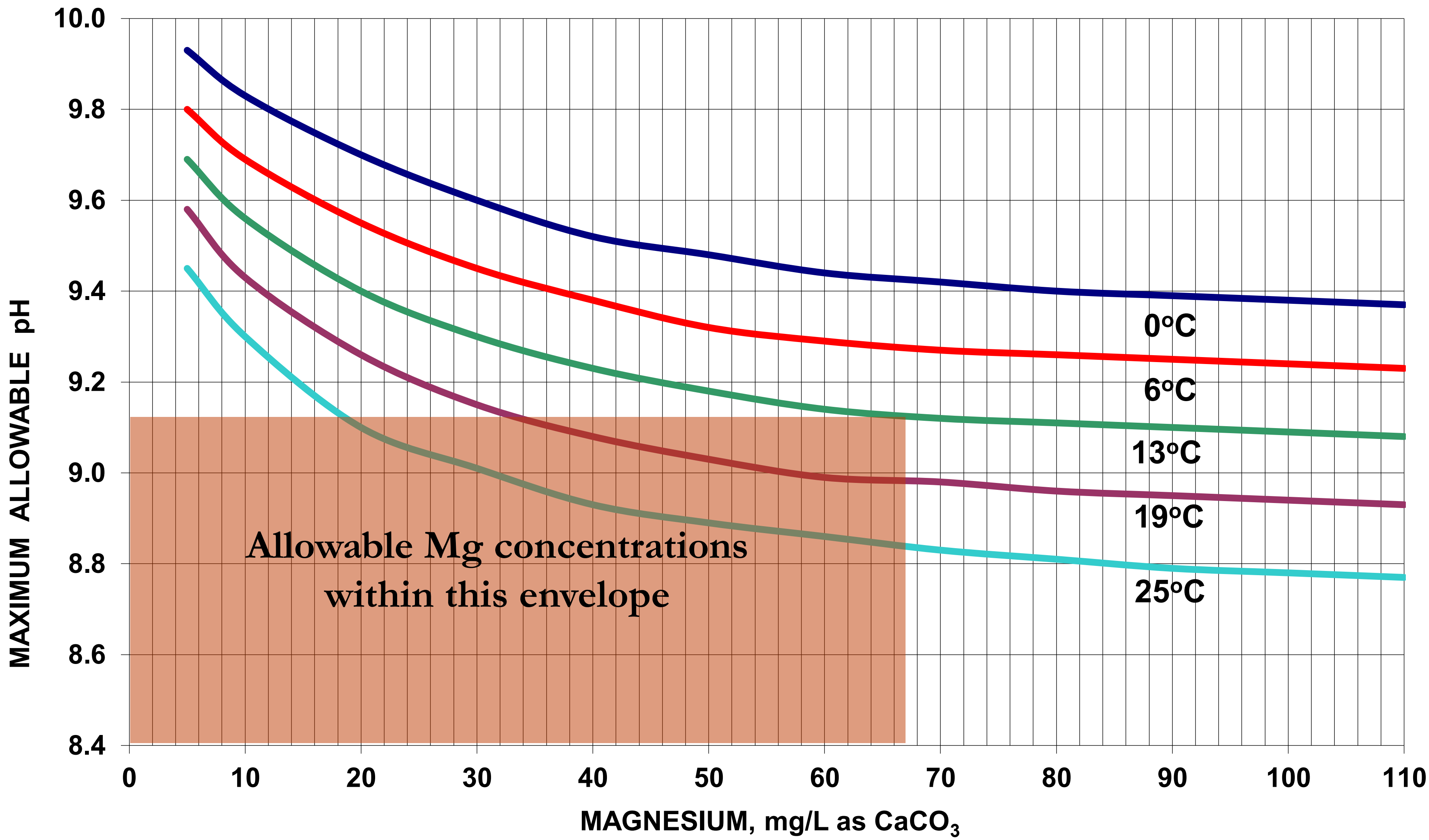

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