Lime Softening for Optimized TOC Removal and Alkalinity Management

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OTCO Water Workshop – Quest Conference Center

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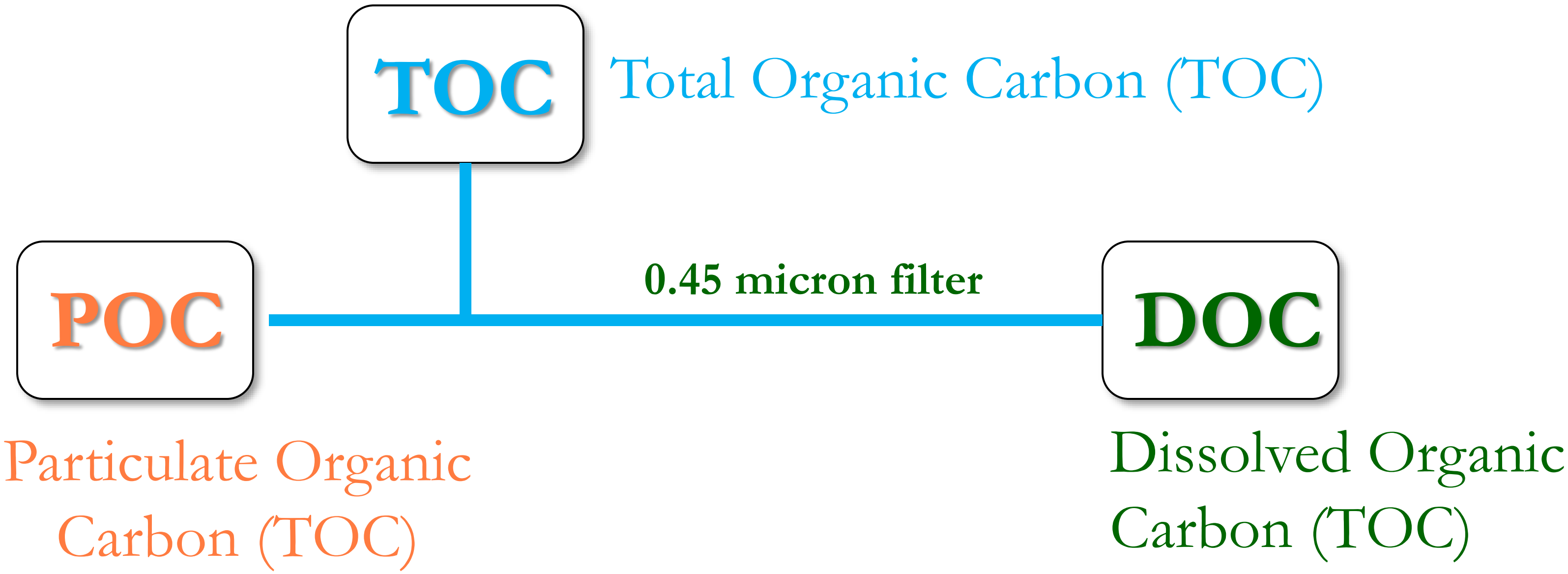
Agenda

- Review technical aspects and best practices for lime softening
- Discuss TOC reductions due to lime softening operations, impacts from coagulant addition, and alkalinity management
- Case studies - water treatment plant data examined using techniques presented
- Summary and Questions

Before We Begin: TOC = POC + DOC



DOC is often 80% to 95% of TOC, **today's presentation is for enhanced removal of DOC by coagulation/lime softening**

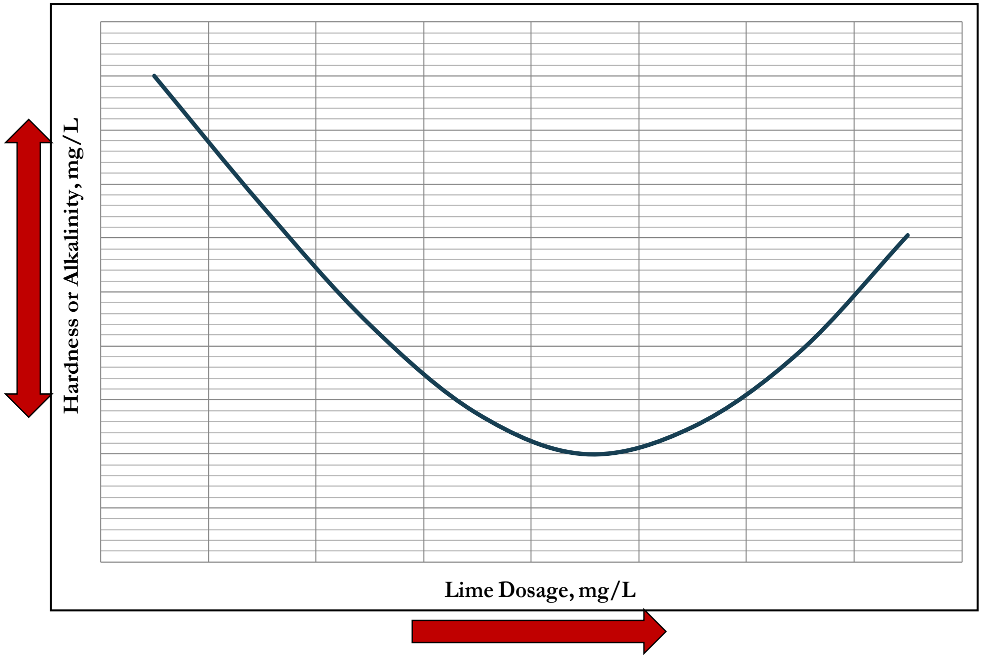
"**Lime Softening for Optimized TOC** Removal and Alkalinity Management"

Part 1

Technical Background on Lime Softening

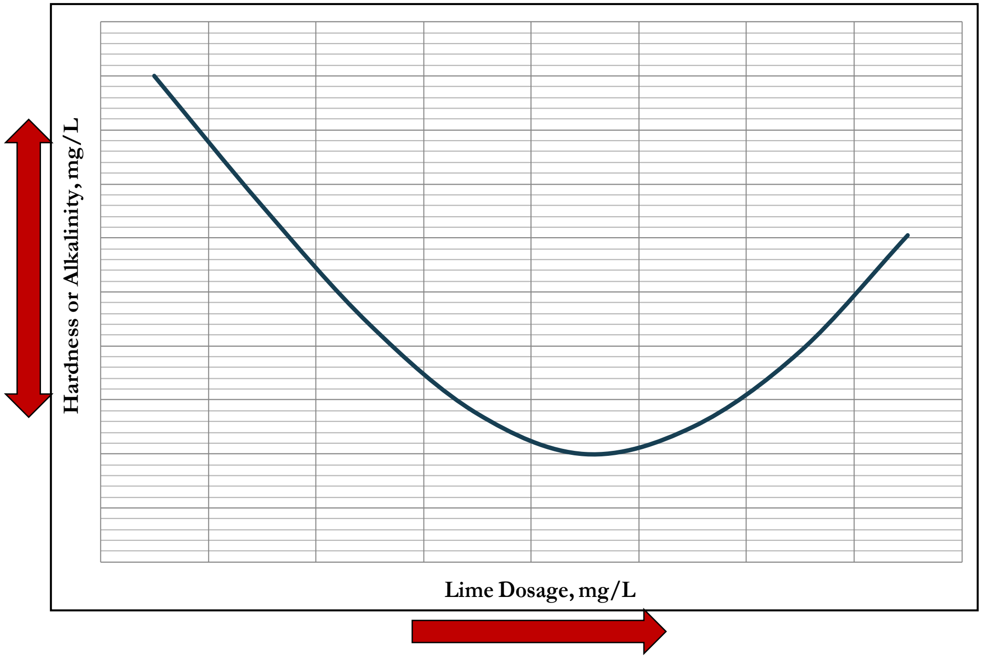
Technical Background: Lime Softening

- Chemical equations are well-known, and we will not review those today
- Relationships between pH, calcium, magnesium, alkalinity are dictated by softening chemistries
- Lime demand curve depicts lime softening operations most effectively

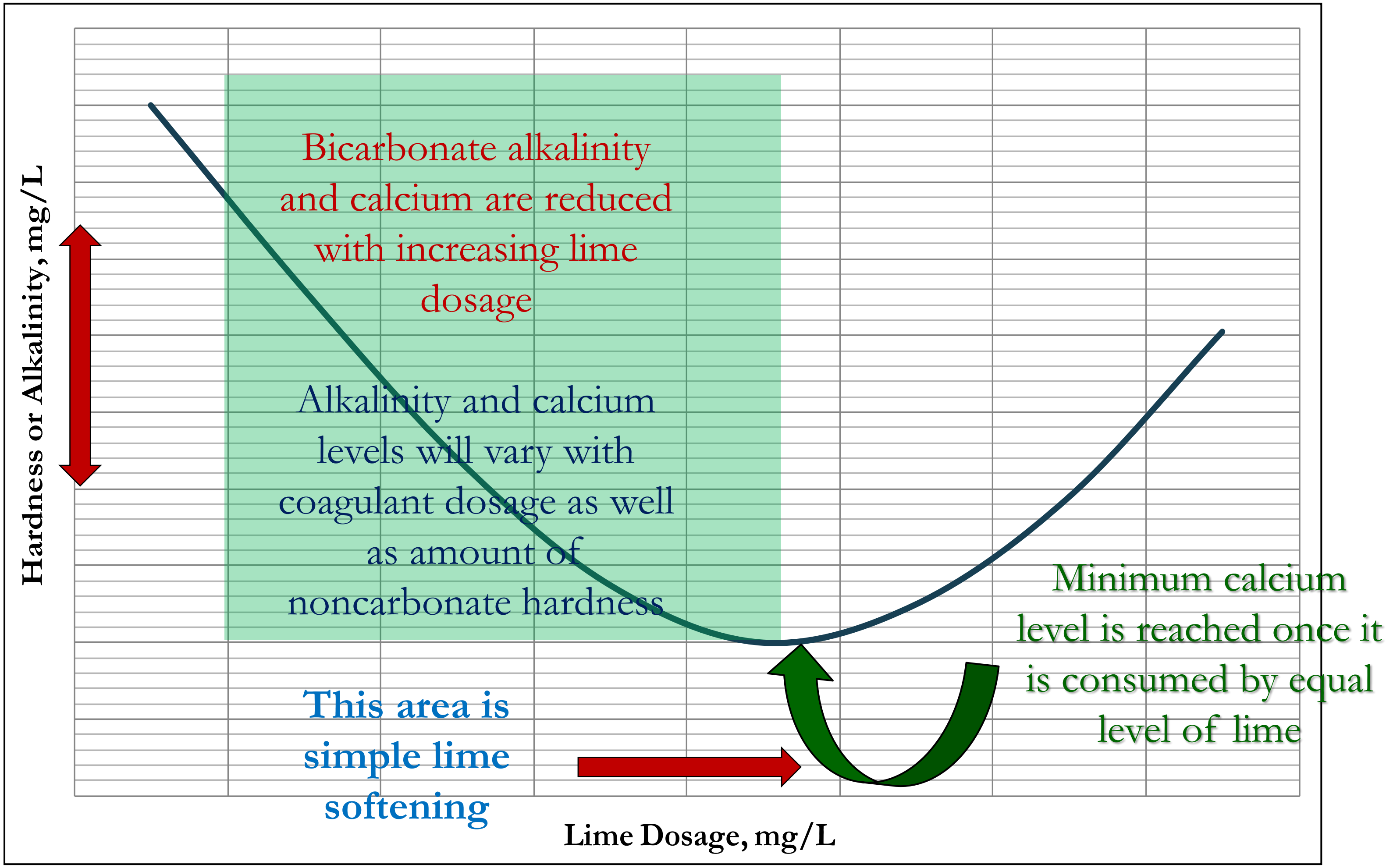


Technical Background: Lime Softening

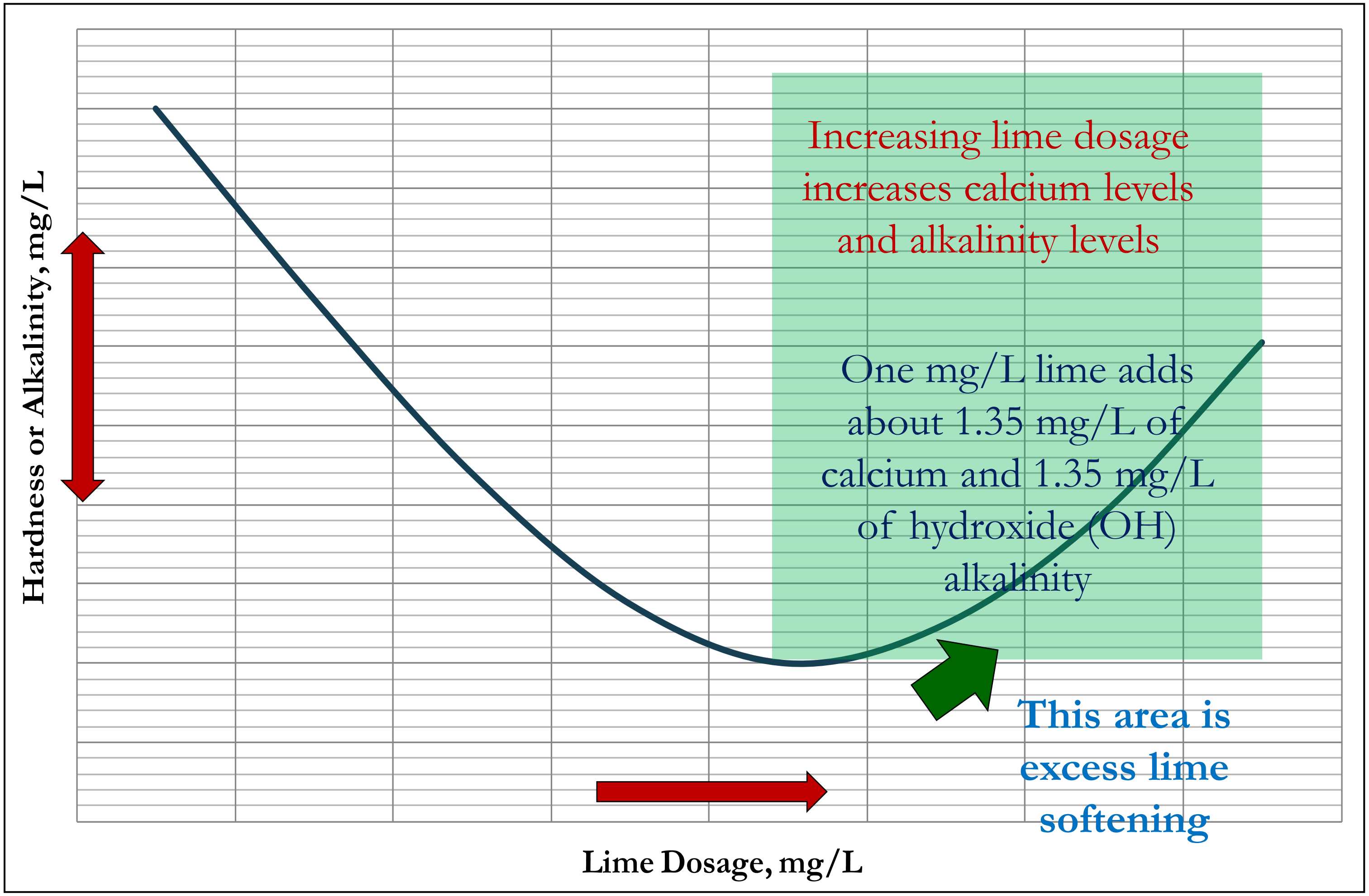
- As lime is added – changes occur in alkalinity, calcium, magnesium, pH, (and TOC shown later)
- Treatment operators should understand where they are operating on the demand curve



