Lead & Copper Control with Phosphates
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Agenda

- U.S. EPA Lead & Copper Rule
- Factors that Effect Corrosion and Prevention
- History of Phosphates
- Selection of Phosphates/Benefits of Phosphates
- Dosage Rates
- Case Studies
- Monitoring Corrosion Control Success
Lead and Copper Rule

June 7, 1991 EPA Document in Effect

<table>
<thead>
<tr>
<th></th>
<th>Interim</th>
<th>1991 MCLG</th>
<th>1991 Action Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>0.05 mg/L</td>
<td>Zero</td>
<td>0.015 mg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>1.00 mg/L</td>
<td>1.30 mg/L</td>
<td>1.30 mg/L</td>
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</tbody>
</table>

Health Effects:
Lead: Delays in physical and mental development of children, kidney problems, & high blood pressure

Copper: Gastrointestinal/liver/kidney problems
Lead and Copper Rule

90\textsuperscript{th} percentile is the value to determine compliance with the action level.

All customers samples are arranged from lowest to highest in a list, the value at 9/10 of the way up is the value to determine compliance with action level.
Lead and Copper Rule

Monitoring is based on the size of the distribution system and high risk sites (lead service lines). Frequency is every 6 months for initial monitoring. Systems consistently meeting the Action Level can reduce monitoring to once a year and half of the samples. Finally to once every three years.
Lead and Copper Rule

Sampling of “First Draw”
1-Liter of water from a cold water tap that has not been used for at least 6 hours.
No upper limit on stagnation time.

2016 Recommendations
No pre-flush
Use wide mouth bottles
Higher flow rate
Don’t remove faucet aerators
**Lead and Copper Rule**

**Actions Required** after an exceedance occurs

- Distribution of Public Education
- Increased Monitoring of Consumer Taps
- Develop and Submit a Corrosion Control Plan
- Adjust pH, Alkalinity, Hardness, or Corrosion Inhibitor
- Lead Service Line Replacement

7% per year
Corrosion Increases.

- Tuberculation & Deposits
- Cost to Pump Water
- Fire Insurance Ratings
- Chlorine Demand
- Bacterial Re-Growth
- Flushing Frequency
- Leaks & Main Breaks
- Water Heater Replacement
- Decay of Water Quality
- Customer Complaints
Corrosion-Influencing Factors

- Electrical
- Chemical
- Physical
- Biological
## Chemical Factors Influencing Corrosion

<table>
<thead>
<tr>
<th>Factor</th>
<th>Effect</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>Low pH increases corrosion, High pH protects</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>Help form protective CaCO3 coating, controls pH</td>
</tr>
<tr>
<td>D.O.</td>
<td>Increases rate of corrosion</td>
</tr>
<tr>
<td>Chlorine Residual</td>
<td>Increases metallic corrosion</td>
</tr>
<tr>
<td>TDS</td>
<td>High TDS increases conductivity and corrosion</td>
</tr>
</tbody>
</table>
Methods to Reduce Corrosion

- pH Adjustment
- Passivation Techniques
  - Carbonate Adjustment
  - Calcium Adjustment
- Corrosion Inhibitors: Phosphates/Silicates
- Reduction of DIC
  - Aeration
  - Lime Softening
  - Ion Exchange
- Physical: Cathodic protection
Phosphates in Water Treatment

1887 First recognized use of phosphates in water treatment.

1930's “Threshold Treatment”- use of few ppm sodium hexa-metaphosphate powder to potable water for control of calcium carbonate scale.

1970's Zinc phosphates introduced for the treatment of low hardness aggressive water supplies (Murray AWWA 1969)

1990's Lead & Copper Rule: Set limitations on the amount of permissible lead and copper in drinking water
Phosphates in Water Treatment

- Potable Water Treatment
  - Corrosion Control (Lead & Copper)
  - Sequestration: Color Control/Scale Control
- 2001 Used by 56% of water utilities
- AWWARF (corrosion control): $200 million spent annually on phosphate products
  - Resulted in $4 billion in savings (20 fold ROI)
- Cost range $0.30 - $2.00/lb
  - or 1¢ - 10¢ thousand gallons
Uses of Phosphates

- **Food Additive**
  - Leavening Agent
  - Dairy Emulsifier
  - Beverages >1% Phosphoric Acid

- **Pharmaceutical Additive**
  - Toothpaste: Plaque Inhibitor, Whitening
  - Drug Manufacture

- **Fertilizers**

- **Cleaners and Detergents**
Improving Finished Water Quality

**Calcium Carbonate Scale Control**

**Iron and Manganese precipitation**

**Pipe Corrosion**

**Lead/Copper**
Uses of Phosphates

Corrosion Control for Lead and Copper

Use when USEPA Action Levels exceeded

- Lead < 0.015 mg/L (15 ppb)
- Copper < 1.30 mg/L

Used in Soft Waters, Surface WTP

- Hardness = <50 mg/L
- Alkalinity = <20 mg/L
Uses of Phosphates

**Color Control preventing Fe/Mn Precipitation**

Used when Fe/Mn are above
USEPA SMCL’s
Fe > 0.30 mg/L
Mn > 0.05 mg/L

Used in ground waters in place of oxidation
Uses of Phosphates

Calcium Carbonate Scale Control

Used in high hardness ground waters
Ranging from 150-400 mg/L as CaCO₃
Phosphate Classes