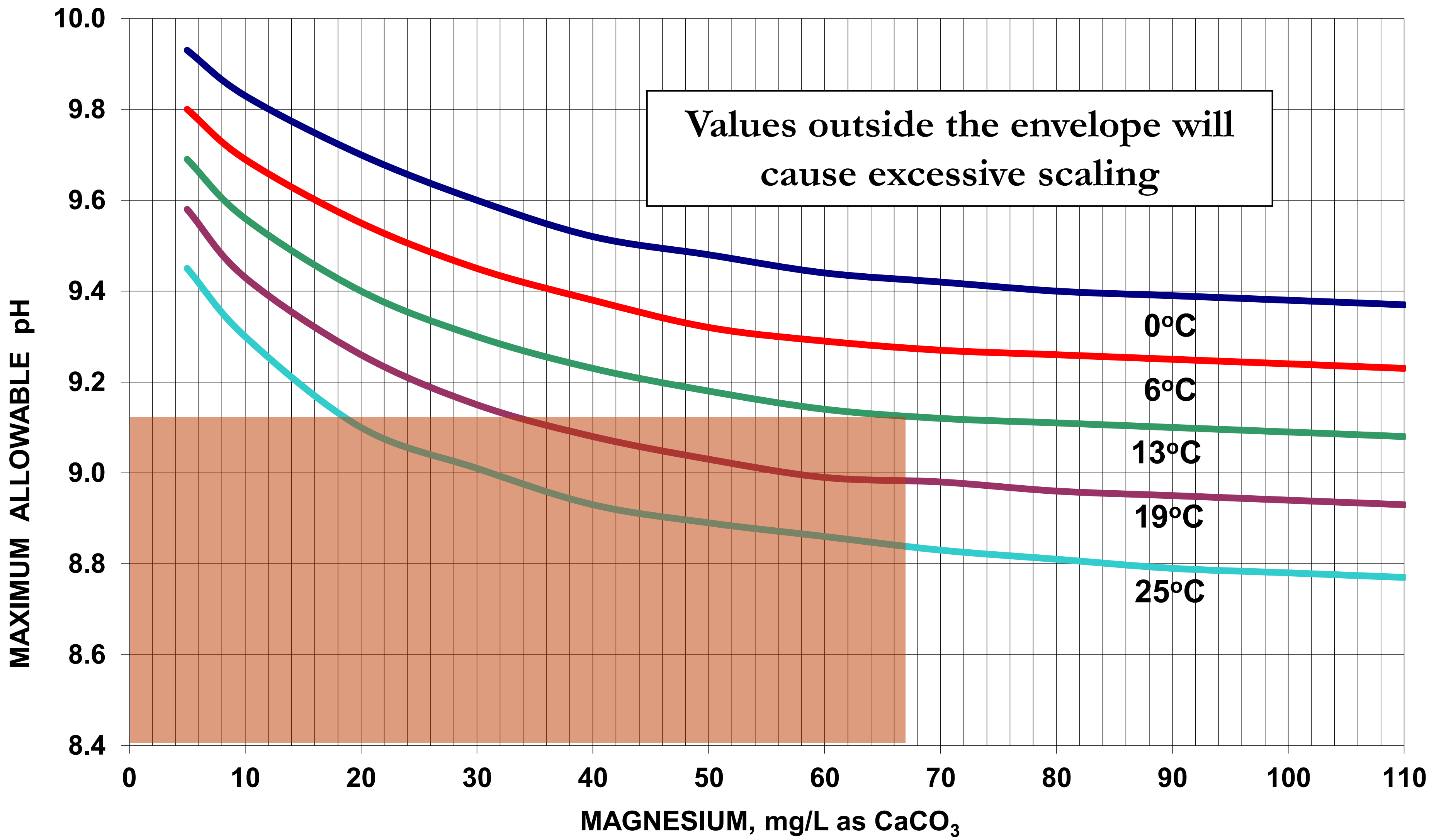
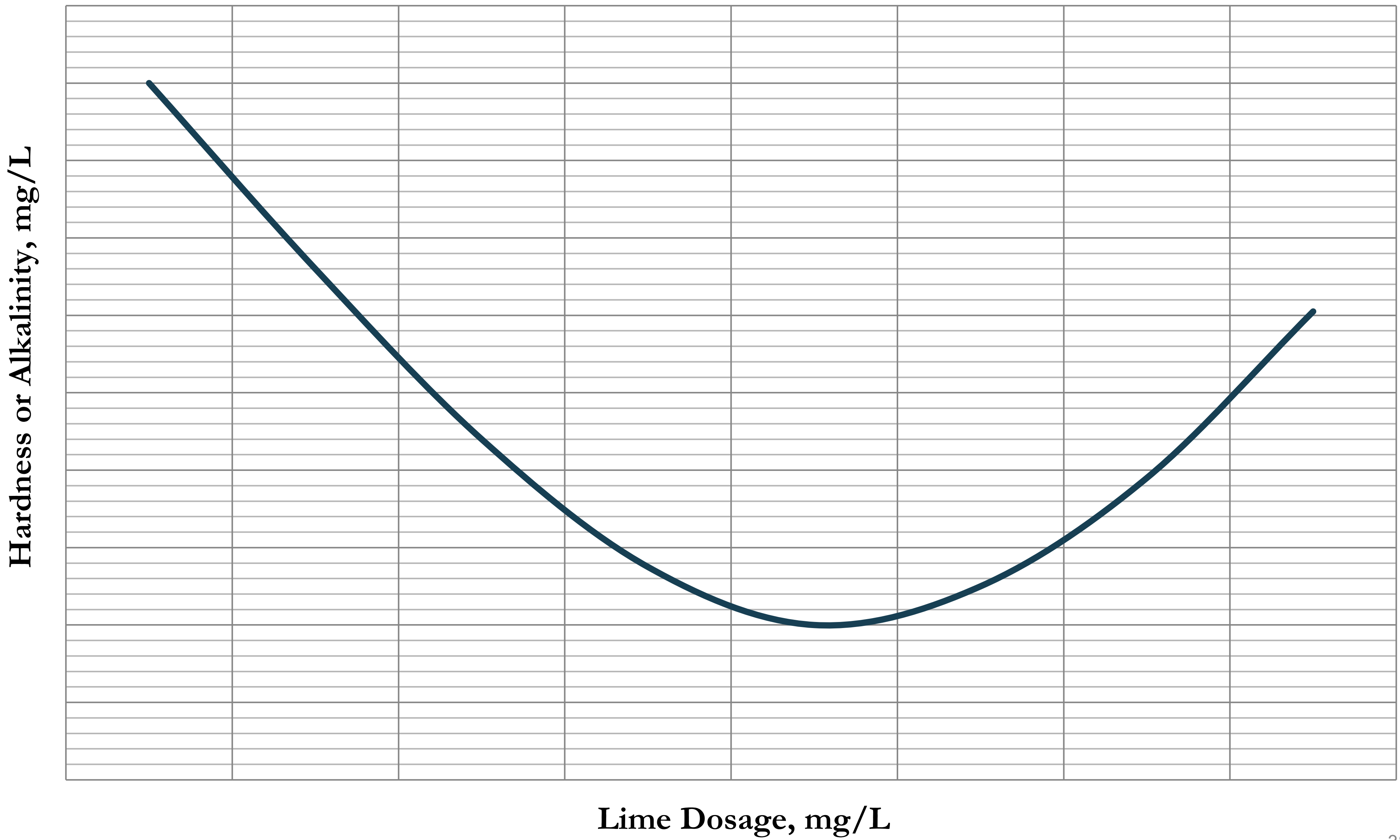