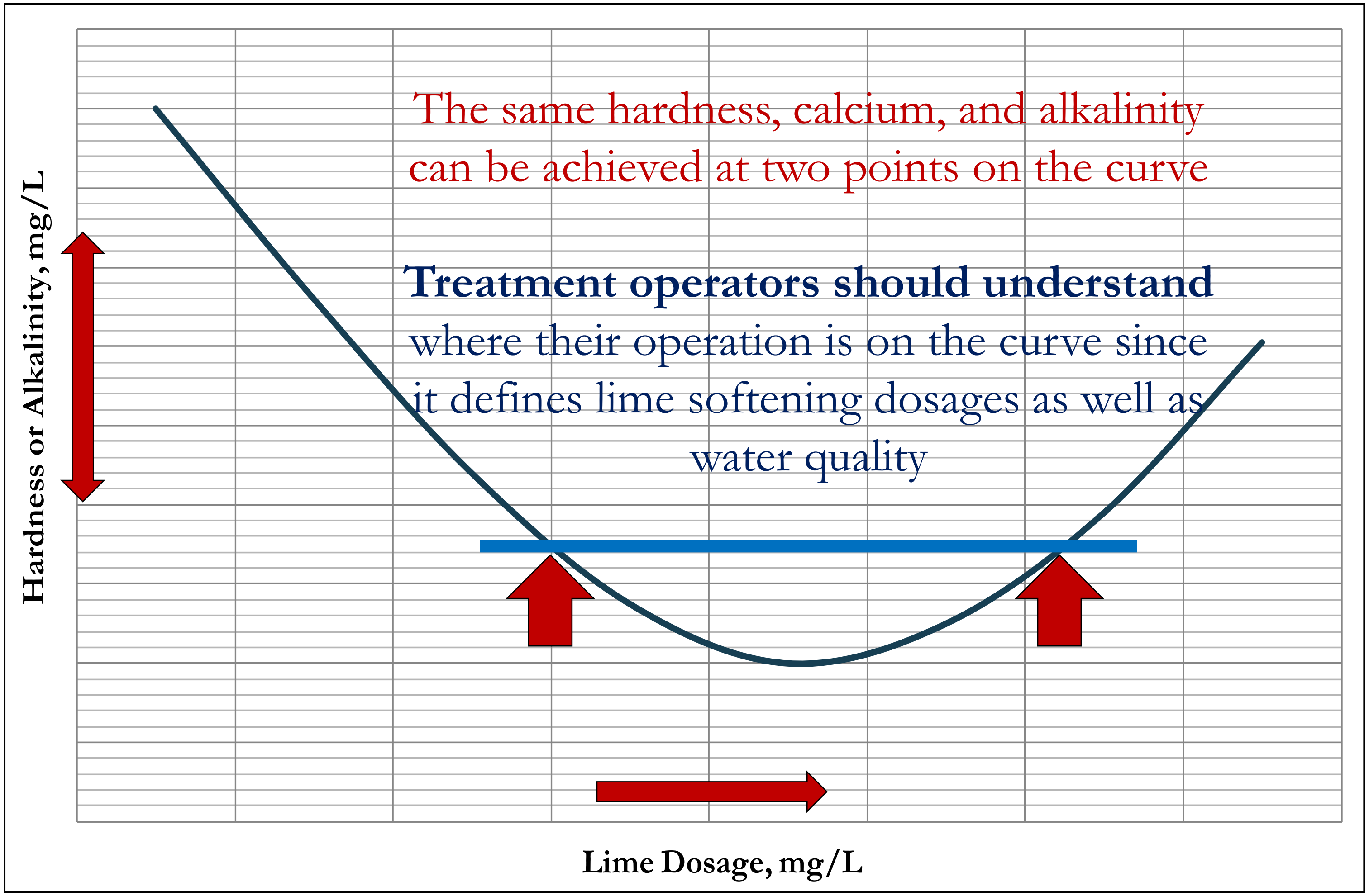
Lime Softening: Simple Softening



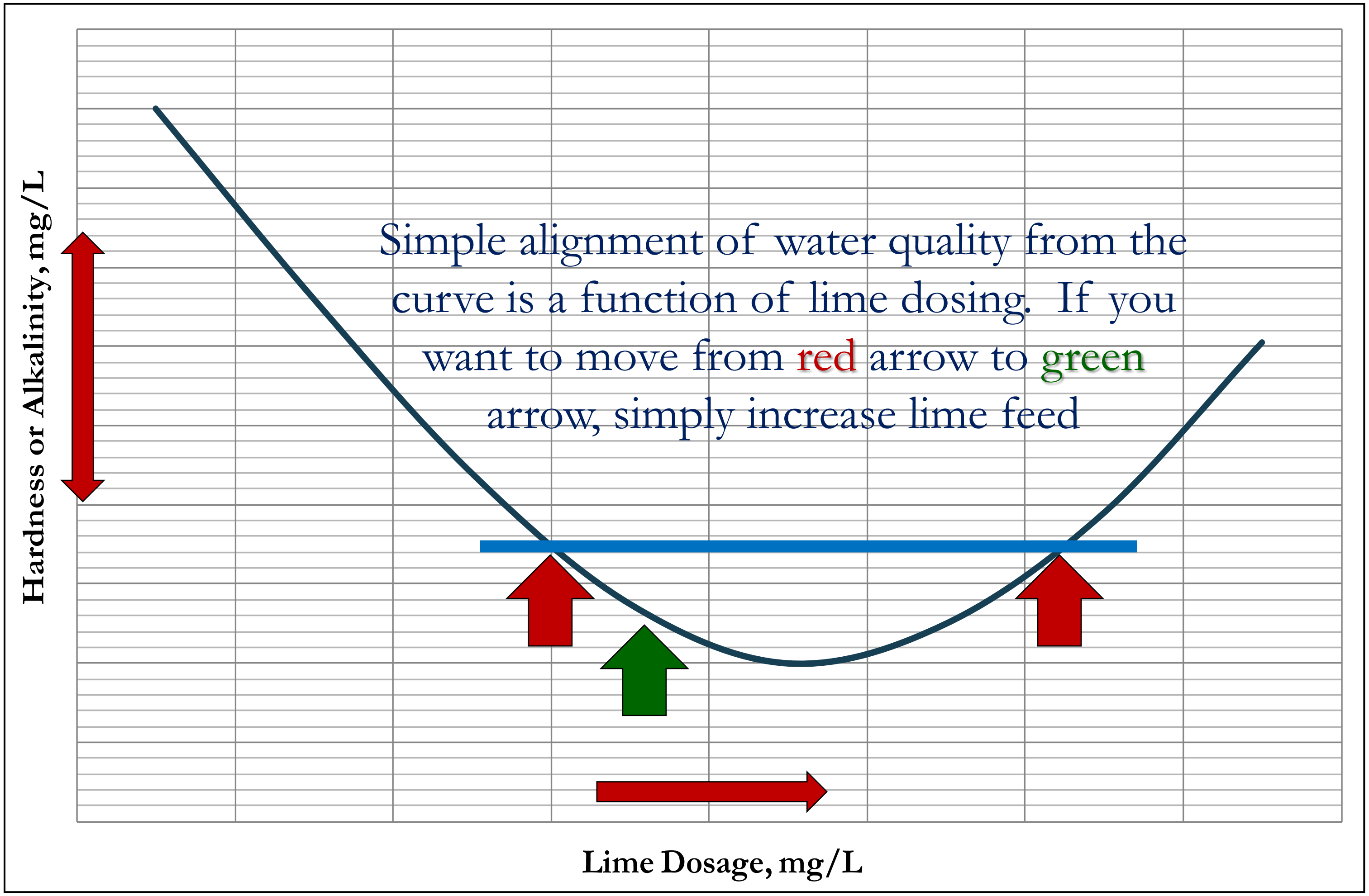
Lime Softening: Excess Lime Softening



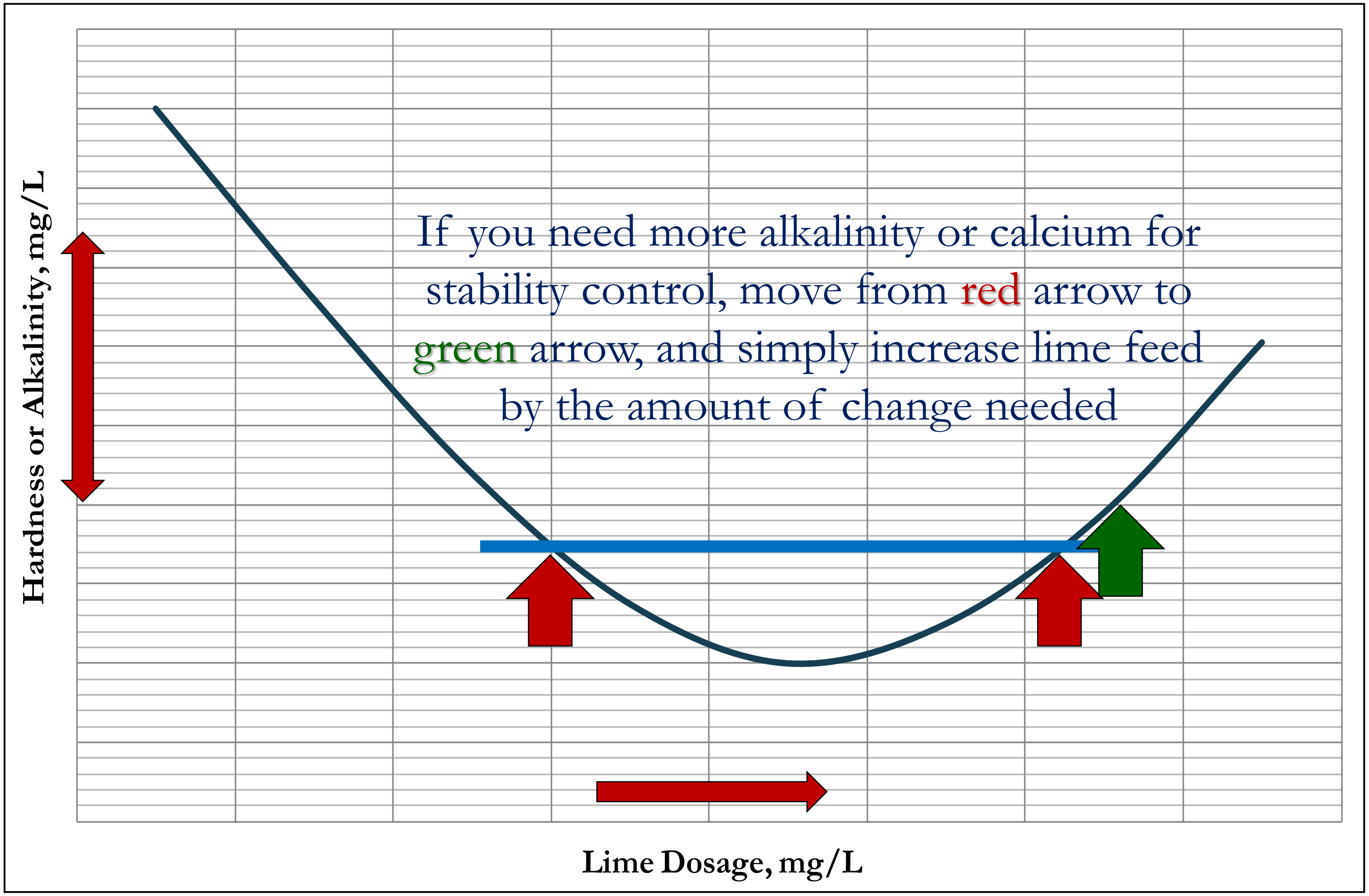
Lime Softening



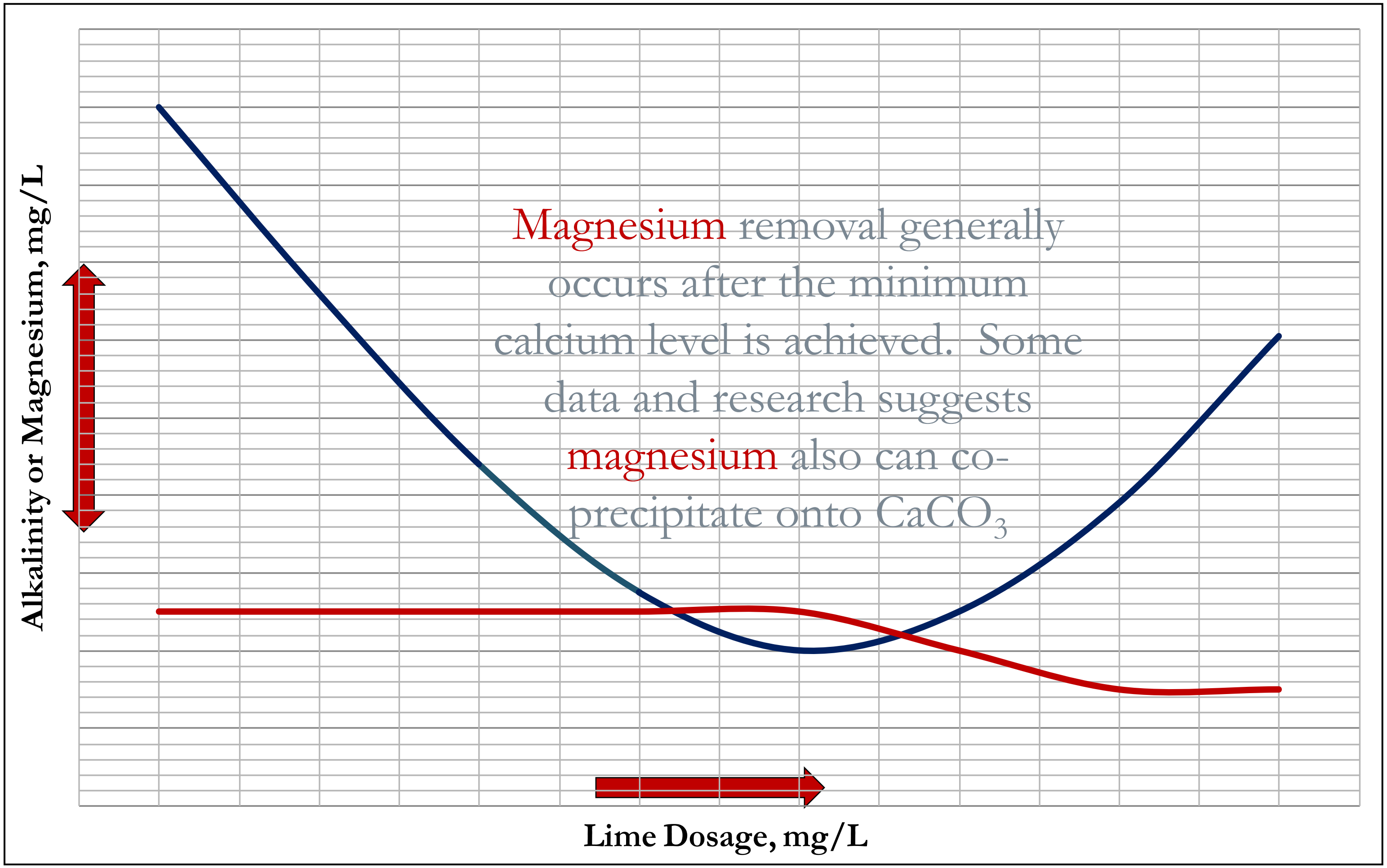
Lime Softening



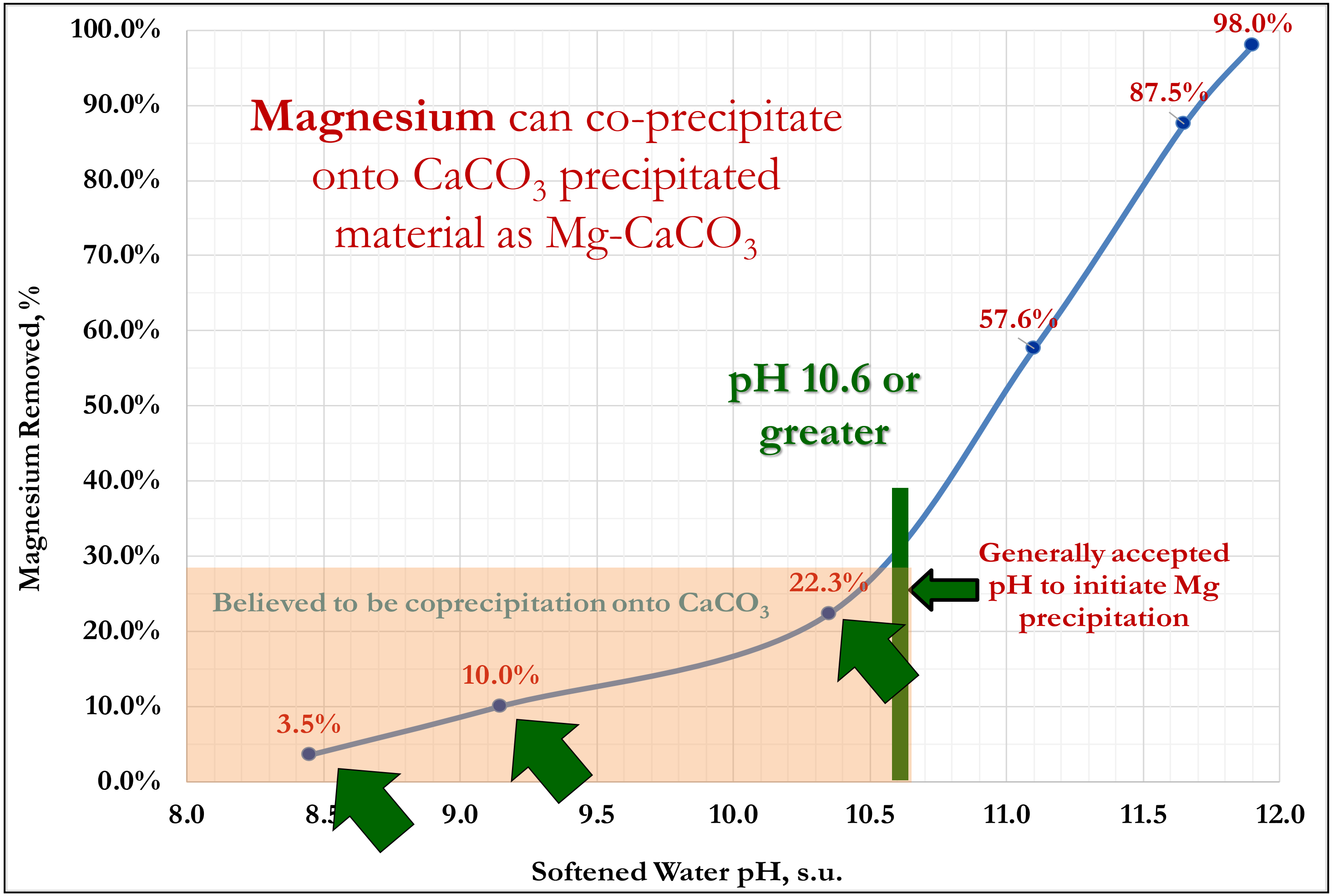
Lime Softening



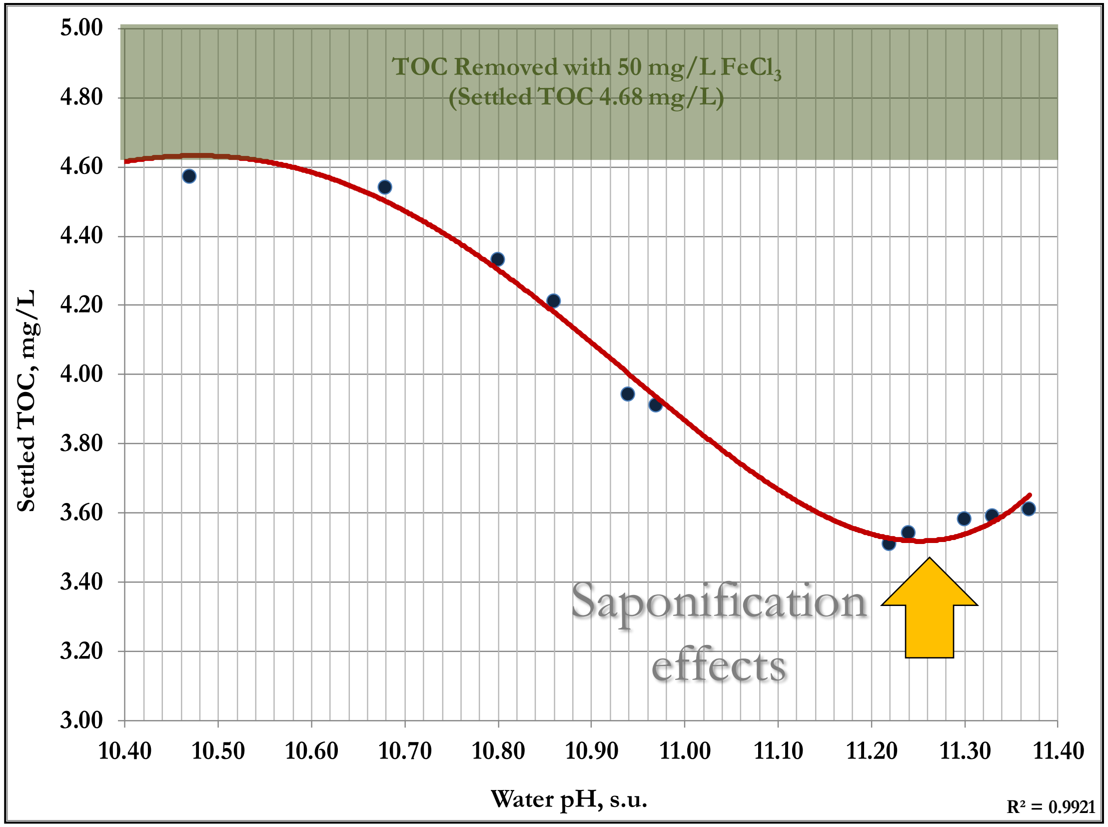
Lime Softening



Lime Softening