- Two distinct classes
  - Each has different properties
- Orthophosphate
  - Contains one $\text{PO}_4^-$ unit
- Condensed (poly) phosphate
  - Contains several $\text{PO}_4^-$ units “chained” together
Phosphate Classes

Orthophosphate

- Contains one $\text{PO}_4$ unit
Phosphate Classes

Polyphosphate

- **Contains two or more PO$_4$ units**

- **Metaphosphate**: contains 3 or more PO$_4$ units in a ring structure
Corrosion Control Mechanism

- Phosphate forms film over pipes or metals
  - Anodic film formers
  - Cathodic inhibitors - Cationic complex provides a diffusion barrier for oxygen
- **Microscopic Film**
  - Very insoluble compounds - phosphate salts
  - Mechanisms are still being researched
Orthophosphate Research

- Precipitates with $2^+$ valence metals
  - Ca, Mg, Pb, Fe, Mn, Cu  \([\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}]\)
- Formation of insoluble film (Schock, 1989 et al)
- PO$_4$ with two Fe$^{3+}$ ions forming Fe-PO$_4$-Fe linkages (Stumm, 1996 et al)
- May bond directly with pipe or soluble ions (Vik, 1996 et al)
  - 0.5 -1.0 mg/L PO$_4$ reduced Fe release two-thirds
- Reduce corrosion in distribution system
Zinc Orthophosphate (ZOP)

- Orthophosphate & Zinc Salt
- Corrosion Control Only
  - Cannot sequester metals
- Quick to form film on pipes
  - 'Passivation' can take place in weeks
- Doses range: 0.10 to 0.25 mg/L as Zinc
  0.50 to 2.00 mg/L as PO$_4$
- Zinc loading limit in wastewater
Optimal Orthophosphate

- Typically > 0.50 mg/L PO₄ reduces Pb and Cu solubility in a pH range 7-9
- Excess of 3.00 mg/L PO₄ yields little change
- Maintenance levels typically 1.00 mg/L
Sequestering Mechanism

- Bonding of condensed phosphate to metals
- Prevents chlorine from oxidizing metal
  - Typically, iron and manganese
- Result is clear water
  - Prior water was rusty orange (Fe$^{3+}$)
  - Prior water was black or brown (MnO$_2$)
- “Threshold Treatment”
  - calcium & bicarbonate ions—“ion-pairs”
  - phosphate attracted to these clusters
  - inhibit/retard crystal growth
“Polyphosphate” linear chains of P atoms (Van Wazer, 1958)

Sequestering of metals depends on water chemistry (Klueh & Robinson, 1988)

Reduces apparent color and turbidity in Fe\(^{3+}\) colloids (Lytle, 2002)

Revert to ortho over time (Thilo, Chem, 1957)

  - Change to ortho as they age
Polyphosphate Dosing

- Doses range **0.50 to 4.00 mg/L** as Total- PO$_4$
- Dose is dependent on soluble cations in water
- Objective may also determine dosing
  - Sequestering: higher dose
  - Flushing: higher dose
Polyphosphate Controls Color Problems
Polyphosphate Controls Color Problems
Sequestering Total Hardness

CONCENTRATION OF HARDNESS AS CALCIUM CARBONATE, IN MILLIGRAMS PER LITER

Mean hardness as calcium carbonate at USGS NASQAN stations during 1975 water year.
The Hidden Energy Loss In Pipe

- Scale reduces a 20” pipe to 12”
- Electrical costs increased > ten fold
Poly/Ortho Blended Phosphates

- Became very popular in 1990’s
  - Promulgation of Lead and Copper Rule
- Sequesters (Fe$^{2+}$, Mn$^{2+}$, Ca$^{2+}$)
- Moderate Corrosion Control
  - Provides Lead and Copper Control
- Prevents and Removes Scale Deposits
- Improves Disinfection
  - Chlorine doesn’t react with dissolved metals
Poly/Ortho Blended Phosphate Dosing

- Doses range: 0.20 to 1.50 mg/L as Ortho- PO$_4$
- Doses range: 0.50 to 4.00 mg/L as Total- PO$_4$
- Dose is dependent on water quality or equation
- Objective may also determine dosing
  - Sequestering: higher dose
  - Flushing: higher dose
  - Corrosion Control: lower dose
Problem:

- Reduce Lead Below Action Level
  - Action Level of 22 ppb
- Reduce Discoloration in Households
- Reduce Long Hydrant Flushing Times
  - Greater than 30 minutes
Case Study 1
Blended Phosphate

- **Plant Operation**
  - Ground Water Filtration Plant/3 Wells
  - Radium Removal with HMO
  - 1.1 MGD (7,500 Customers)