Softening Demand Curves

- 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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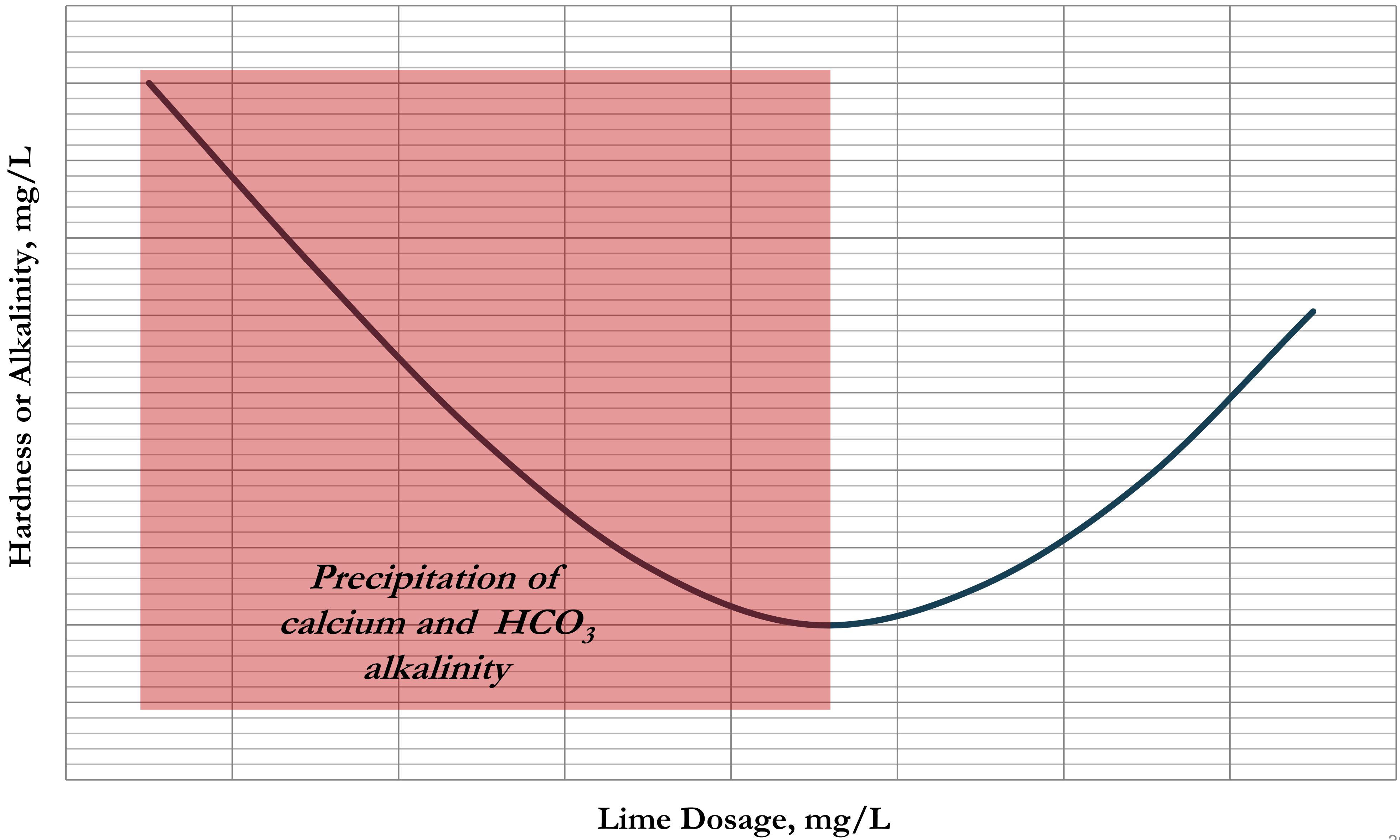

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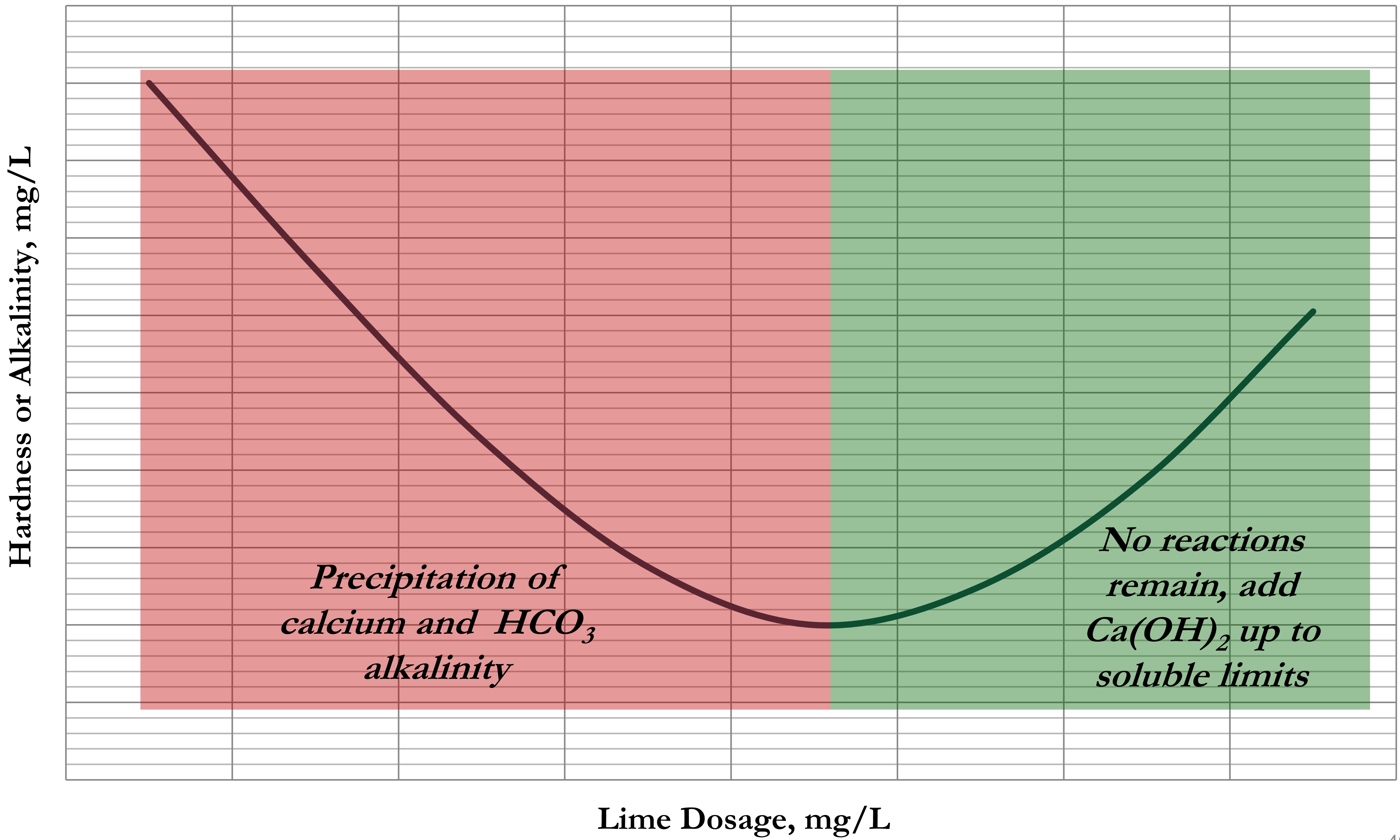