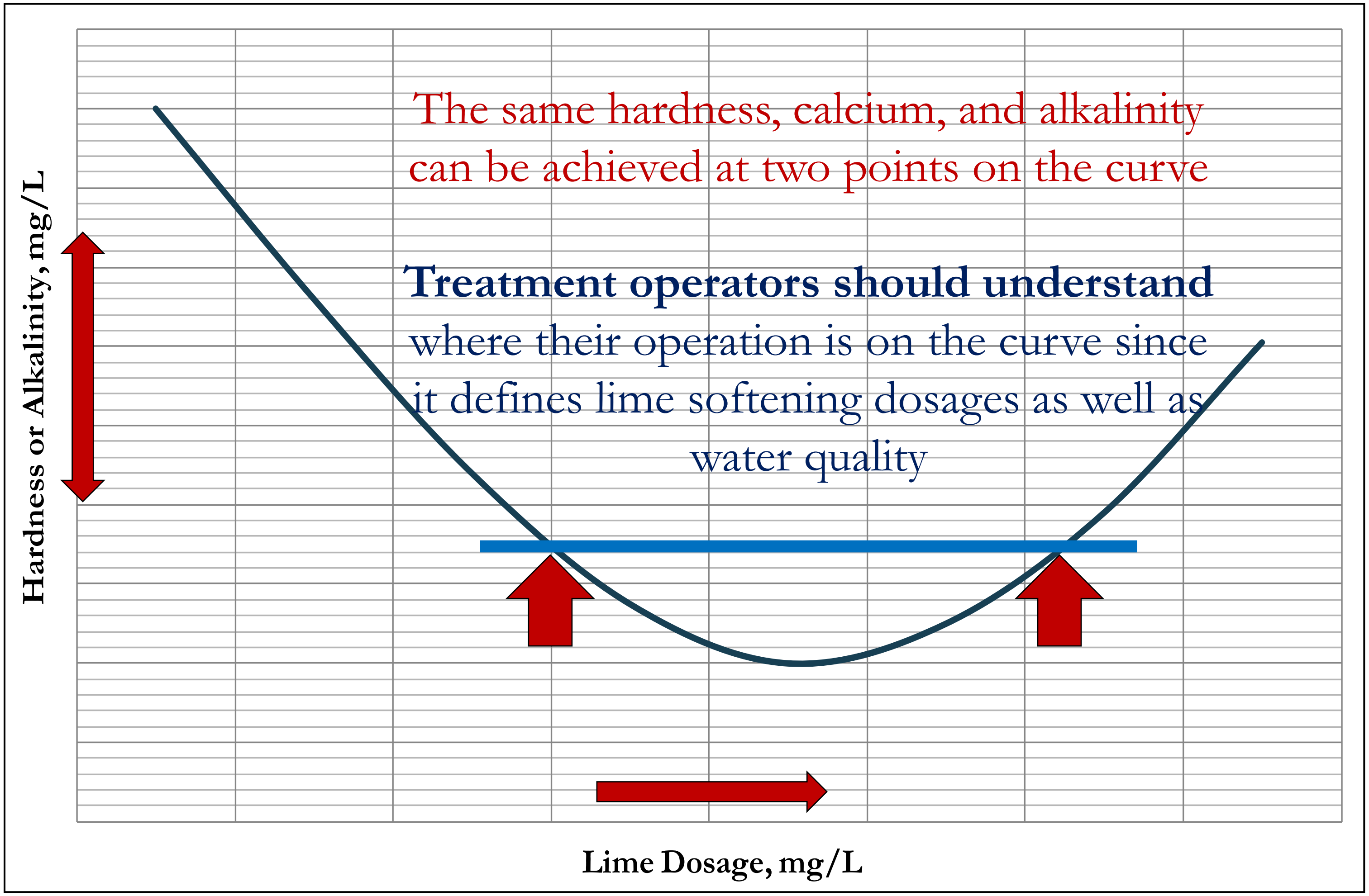


Lime Softening: Avoid high pH

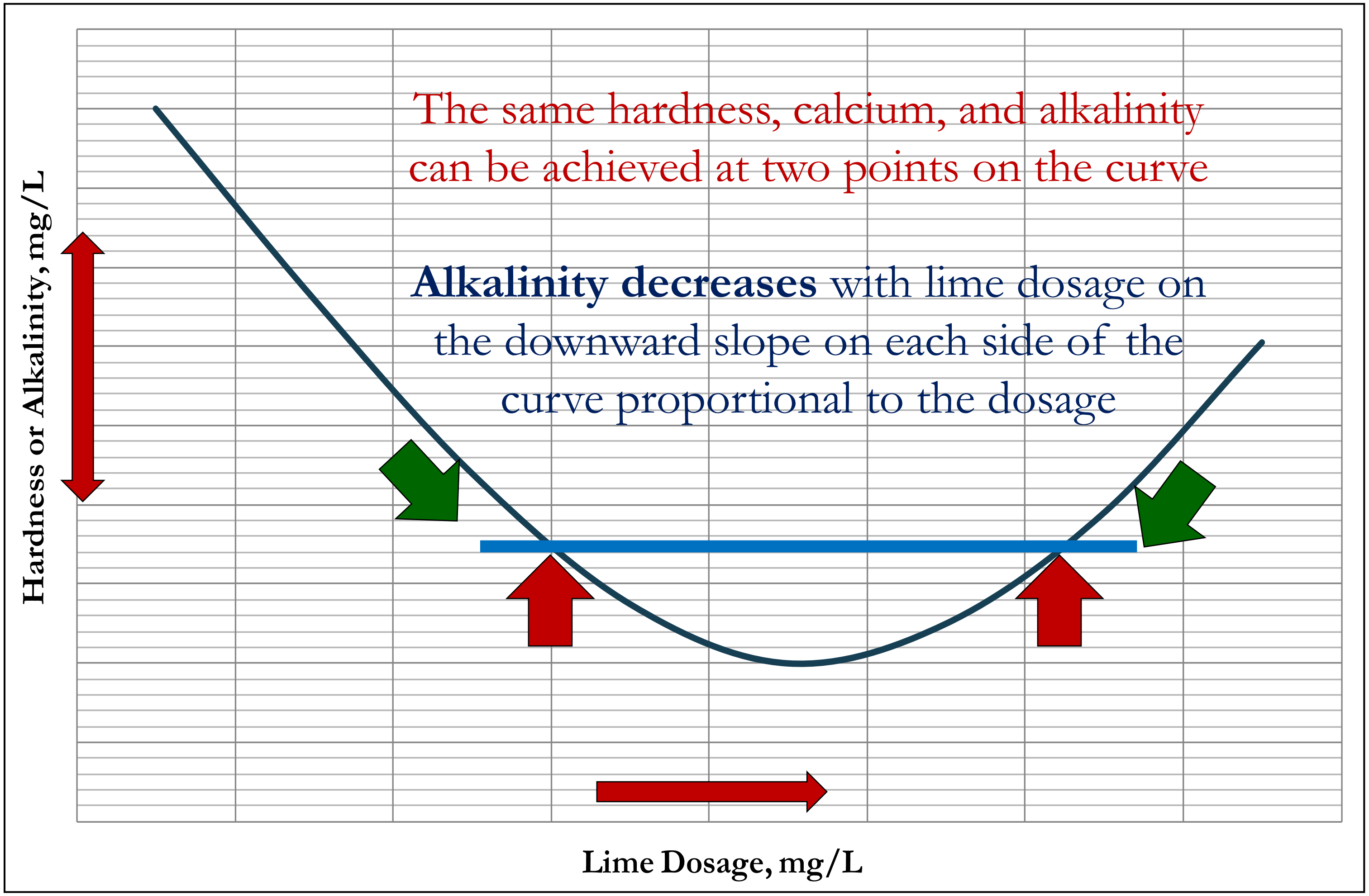


- Avoid high pH conditions in softening treatment
- Creates **saponification of organics** fixing OH onto TOC and inhibits removal under treatment
- Typically occurs at pH levels above 11.2
- **Increases TOC values** beyond the high pH levels due to saponifying impacts of organic matter