- **Water Quality**
  - pH 7.3-7.5
  - Fe 0.1-0.5 mg/L
  - Mn 0.01-0.05 mg/L
  - Hardness 250 mg/L
  - Alkalinity 288 mg/L
Treatment

- Blended Phosphate (50/50 Ratio Poly/Ortho)
- Dosage: 1.5 mg/L as Total PO4
- Feed Rate: 35 lbs per MGD

Results Within 90 Days

- Lead Levels from 22 ppb to 7.5 ppb
- Hydrant Flushing Times from 30 minutes to less than 5 minutes
- Customer Complaints Reduced
Case Study 2
Blended Phosphate

Problem:

- Dirty Water (Red Water) Complaints
  - 10-15 per month
- Scale Formation on Packed Tower Aeration
  - Acid cleaning quarterly
- Long Hydrant Flushing Times
  - Greater than 30 minutes
Case Study 2
Blended Phosphate

- **Plant Operation**
  - Ground Water Filtration Plant/7 Wells
  - Packed Tower Aeration for VOC Removal at 1 Well
  - 3.8 MGD (23,500 Customers)

- **Water Quality**
  - pH 7.5-7.8
  - Fe 0.10-0.25 mg/L
  - Mn 0.01-0.03 mg/L
  - Hardness 340-490 mg/L
Case Study 2

Blended Phosphate

- **Treatment**
  - Blended Phosphate (90/10 Ratio Poly/Ortho)
  - Dosage: 1.5 mg/L as Total PO4
  - Feed Rate: 38 lbs per MGD

- **Results Within 30 Days**
  - Customer Complaints Reduced from 10-15 to 2 in first month and 7 for the rest of the year
  - Scale Formation on Packed Tower Aeration
    - Acid cleaning from quarterly to yearly
  - Hydrant Flushing Times from 30 minutes to less than 5 minutes
Choice of Phosphate

- Which phosphate to use?
  - Choice can be as critical as dosing
  - What types of problems are you having in the distribution system?
  - What is the water quality leaving the plant and in the distribution system?
  - What are your treatment goals?
Need to Determine

- Hardness
- Soluble Fe & Mn (after filtration)
  - The Fe SMCL is 0.30 mg/L for potable water
  - The Mn SMCL is 0.05 mg/L for potable water
- Orthophosphate
  - Background ortho does not aid corrosion
- pH
  - Ortho/poly phosphate 6.0 - 9.0 with 7.0 - 8.0 optimal
  - Zinc orthophosphate 6.7 - 8.2 with 7.3 - 7.8 optimal
Selection of Phosphates

High Fe/Mn
2.0mg/L/0.3mg/L

SMCL
0.3 mg/L Fe
0.05 mg/L Mn

Low Fe/Mn
0.1mg/L/0.02mg/L

Corrosive water

Scale forming water

Orthophosphates
ZOP

Blended Phosphates

Polyphosphates
Phosphate Injection Applications

- Inject Phosphate solution using a corporation stop in main prior to chlorination for sequestering
  - Inject neat or with carry water, static mixer can be used
  - Peristaltic or Membrane chemical feed pump
    Flow paced, SCADA controlled recommended

\begin{itemize}
  \item Inject \text{PO}_4 \text{H}_2 \text{O}CL^{-}
  \end{itemize}
Phosphate Injection Applications

- Typical Phosphate Feed Rate Measurements
  - Calibration of Metering Pump (mLs/min or gals/hr)
  - Weigh Scale for Day Tank (pounds used per day)
  - Level Indicator for Day Tank (gallons used per day)
How Do I Monitor Phosphate?

- USEPA Approved Ascorbic method 8048
- Measures orthophosphate residual in mg/L
- Two minute reaction - turns light blue
Monitoring a Phosphate Product?

- Test at Finished Water Tap, Distribution System, & Dead Ends
- Results should be at or above the target level throughout the distribution system
Pipe Loop Design

- Coupon Based Monitoring (NACE Protocol)
- Test Exposed Coupons for MPY
  "Mils penetration per year"
  - Test Duration (30, 60, 90 days exposed)
  - Need non-treated, treated, & distribution loops
  - Focus on “trend of data” not numerical data
Coupon Testing Results

Coupon Exposure
90 Days

Matrix
Florida Surface
Water

No Treatment  50:50 Blend Treated
PPE required for phosphoric acid and zinc orthophosphate

- pH is < 1 (corrosive inorganic liquid)
  - Goggles and/or face shield
  - Rubber or appropriate polymer gloves
  - Rubber apron
  - Complete acid resistant suit
  - Rubber boots
- DOT hazardous for shipping
Personal Protection Equipment (PPE)

PPE required for pH adjusted orthophosphates and blended phosphates

- pH is typically neutral
  - Safety glasses or goggles
  - Rubber or appropriate polymer gloves
- Not DOT hazardous for shipping
Summary of Phosphates Uses

- Phosphate use is extensive in US
  - Very small systems to very large
- Benefits are worth the cost
  - Reduced lead and copper corrosion
  - Clearer water (sequestering)
  - Reduced flushing times
  - Reduced disinfectant demand
- Overall better water quality
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