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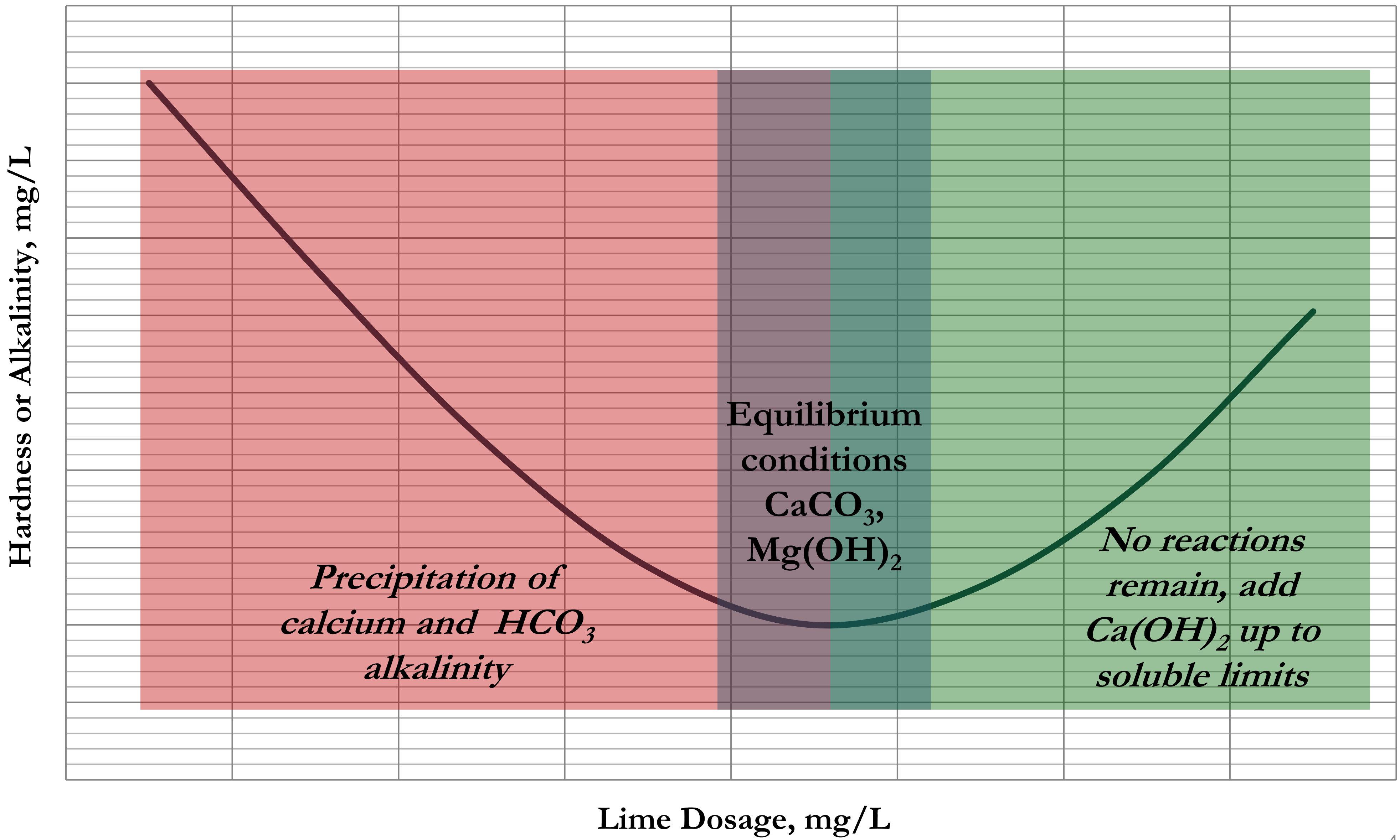