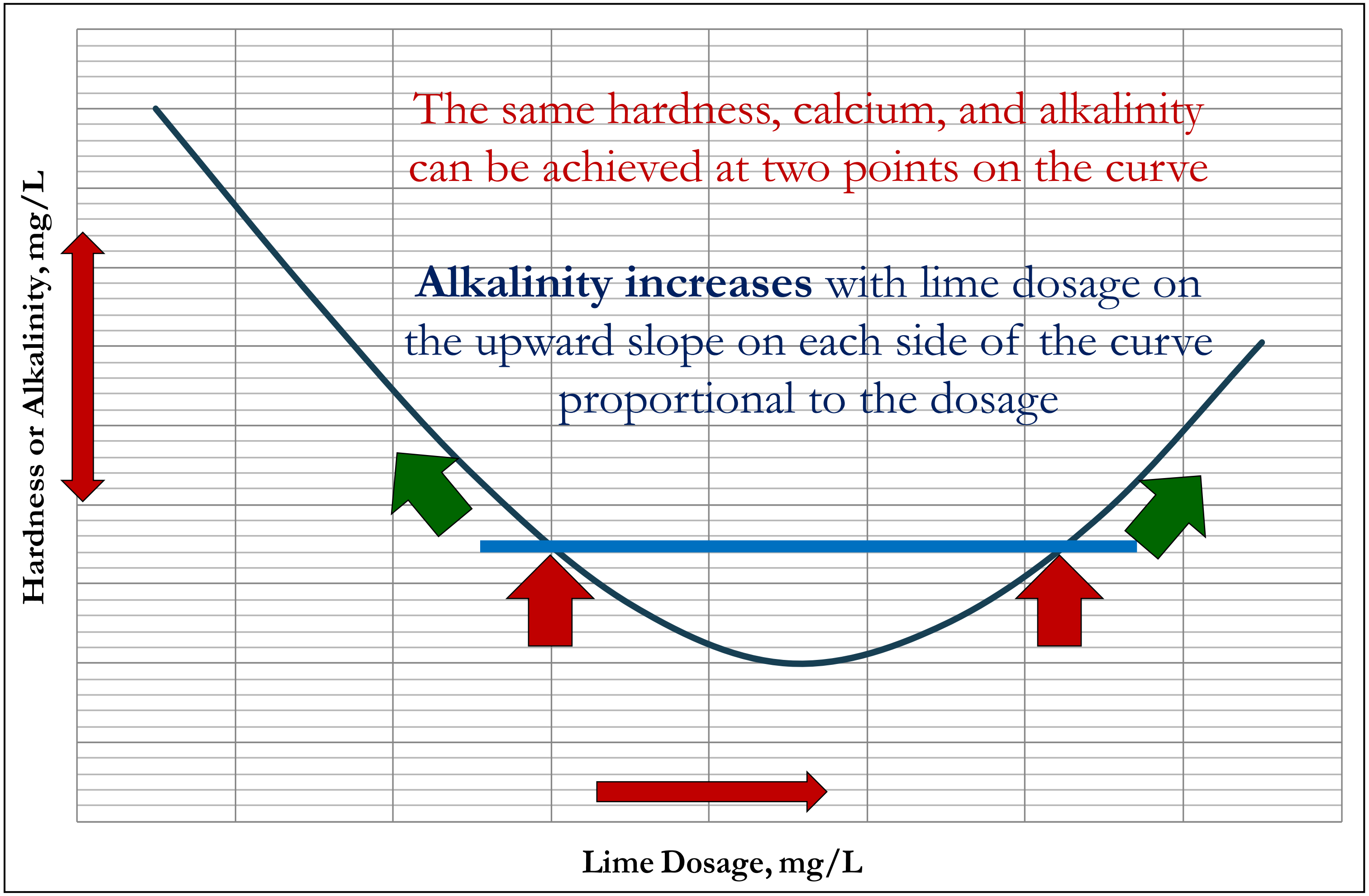
Lime Softening



Lime Softening

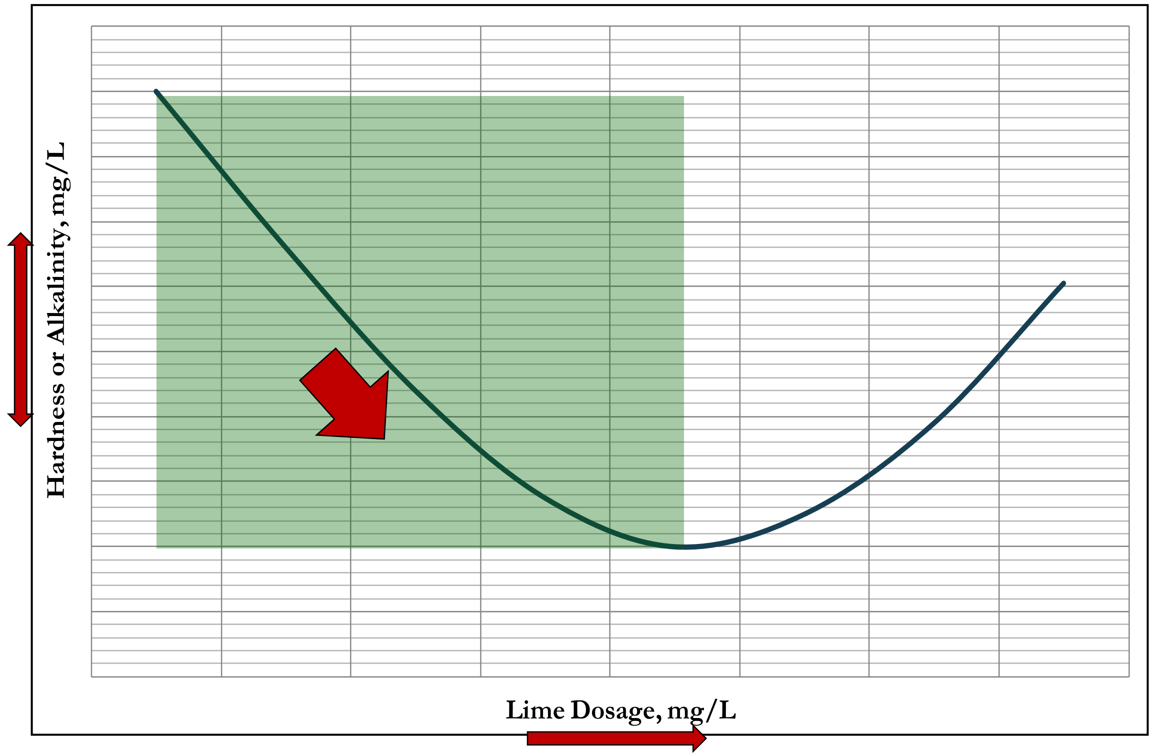


Lime Softening



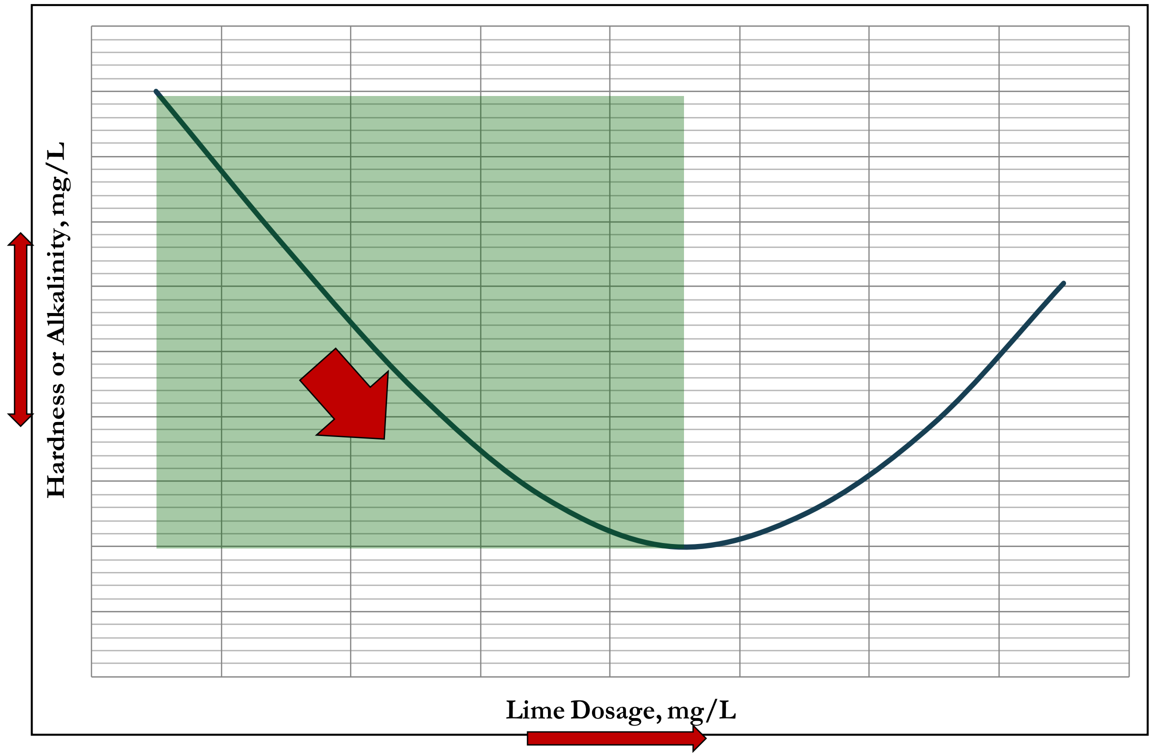
Lime Softening: Best Practices

- **Simple softening** to achieve a desired hardness/alkalinity
- Operate on the downward slope of the curve until hardness or alkalinity level is reached
- Generally, CO_3 alkalinity ranges from **5 mg/L to 35 mg/L** depending on lime ratio (LR explained soon)



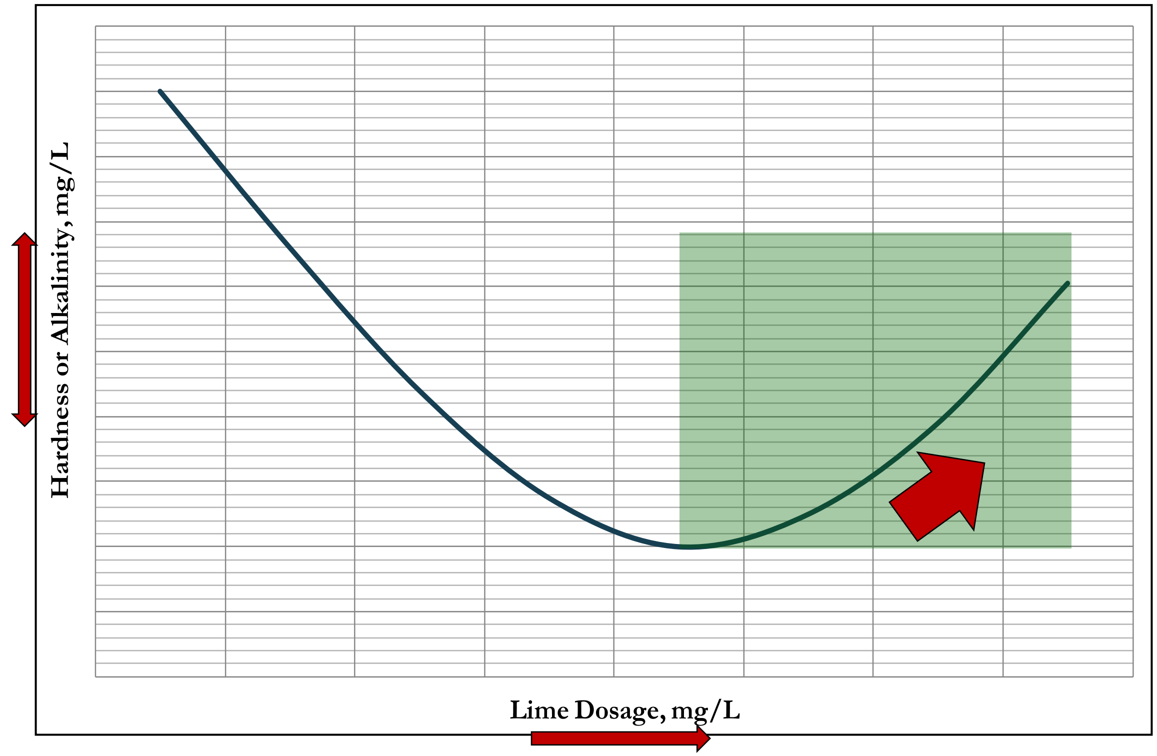
Lime Softening: Best Practices

- TOC removal according to calcium reductions accomplished in the simple lime softening area
    - Calcium precipitation
    - Co-precipitation of magnesium
- Water pH levels typically less than **10.4**



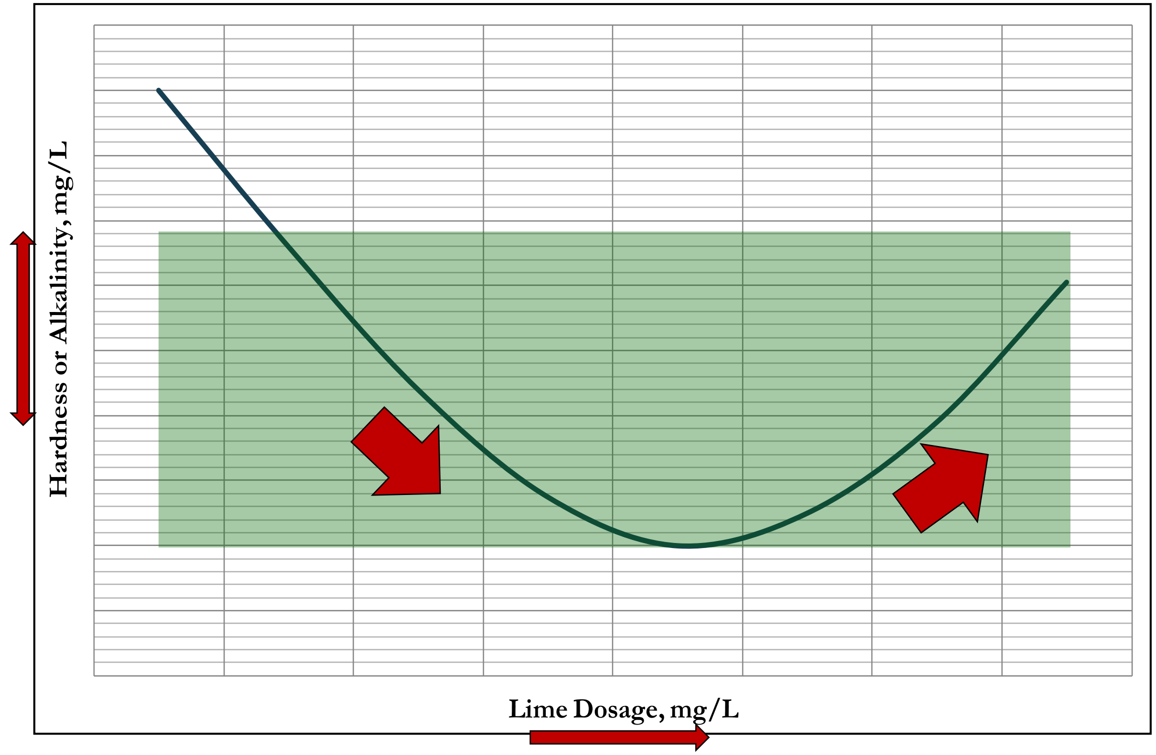
Lime Softening: Best Practices

- **Excess softening** to achieve a desired hardness
- Operate on the upward slope of the curve until alkalinity level is reached
- Generally, OH alkalinity ranges from **5 mg/L to 35 mg/L** depending on lime ratio (LR explained soon)



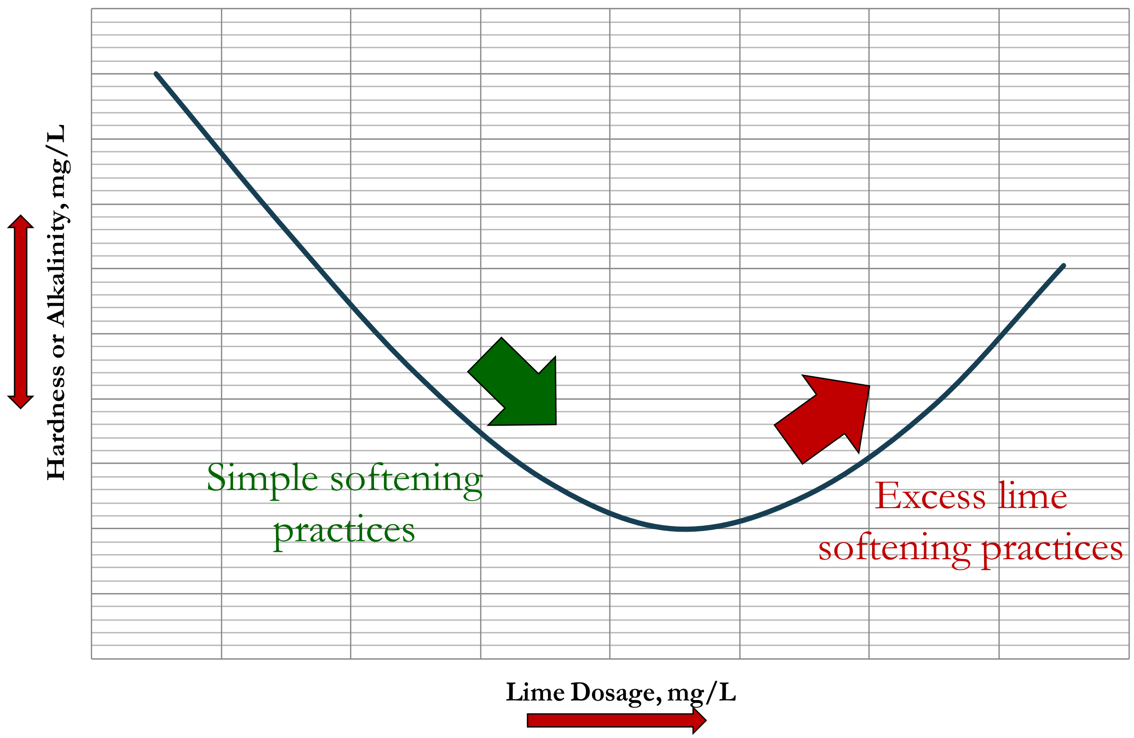
Lime Softening: Best Practices

- TOC removal according to calcium and magnesium reductions accomplished in both simple softening and excess lime softening areas
- Water pH levels typically less than 11.2



Lime Softening: Best Practices

- Lime ratio (LR) concept discussion in next segment, but…
- Most plants operate at a lime ratio of **1.0 to 1.6** for **excess lime softening**
- **Simple softening** practices operate at lime ratios between **0.6 to 0.9** range



"**Lime Softening for Optimized TOC** Removal and Alkalinity Management"

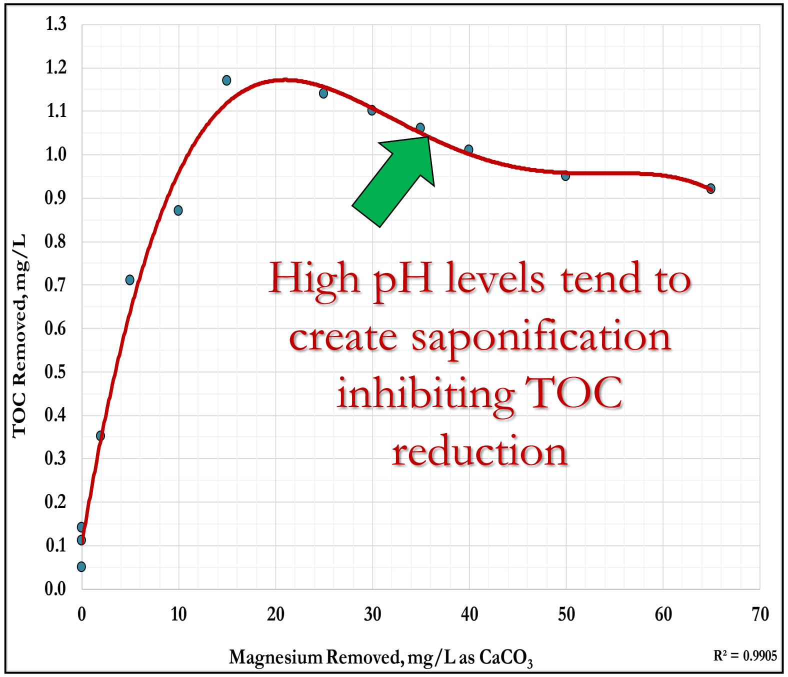
Part 2
Research Data Related to Lime Softening and DOC Removal

Softening Research Related to TOC Removal

- 2002 Disinfectants/Disinfection Byproduct Rule (D/DBPR) introduced enhanced softening as a means of TOC reduction if magnesium was removed during softening – part of TOC removal matrix

- $Mg(OH)_2$ believed to be adsorptive for TOC – up to ≈2 mg/L observed in studies

- Several studies confirmed $Mg(OH)_2$ helps remove TOC



Softening Research Related to TOC Removal

Subject was described in **AWWA Journal Article 2006** – research specific to TOC treatment and DBPs using only lime softening

Enhanced softening: Effects of source water quality on NOM removal and DBP formation

BY KATHRYN N. KALSCHEUR, CAROLINE E. GERWE, JIHYANG KWEON, GERALD E. SPEITEL JR., AND DESMOND F. LAWLER

Softening is the removal of hardness from drinking water sources by precipitating calcium (and in some cases, magnesium) and is practiced by many facilities in the central United States and Florida. Since the discovery of disinfection by-products (DBPs) in the early 1970s, researchers have investigated the potential for softening to be "enhanced" for removal of natural organic matter (NOM) by coprecipitation with or adsorption onto the calcium and magnesium precipitates. NOM removal in softening has been demonstrated at bench scale (Thompson et al, 1997; Shorney & Randtke, 1994; Qasim et al, 1992; Liao & Randtke, 1985), pilot scale (Clark et al, 1994), and field scale (Wilson, 1960).

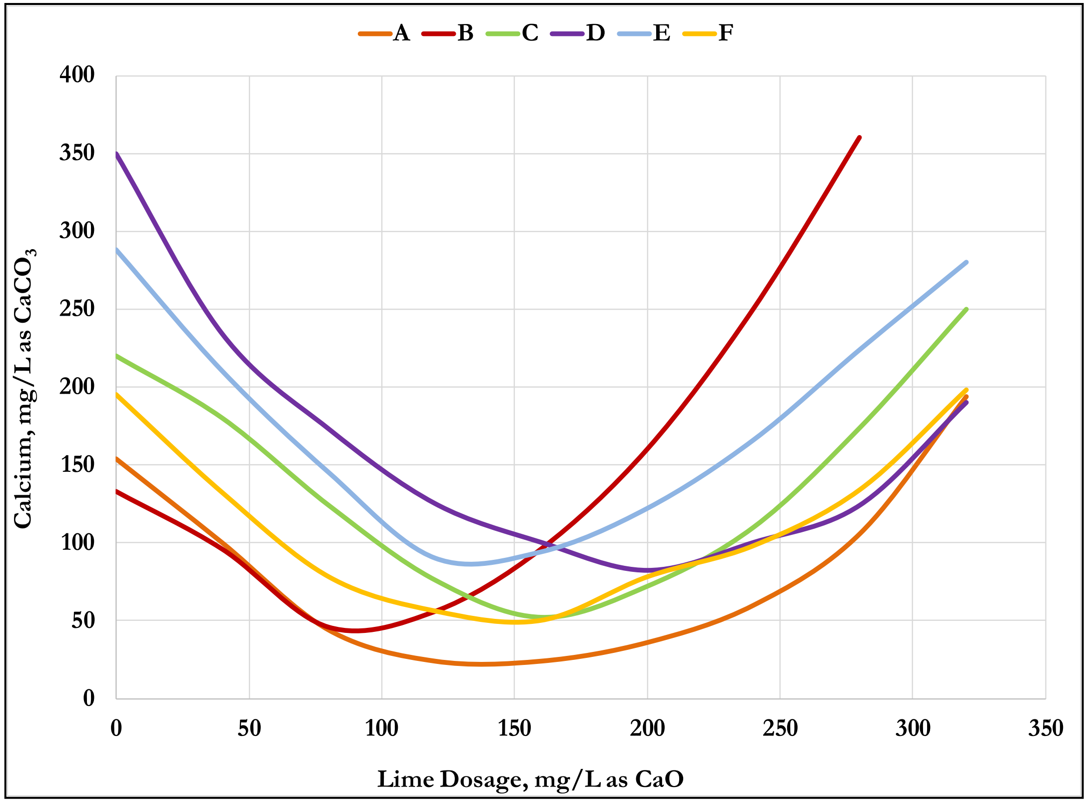
An earlier study (Roalson et al, 2003) reported the effect of different softening conditions on NOM removal and subsequent DBP formation on a single natural water—Lake Austin, the water supply source for Austin, Texas. The specific objective of the research described here was to extend that earlier study by performing similar experiments on several source waters from a wide geographic area to determine general guidelines for softening plants seeking to enhance NOM removal.

Softening plants are required by the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR) to remove NOM, measured as total organic carbon (TOC) (USEPA, 1998). The requirements are the same as for nonsoftening plants with alkalinity >120 mg/L as calcium carbonate ($CaCO_3$). Minimum TOC removals of 15, 25, and 30% are required for plants with raw water TOC values in the ranges of 2–4, 4–8, and >8 mg/L, respectively. As with nonsoftening plants, exceptions to these requirements are made if the raw

KALSCHEUR ET AL | 98:11 • JOURNAL AWWA | PEER-REVIEWED | NOVEMBER 2006 93

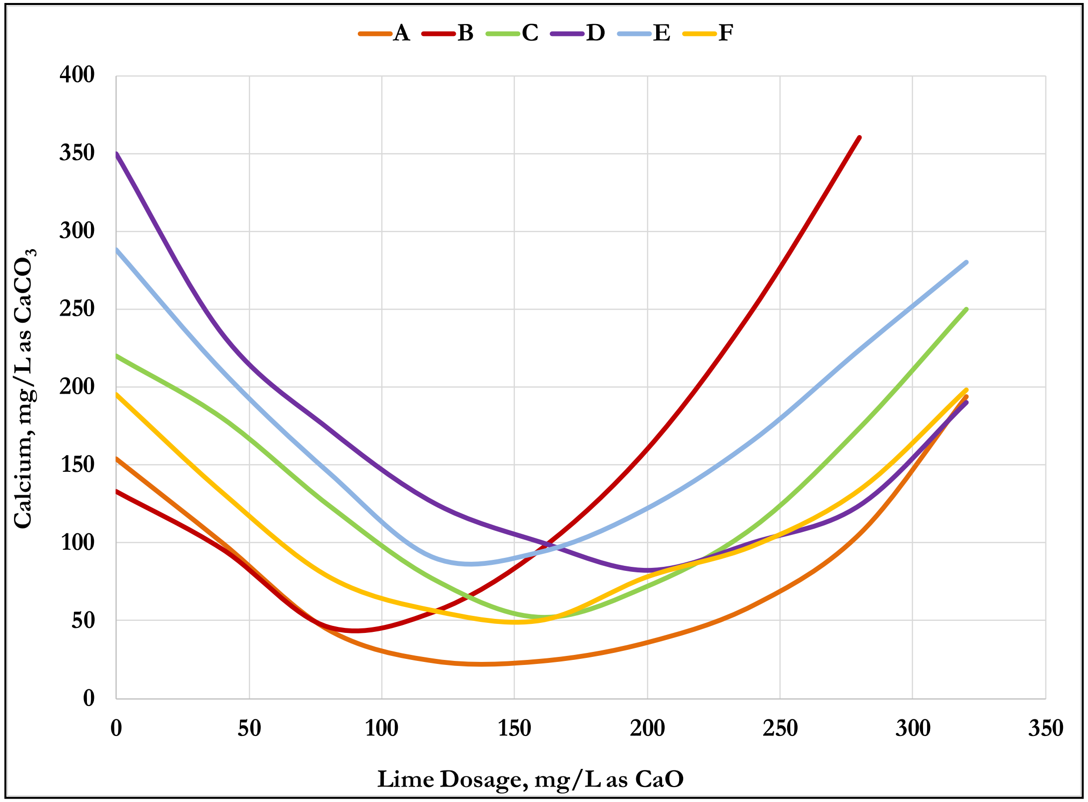
Lime Softening for TOC Removal

- Several treatment plants evaluated using jar tests for lime softening
- Bottom of each curve is minimum calcium level from softening
- Beyond the minimum calcium point, calcium increases proportional to lime dose



Lime Softening for TOC Removal

- Data is poorly aligned since each source takes differing lime dosage to minimize calcium levels
- Lime ratio concept is now introduced to align data between treatment plants



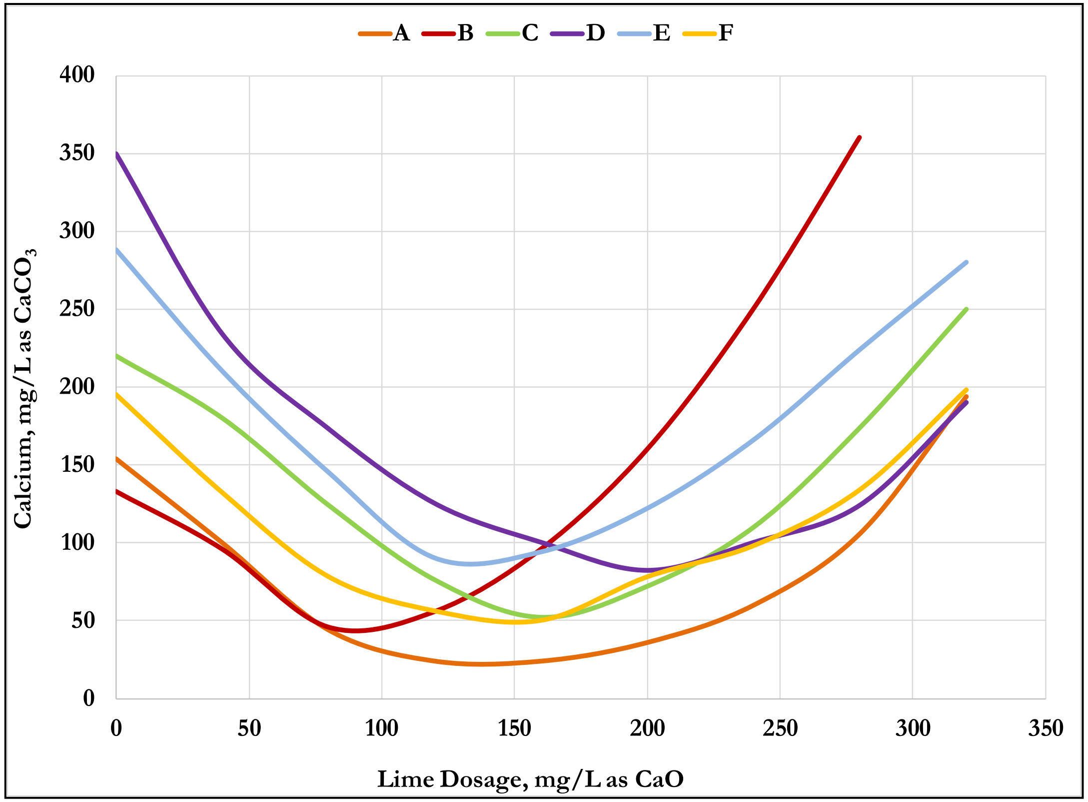
Lime Softening for TOC Removal

- **Lime ratio (LR)** = actual lime dose divided by lime dose required to minimize calcium

- $$\frac{actual\ lime\ dose}{required\ lime\ dose} = LR$$

- Use of lime ratio LR consistently aligns data for each plant in the same area

- **LR 1.0 = LR 1.0**



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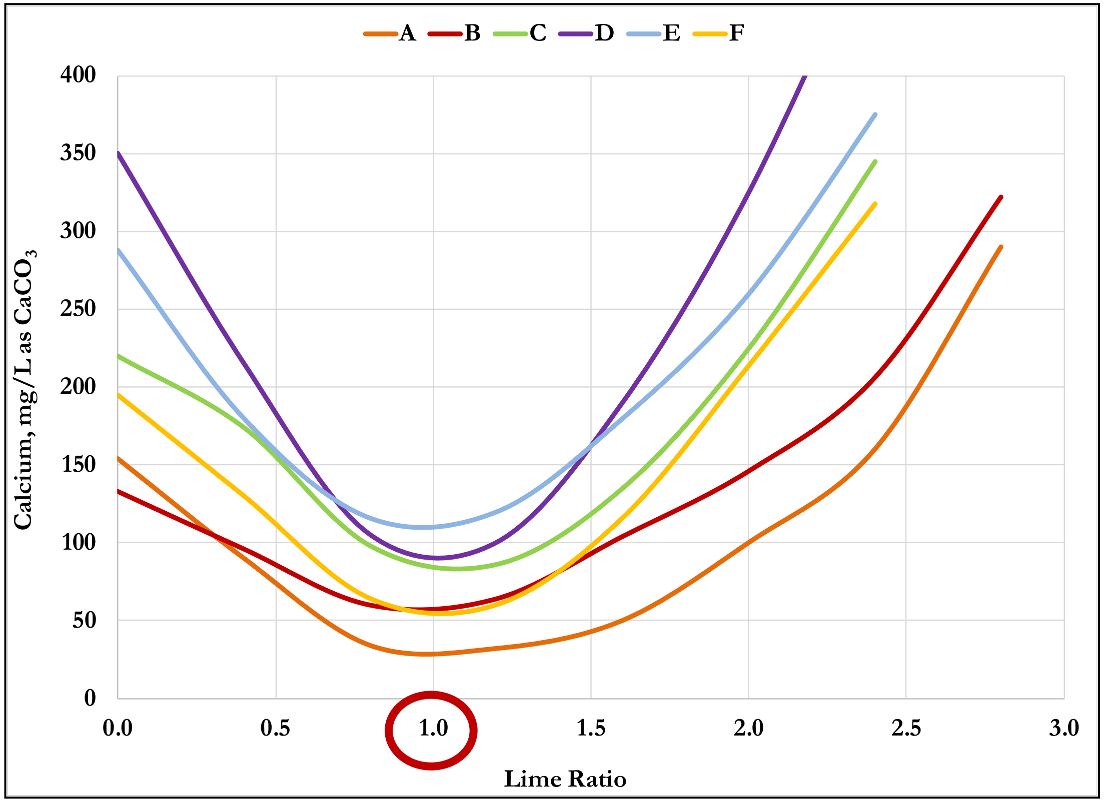
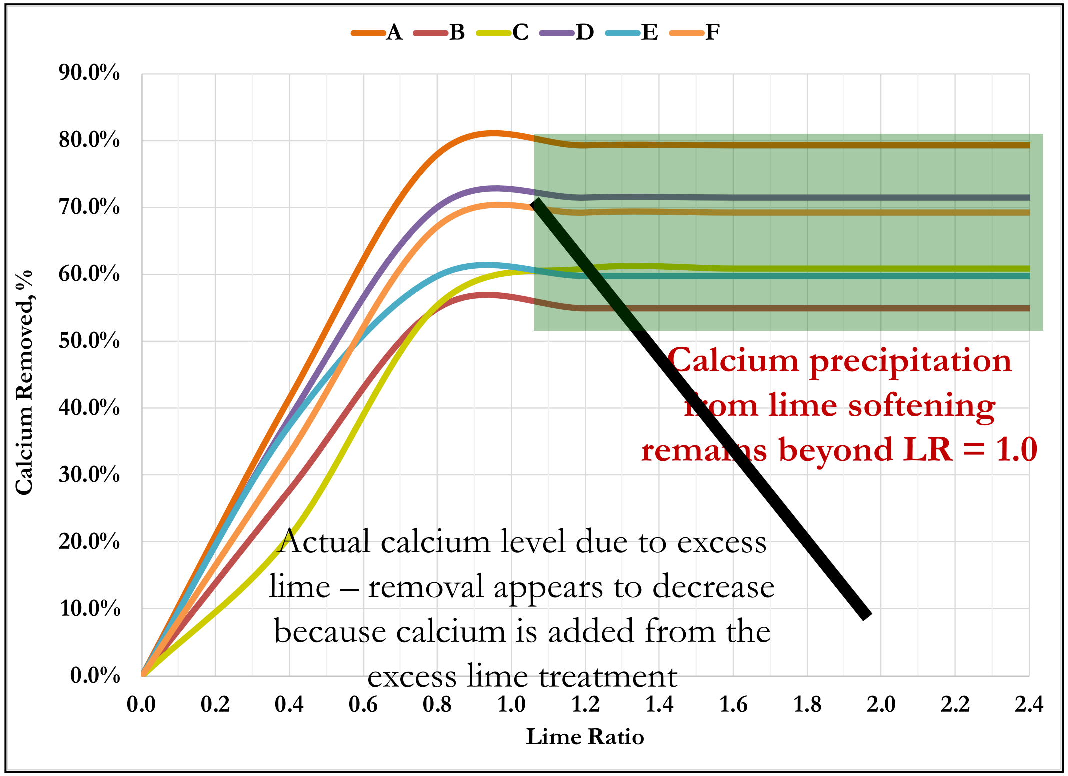


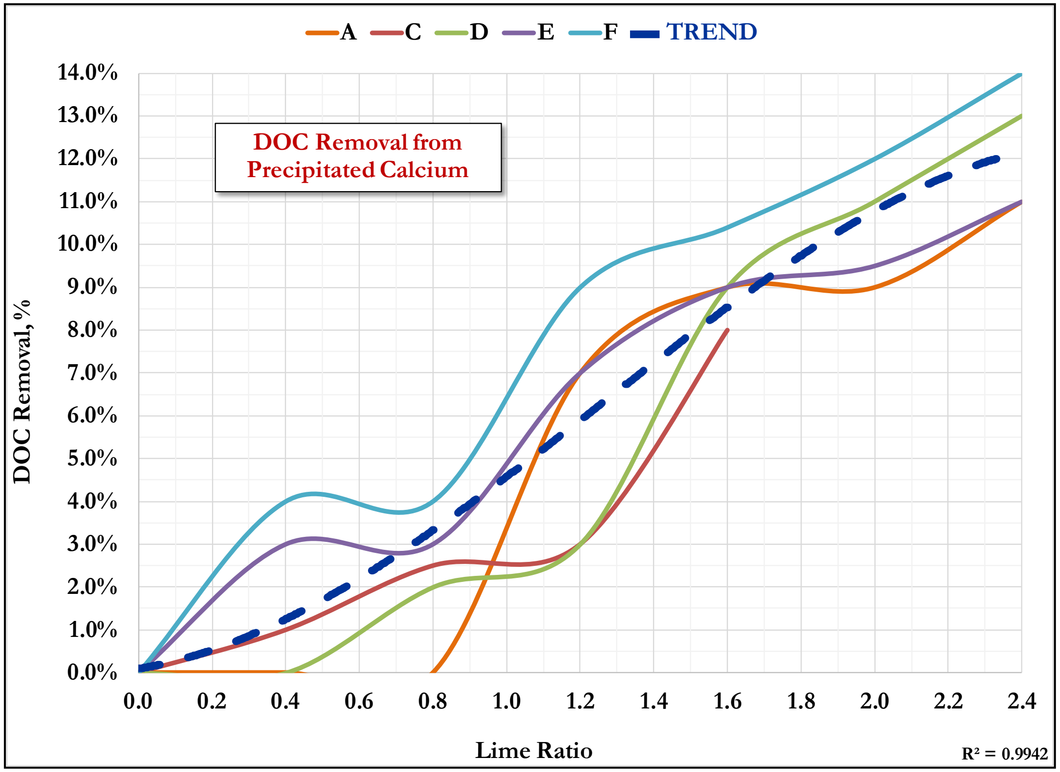
Lime Softening for TOC Removal

- Important to understand that **calcium still precipitates** once excess lime softening is achieved (LR >1.0)
- Calcium concentration increases on the upward slope of the demand curve due to excess $Ca(OH)_2$, but <u>precipitation of calcium remains constant</u> and still results in $CaCO_3$ sludge