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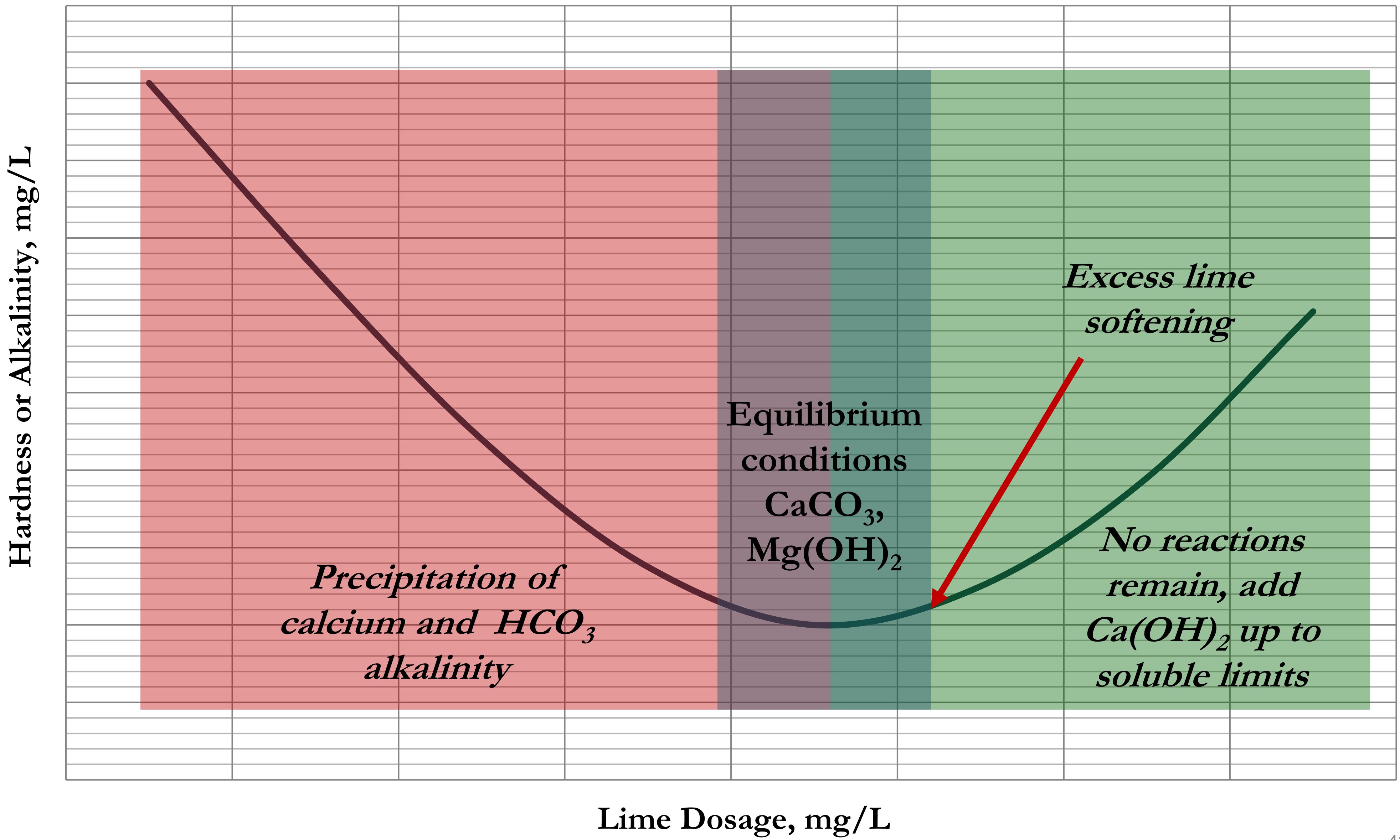

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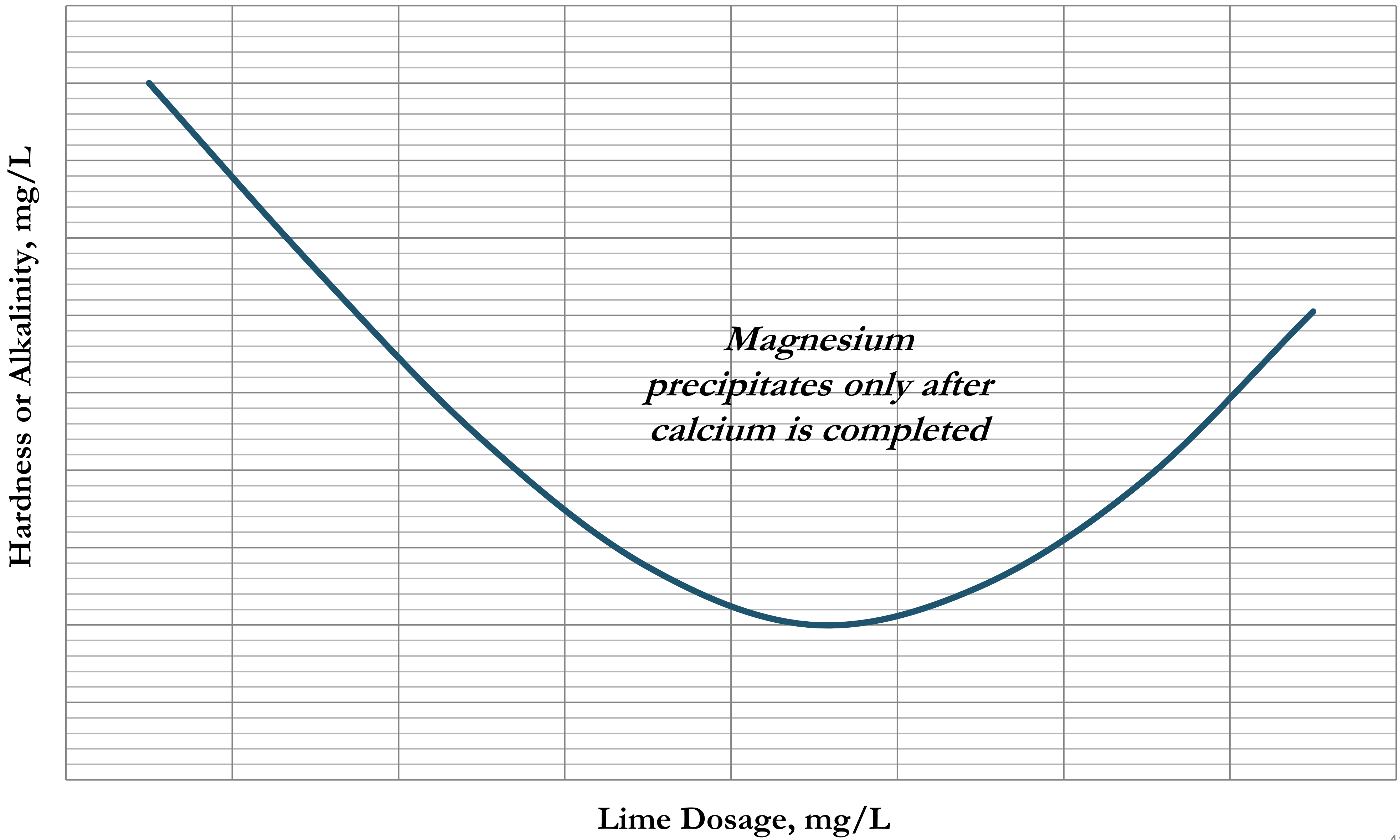