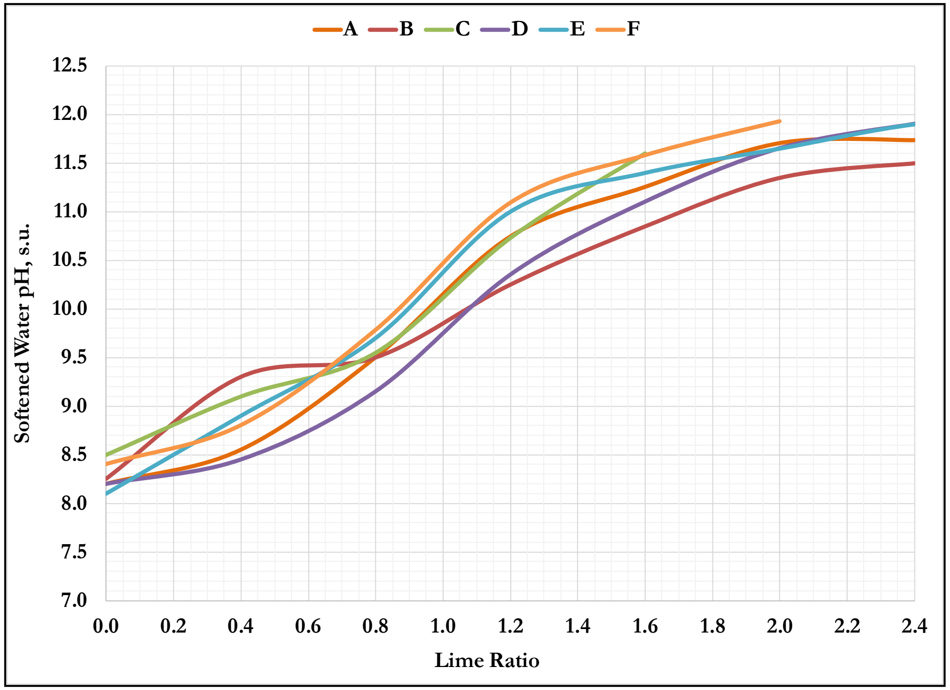


Lime Softening for TOC Removal

- **Calcium removal increases proportional to lime dose** until all carbonate calcium is consumed (noncarbonate remains)
- Calcium precipitation adsorbs some TOC
- Adsorption affinity is not very high – **3% to about 12%**
- **Some co-precipitation of magnesium** may occur until Mg precipitation pH (≈10.6) is reached



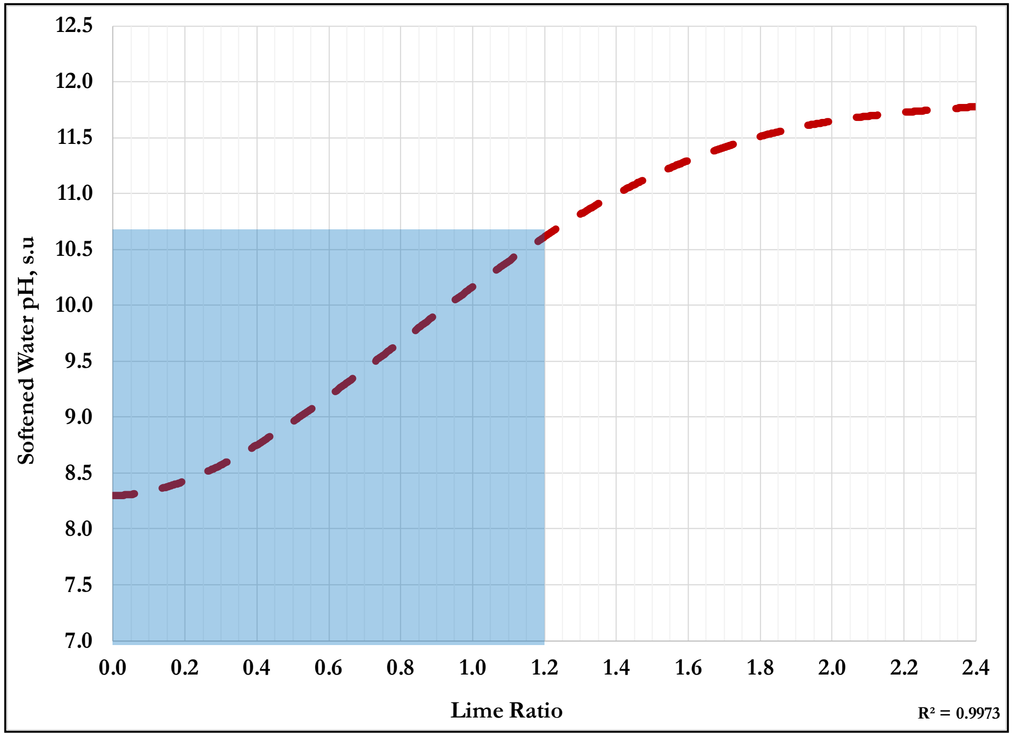
Lime Softening for TOC Removal



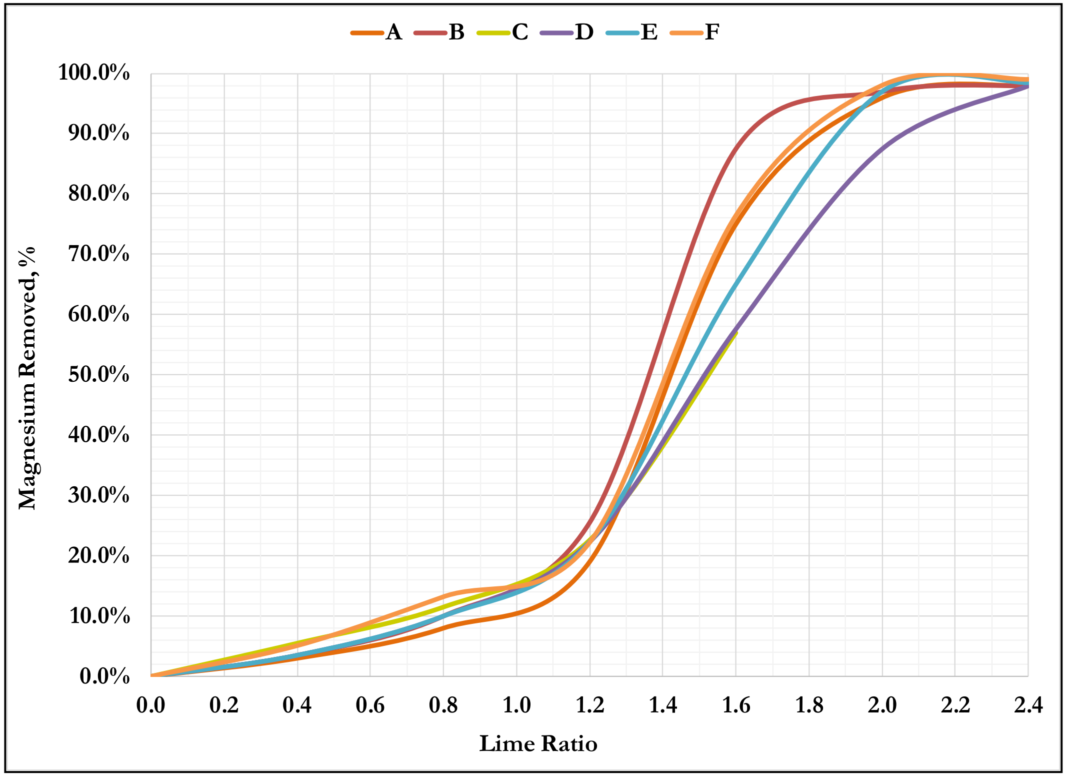
- Lime ratio (LR) consistently results in elevated softened water pH levels
- Some variations between treatment plants but similar shape and magnitude – clustered data trends together
- Follows expected assumptions as lime dose increases, water pH increases proportionally

Lime Softening for TOC Removal

- Water pH trendline from research data shows increasing pH is consistent among treatment plants
- Knowing LR, one can predict softened water pH level
- Useful for fact-checking lime dosages versus actual pH

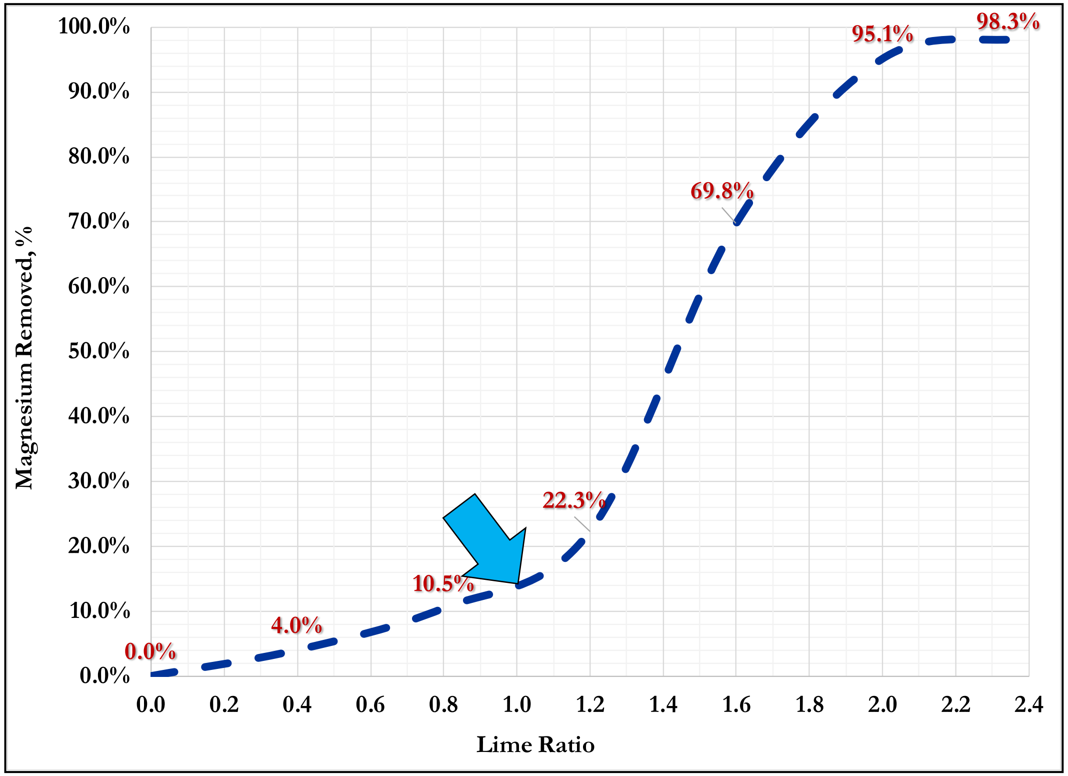


Lime Softening for TOC Removal



- **Magnesium removal** is proportional to lime dose like calcium removal
  - **Some Mg-$CaCO_3$ co-precipitation can occur before LR = 1.0**
- $Mg(OH)_2$ precipitation increases dramatically after achieving LR = 1.0
- $Mg(OH)_2$ important for adsorption of TOC

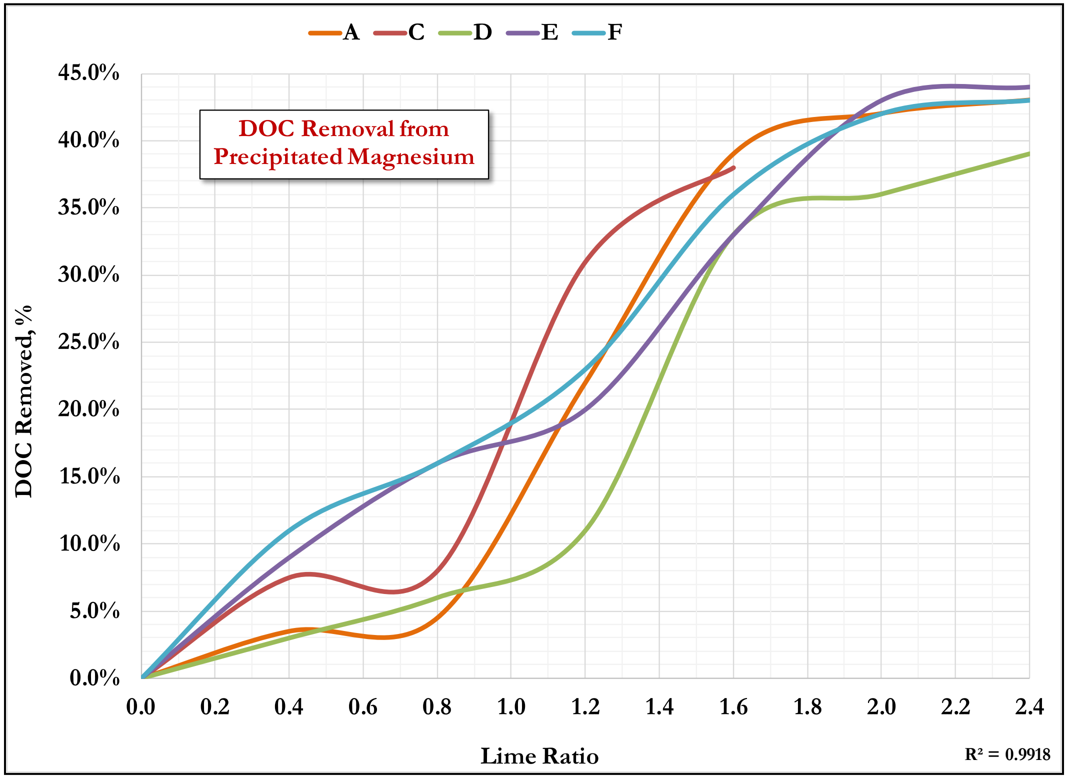
Lime Softening for TOC Removal



- **$Mg(OH)_2$ precipitation increases dramatically after LR = 1.0**
- Some magnesium will always remain due to solubility of $Mg(OH)_2$ in water
- $Mg(OH)_2$ presence during softening **increases probability of TOC reduction**

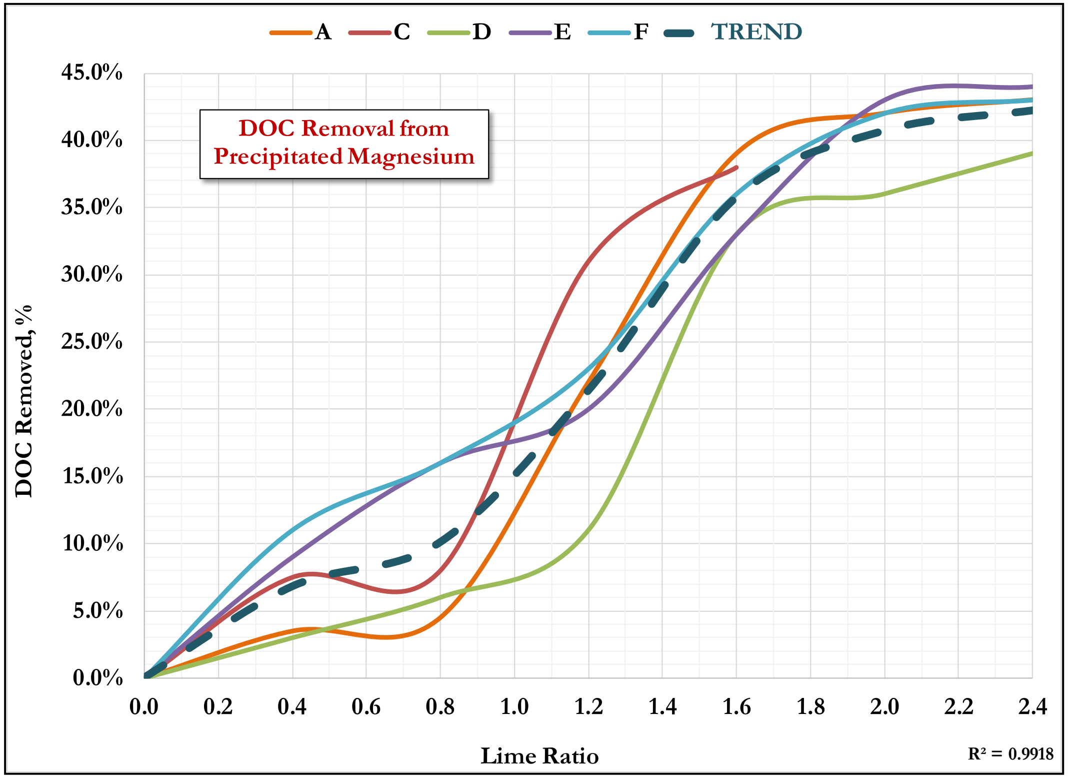
Lime Softening for TOC Removal

- Magnesium removal increases proportional to lime dose once all carbonate calcium is consumed
- Magnesium precipitation adsorbs some TOC
- Adsorption affinity is much higher than calcium – **up to about 44%**
- TOC adsorption is proportional to Mg reduction



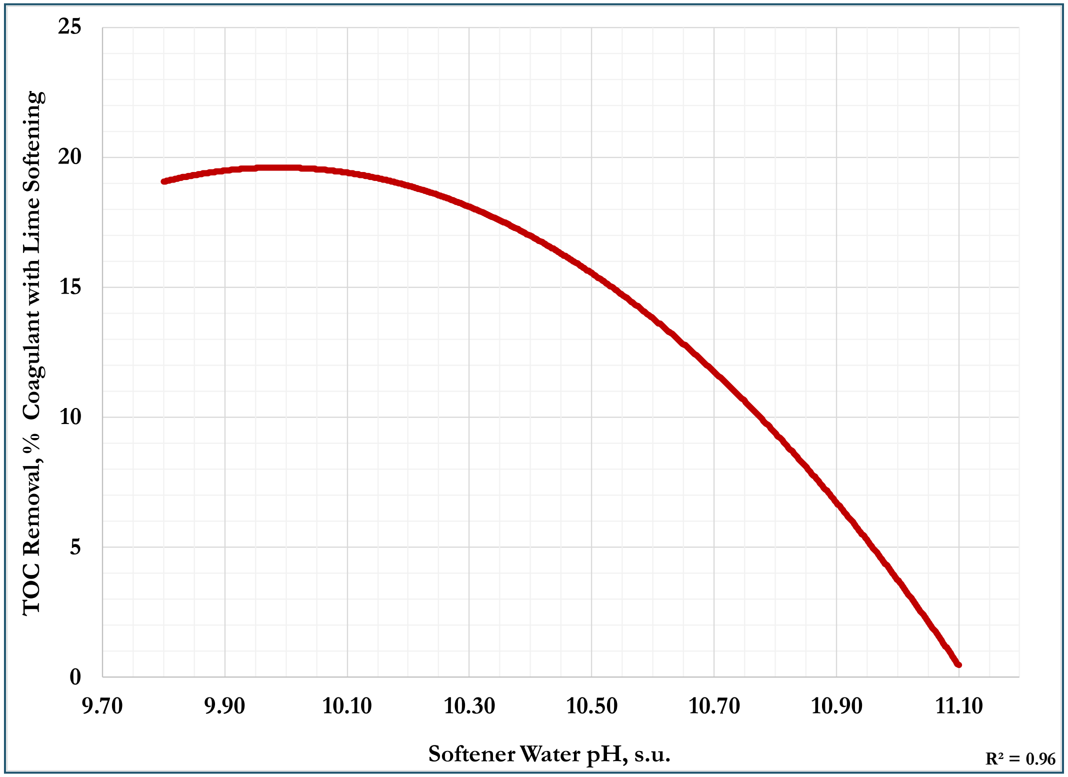
Lime Softening for TOC Removal

- TOC removal increases proportional to lime dose and magnesium removal
  - TOC reduction ceases once minimum magnesium level is achieved
- Trendline suggests possible TOC reductions
- Useful for TOC removal predictions



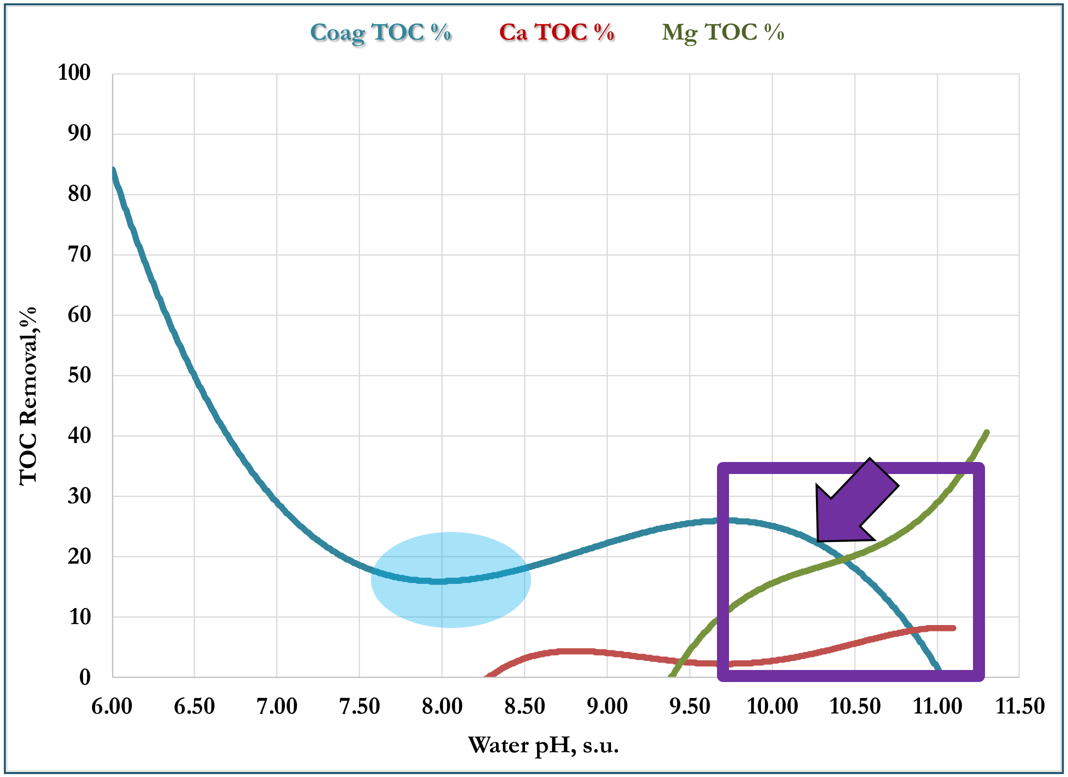
Lime Softening for TOC Removal

- Impacts from coagulant addition during softening
- Higher pH values **negate** coagulant reactions for TOC removal (TOC reduction falls to zero at pH's above 11.0)
- Coagulant reduction of TOC varies then with reduced pH levels
- Can predict TOC from coagulant addition, calcium removal, and magnesium removal

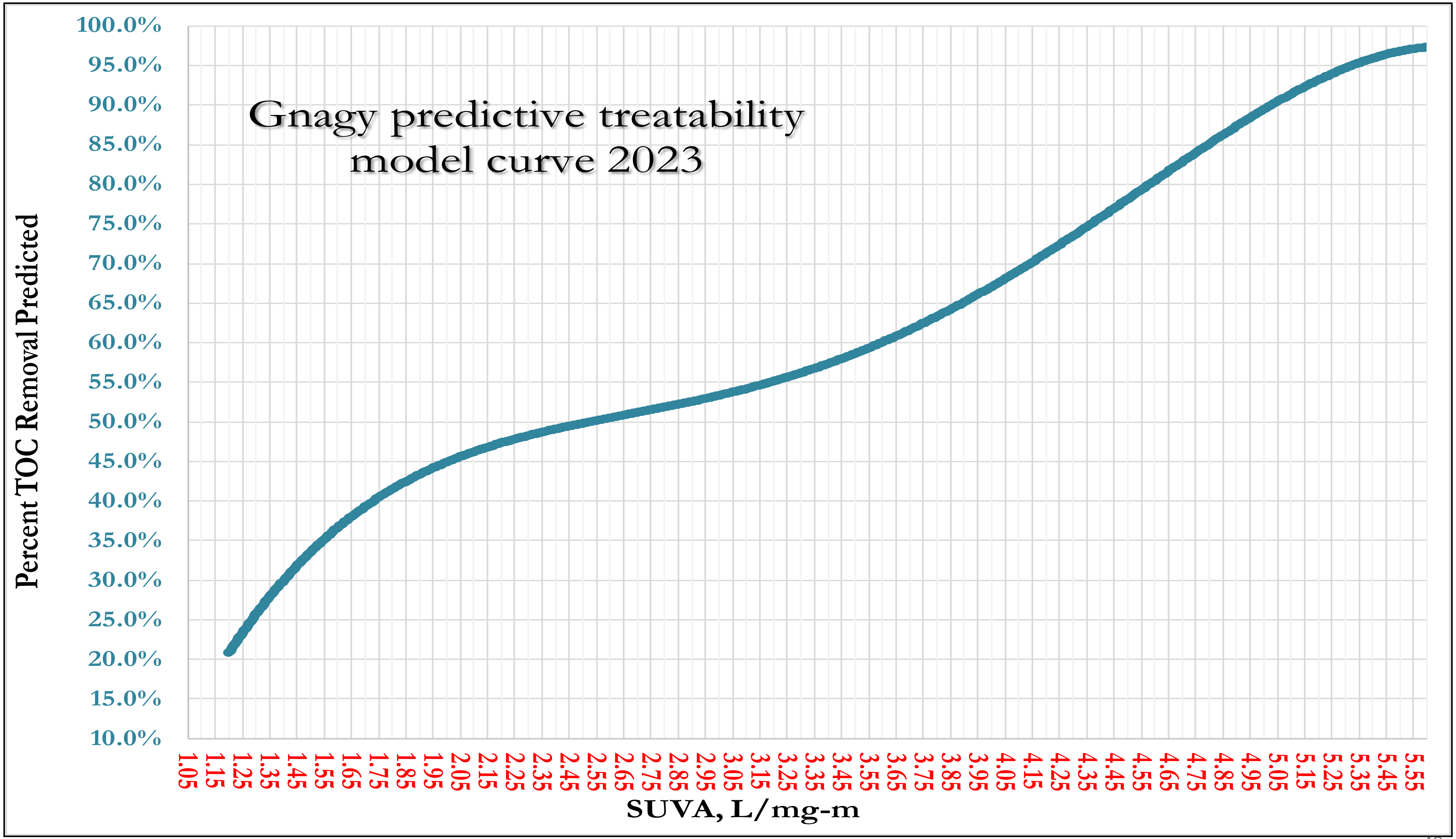


Lime Softening for TOC Removal

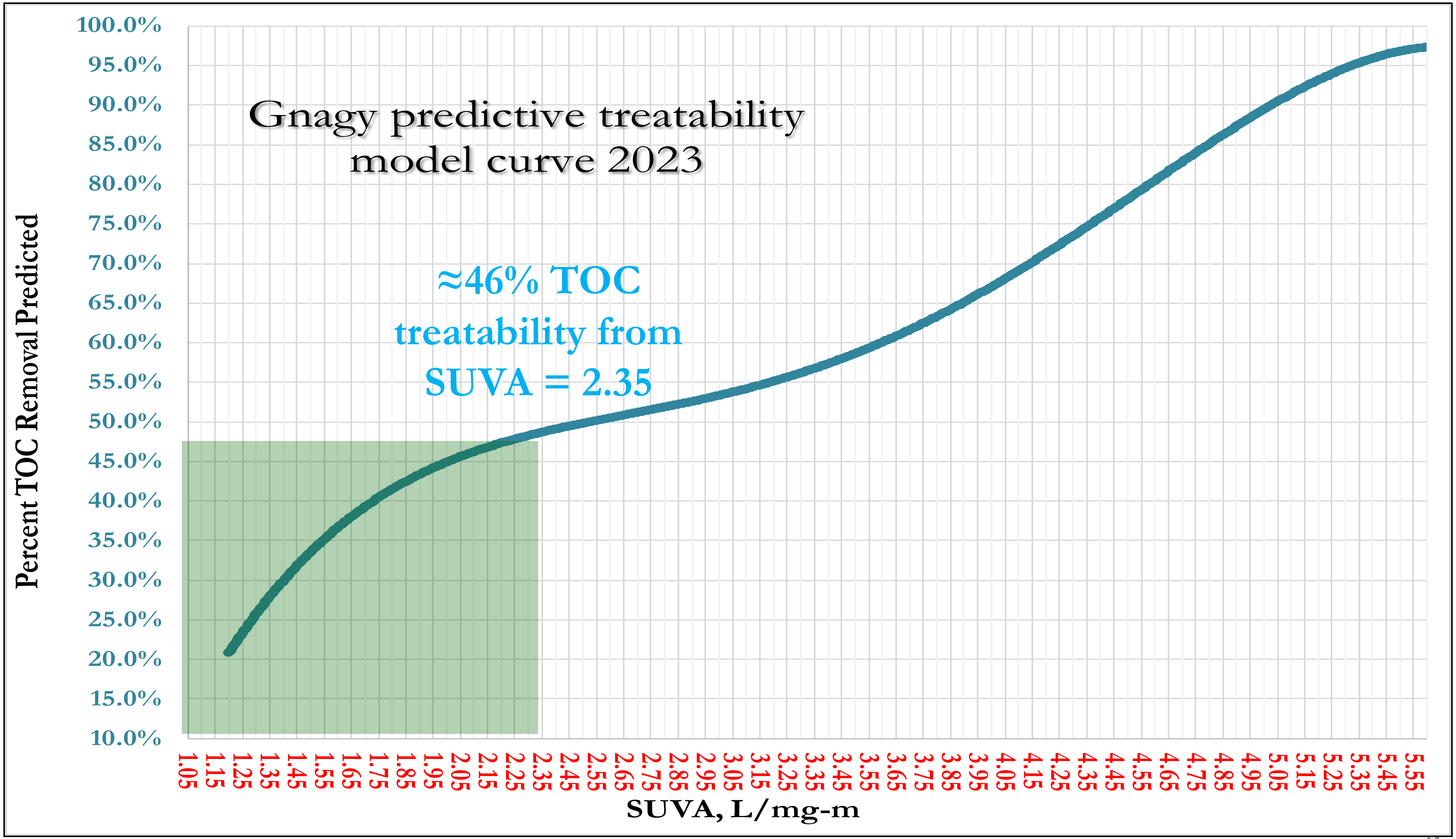
- Impacts from coagulant addition during softening and coagulant addition alone
- Coagulant/TOC reduction varies with water pH levels
- Minimized TOC removal at pH 7.8 to 8.3 believed to be from lower solubility effects of metal hydroxides $M^{+}(OH^{-})_3$



Predicting TOC Treatability



Predicting TOC Treatability



“Lime Softening for Optimized TOC Removal and Alkalinity Management”

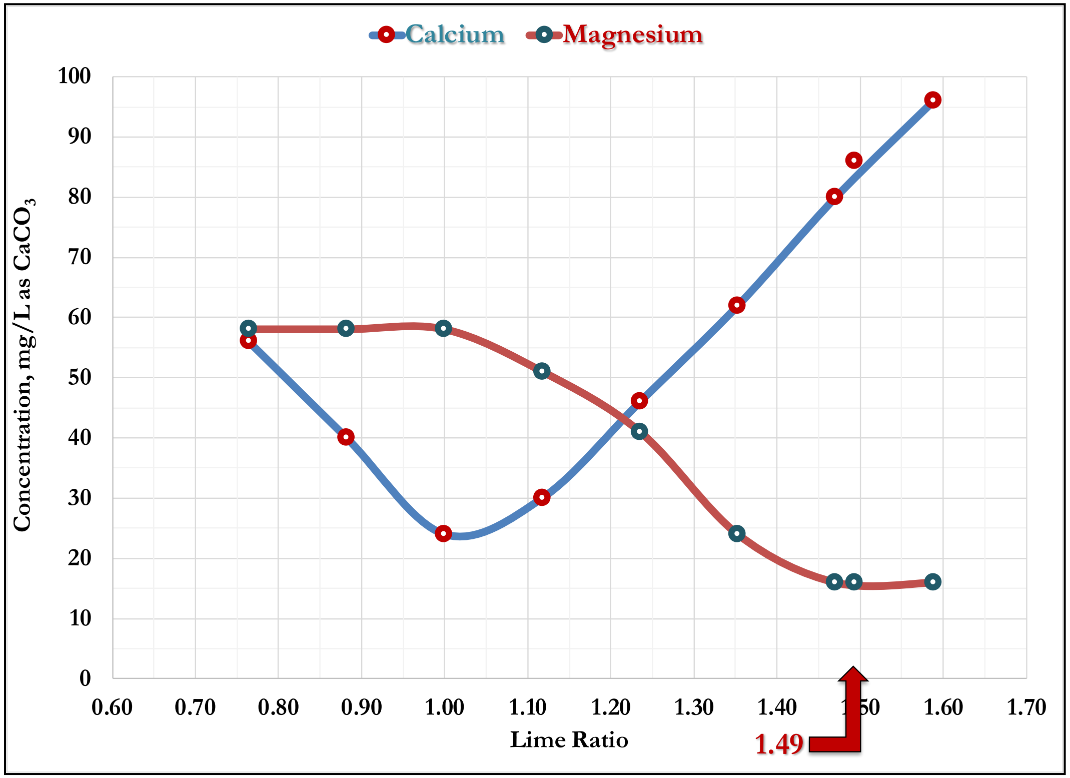
Part 3
Case Studies

Galion, Ohio Case Study

- Reservoir source with moderate TOC and hardness
- $KMnO_4$, PAC (carbon), ferric chloride (pretreatment), ferric and lime to softening treatment
- Two-stage coagulation for TOC removal, split 80/20 between basins, lime softening in Basin 2, NaOH for alkalinity adjustment
- Filtration followed by chlorine disinfection, fluoride, blended phosphate