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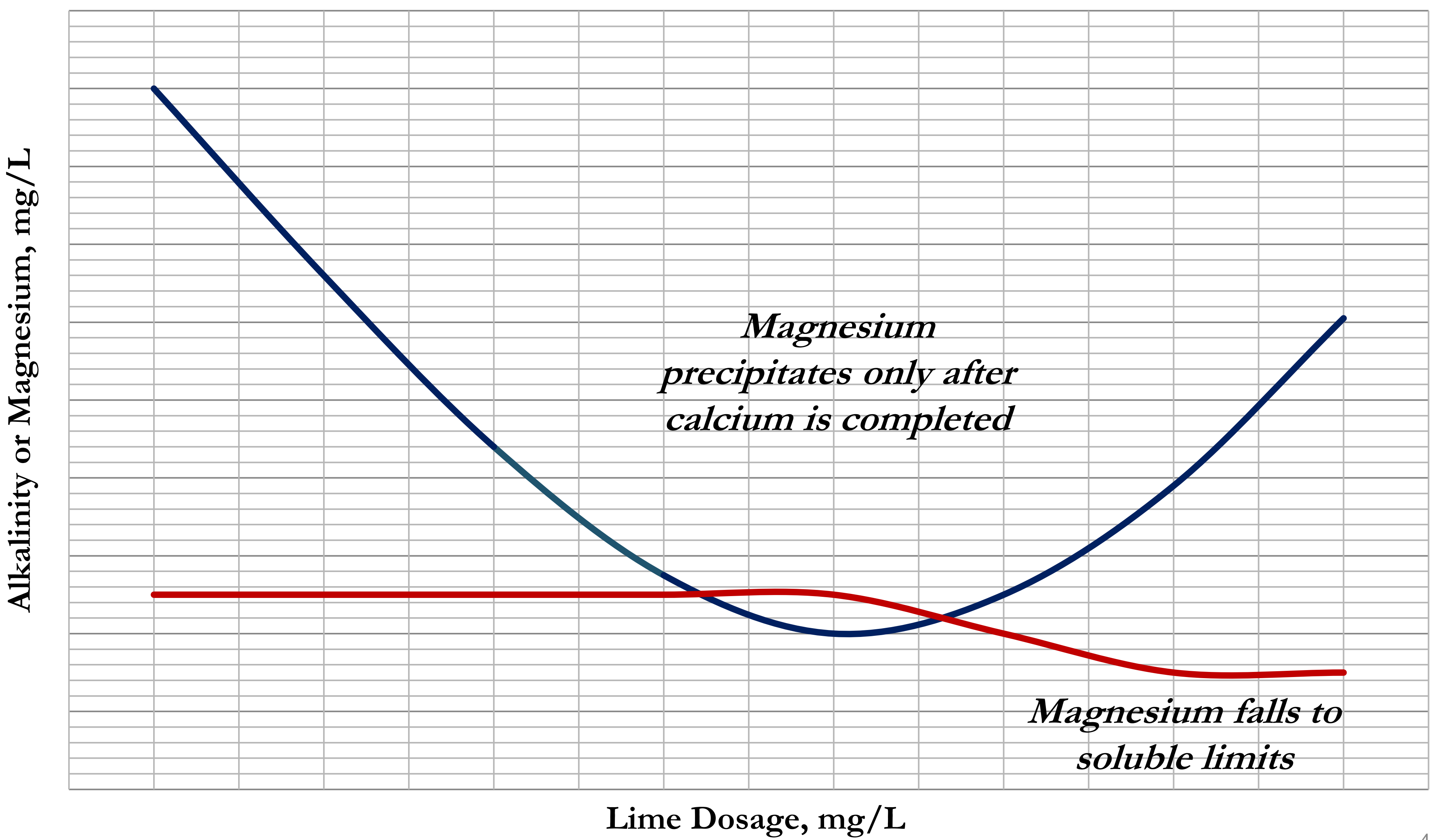