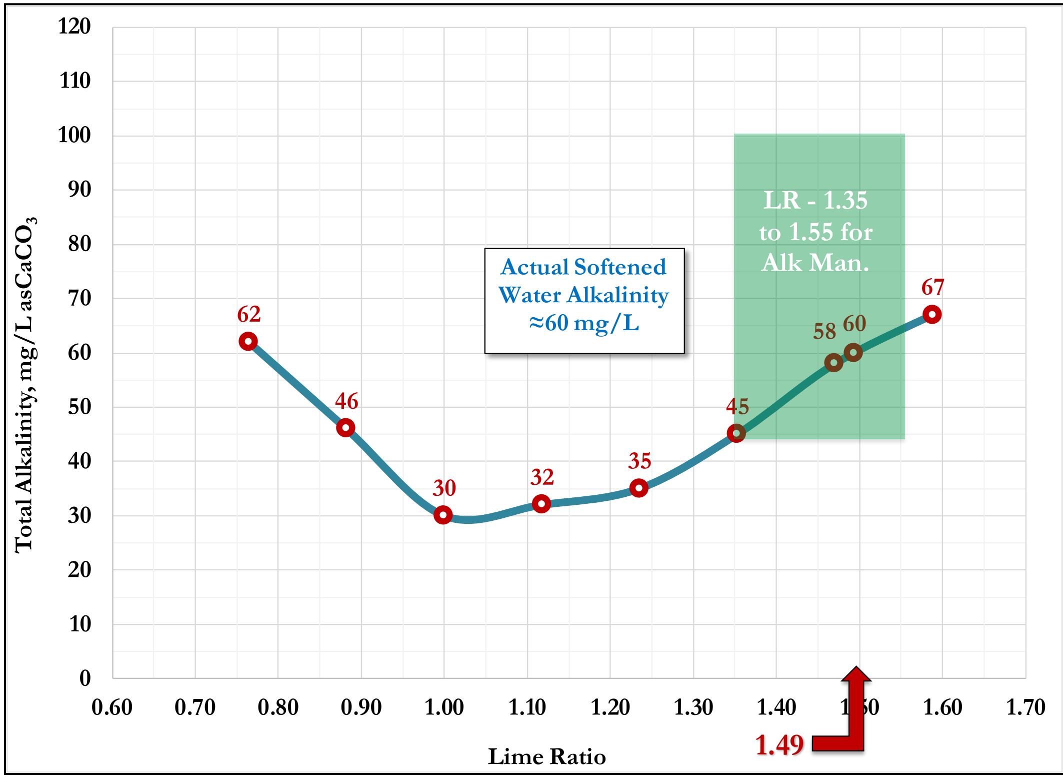
Galion, Ohio Case Study

- Excess lime softening for calcium and magnesium removal to obtain desired alkalinity
- Treatment curve suggests softening to minimum Ca^{+2} then adding hardness and alkalinity back for WQ management
- Lime ratio typically averages 1.49
- Softened hardness averages 98 mg/L

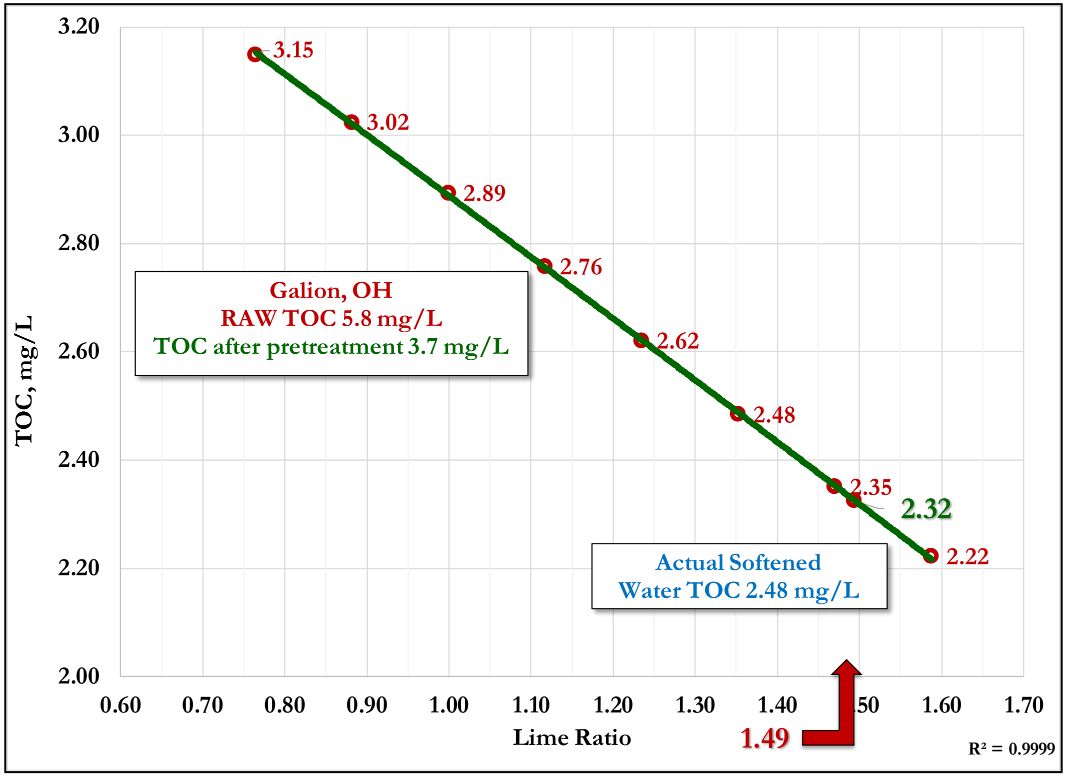


Galion, Ohio Case Study

- Alkalinity managed by excess lime softening and controlling lime ratios in treatment
- Lime ratio range 1.35 to 1.55 for alkalinity management and corrosion control needs
- Maintain softened alkalinity average about 60 mg/L as $CaCO_3$
- Softened water pH levels average 11.04



Galion, Ohio Case Study



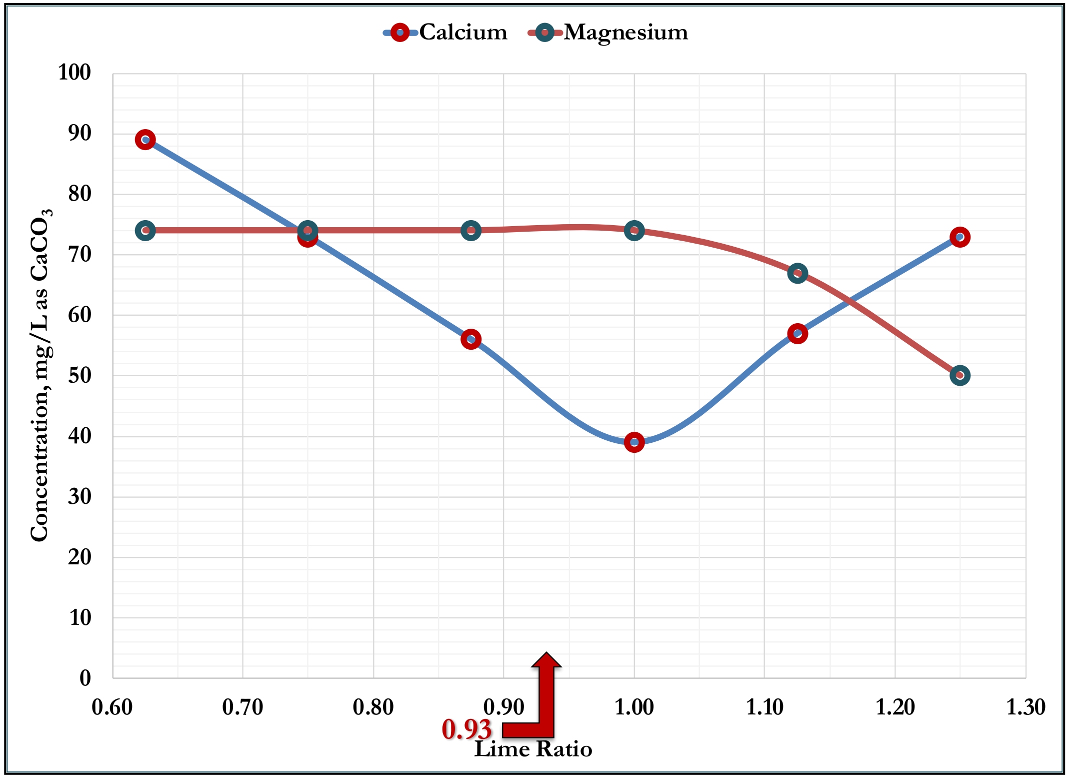
- Lime ratio concept produces some TOC removal from calcium and magnesium precipitation
- Softened water TOC predictions at 2.32 mg/L (1.4 mg/L reduction) at normal lime ratios (1.49)
- Actual softened water TOC levels averaged 2.48 mg/L May 2023
- **94% confidence for TOC predictions**

Oberlin, Ohio Case Study

- Black River source pumped to large reservoir storage with moderate TOC and hardness
- $NaMnO_4$ pretreatment with alum, lime softening, CO_2, polyphosphate, fluoride
- Filtration followed by chlorine disinfection and CT

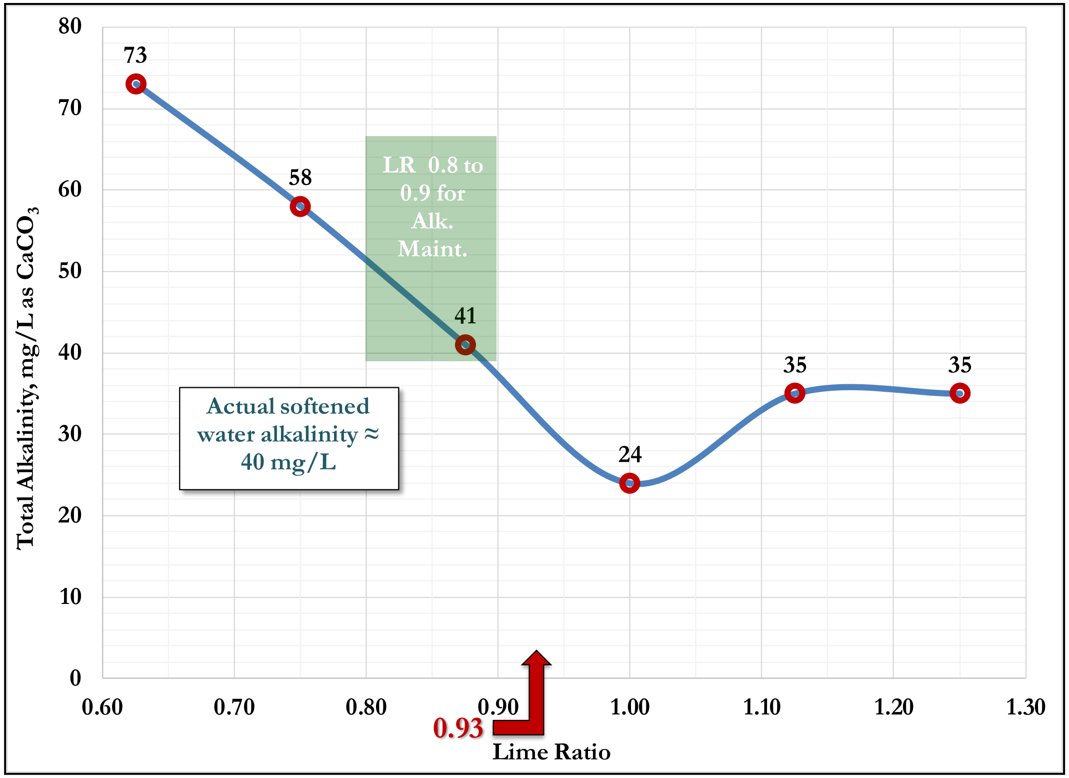
Oberlin, Ohio Case Study

- Simple lime softening for calcium and co-precipitation of magnesium to obtain desired hardness
- Treatment curve suggests simple softening to minimize Ca^{+2} and maintain alkalinity for WQ management
- Lime ratio typically averages 0.93
- Softened hardness averages 130 mg/L

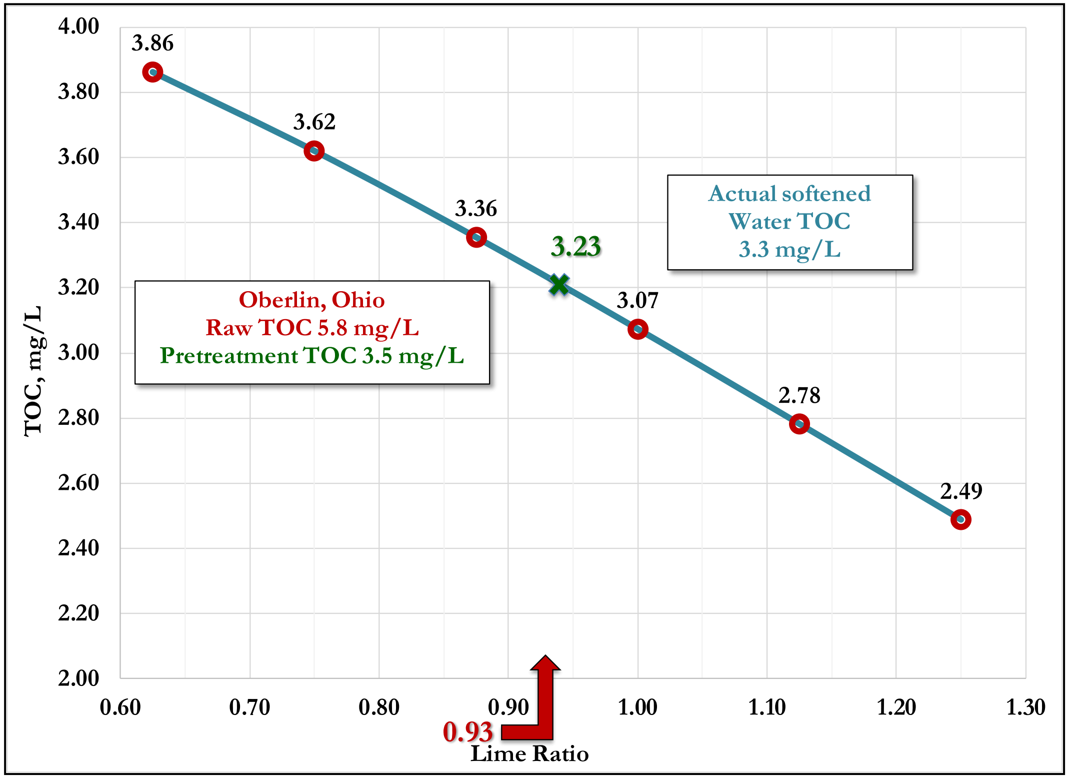


Oberlin, Ohio Case Study

- Alkalinity managed by simple lime softening and controlling lime ratios in treatment
- Maintain total alkalinity average at about 40 mg/L as $CaCO_3$
- Lime ratio range 0.8 to 0.9 for alkalinity management and corrosion control needs
- Softened water pH levels average 10.20



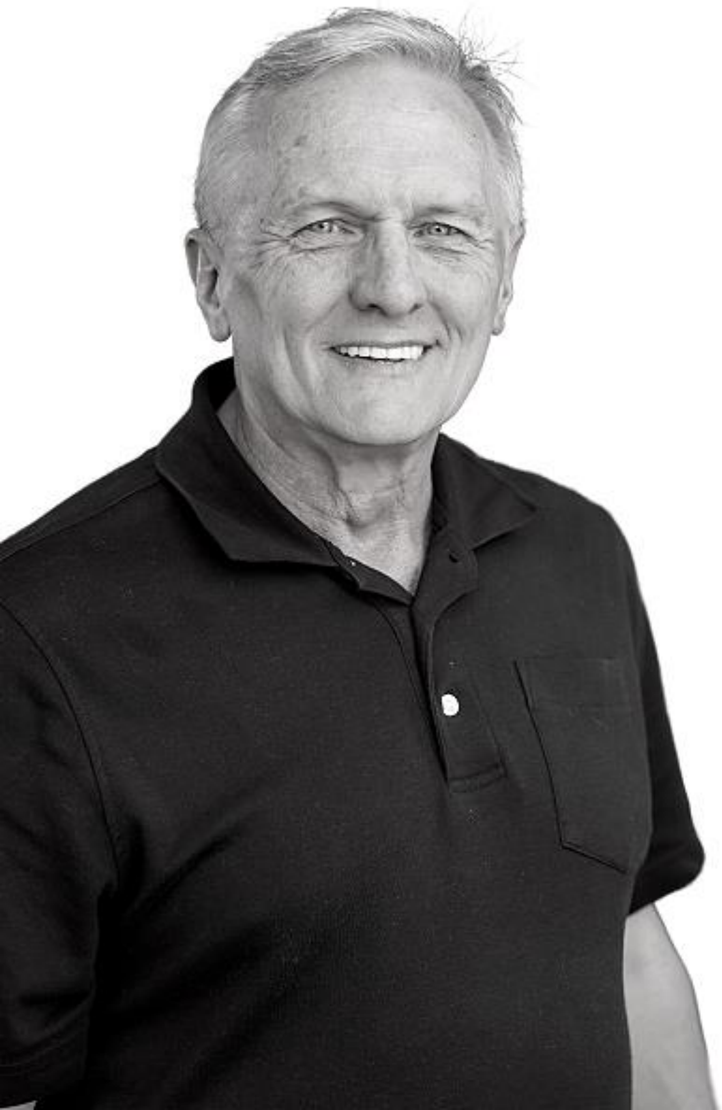
Oberlin, Ohio Case Study



- Lime ratio concept produces some TOC removal from calcium and magnesium coprecipitation
- Softened water TOC predictions at 3.23 mg/L (2.57 mg/L reduction) at normal lime ratios (0.93)
- **Actual softened water TOC levels averaged 3.3 mg/L October 2023**
- **98% confidence for TOC predictions**

Summary and Conclusions

- Lime ratio (LR) concept aligns calcium and magnesium content, follows research data closely
- Target LR benefits water quality with optimized TOC removal
- LR allows predictive assumptions of softened water TOC, hardness, and alkalinity
- LR enhances alkalinity management for final corrosion control treatment
- Other "key" water quality measures will improve such as turbidity, THMs, and HAAs



Questions

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