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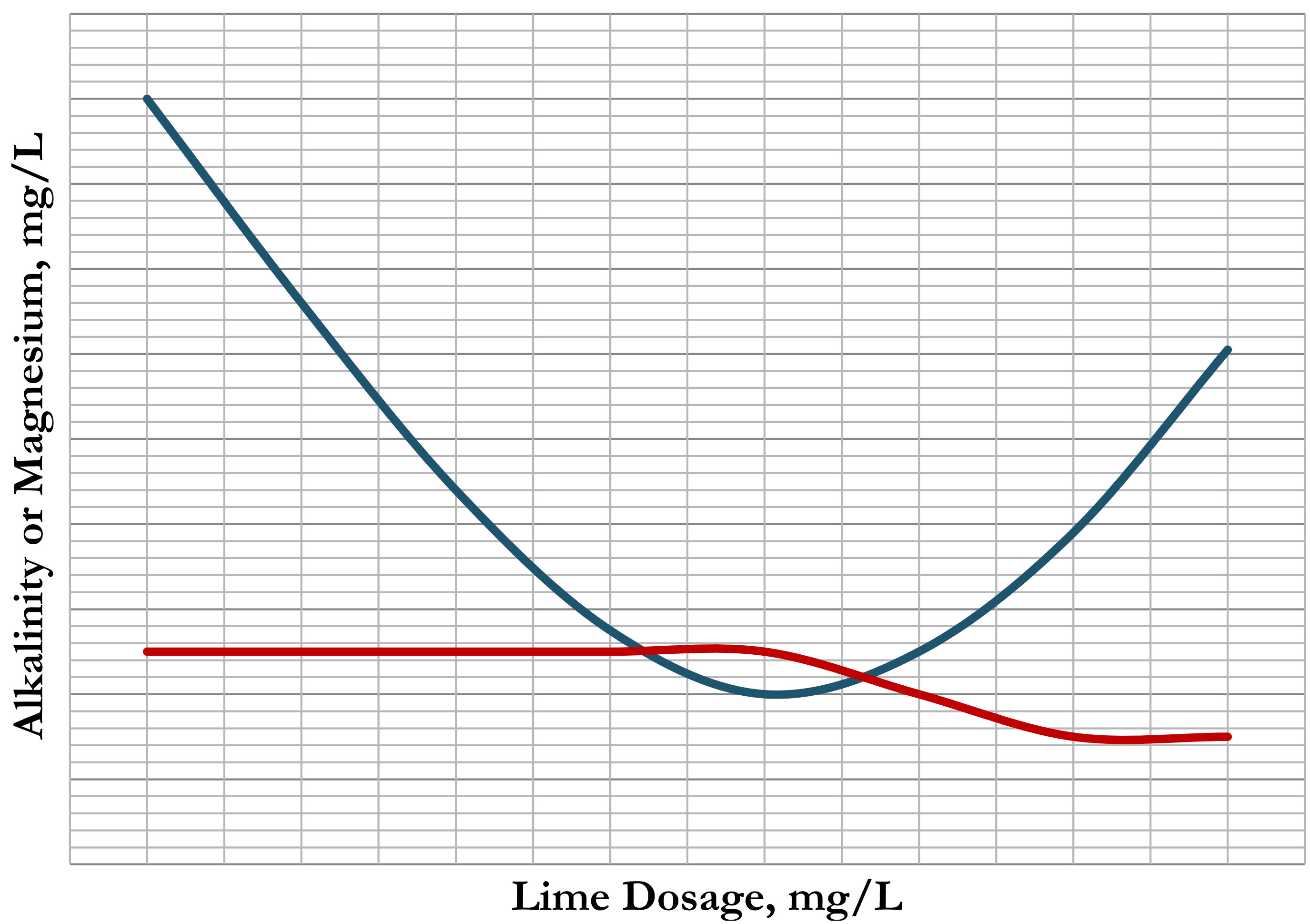
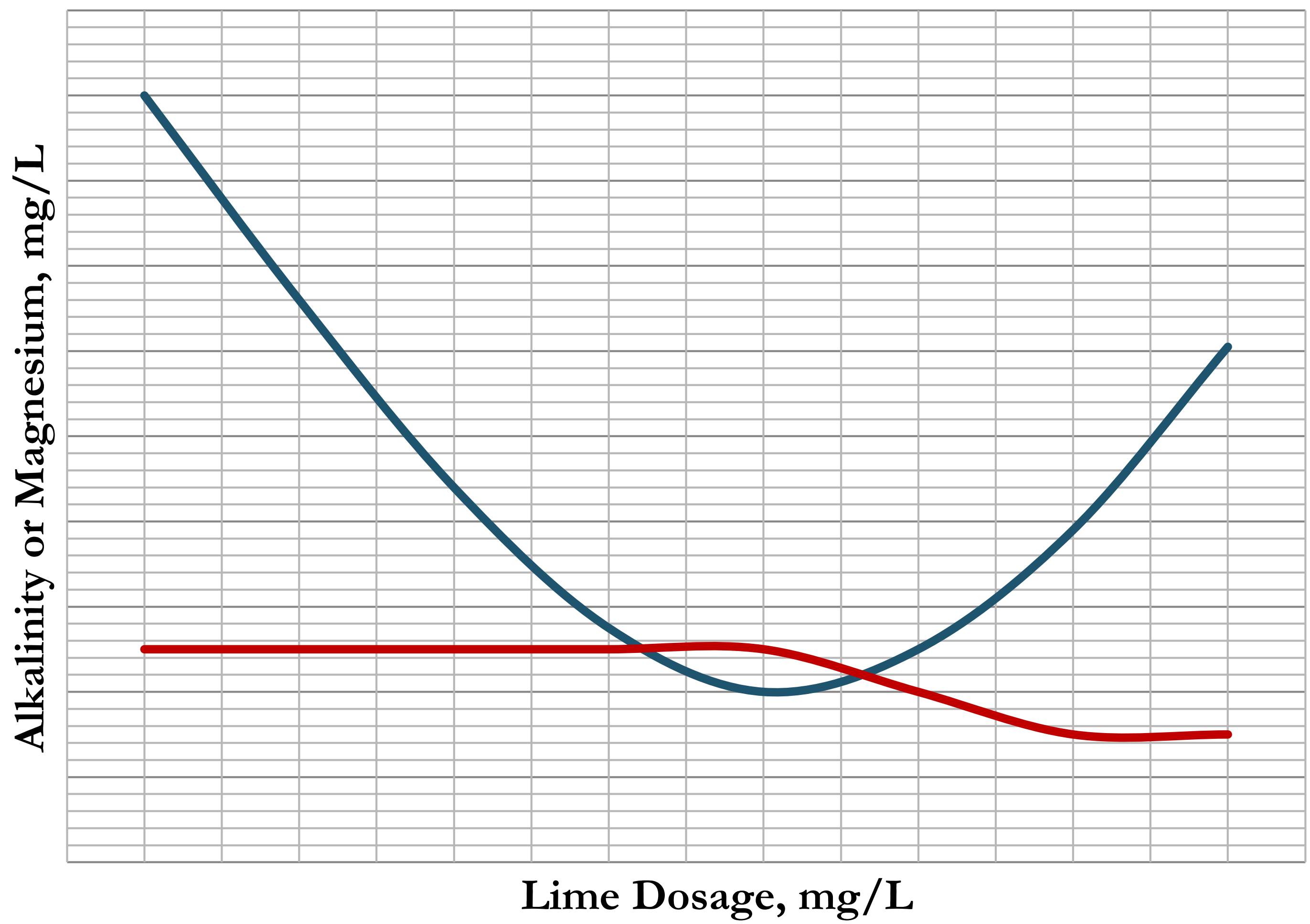


Demand Relationships

- Calcium and alkalinity precipitate first
  - At pH ≥8.49
- Magnesium precipitation occurs after calcium completed
  - At pH ≥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

CO_2 Determinations

$$CO_2 + Ca(OH)_2 \Rightarrow CaCO_3 + H_2O$$

- **CO_2** creates demand for lime
- High **CO_2** should be removed with aeration
  – >10 mg/L **CO_2** aeration more cost effective
- Calculation in Standard Methods

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

- Nomograph method also available

Coagulant Reaction Byproducts

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \Rightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2$$

- Alkalinity consumed during coagulation reactions
- Alkalinity essentially converted to ***noncarbonate*** hardness, soda ash or caustic soda needed for removal
- **CO_2** creates additional lime demand

Coagulant Reaction Byproducts

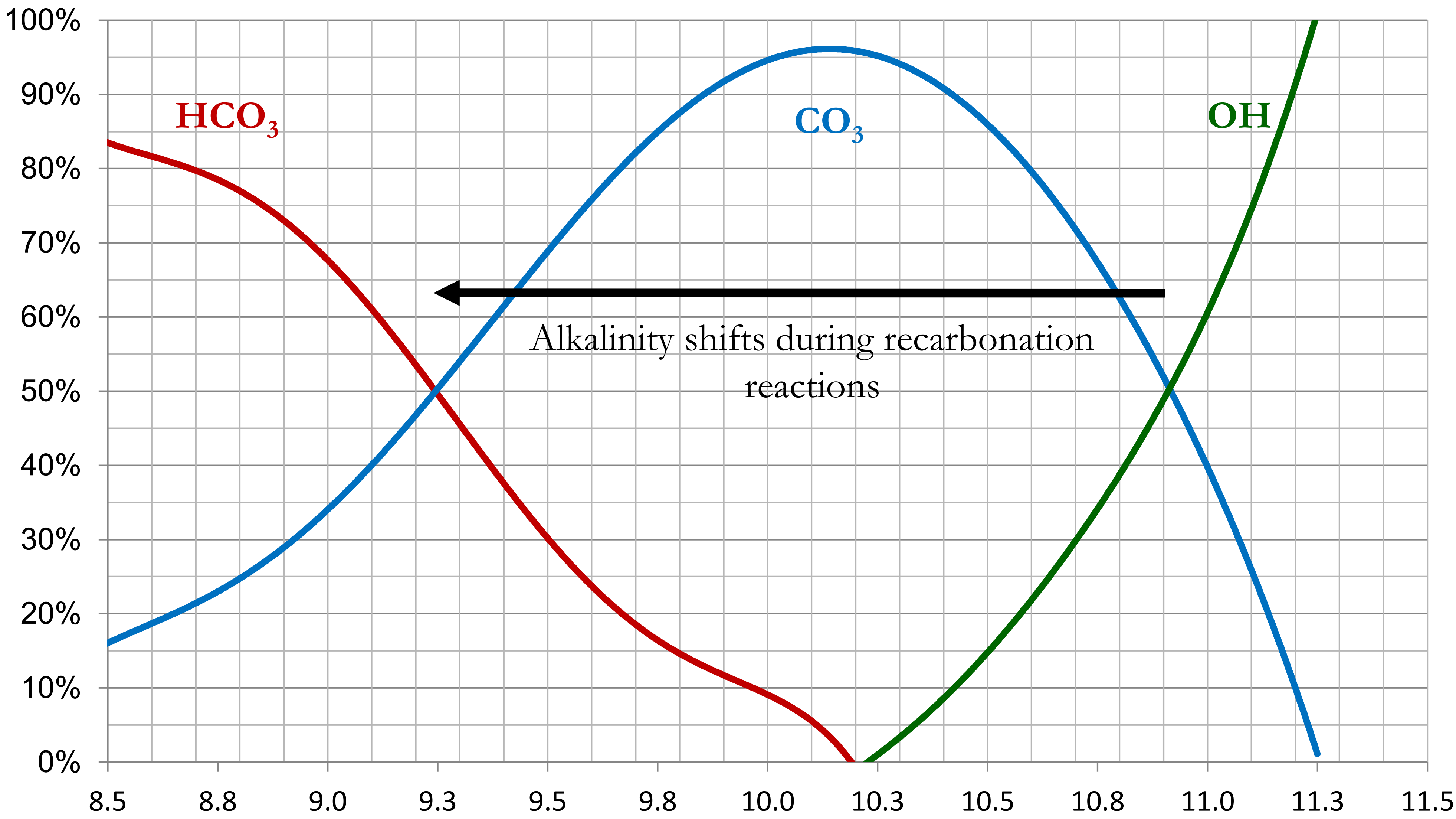
Coagulant	Alkalinity Consumed, mg/L	Dissolved CO_2 Formed, mg/L
Alum	0.5	0.44
Ferric Chloride	0.46	0.40
Ferric Sulfate	0.53	0.23
Aluminum Chlorohydrate (ACH)	0.29	0.25
Polyaluminum Chloride (PACl)	0.71	0.62
Polyaluminum Chlorosulfate (PACS)	0.36	0.31

Recarbonation Chemistry

$$CO_2 + H_2O \Rightarrow H_2CO_3$$

- 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 **CO_3** alkalinity

$$Ca(OH)_2 + H_2CO_3 \Rightarrow CaCO_3 + 2H_2O$$

- **CO_3** alkalinity reacts to form **HCO_3** alkalinity

$$CaCO_3 + H_2CO_3 \Rightarrow Ca(HCO_3)_2 + H_2O$$

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 CO_2 dosage
- If **OH** absent, one iteration needed

Questions

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