The Use of Phosphates in Water Treatment for Corrosion Control & Sequestration

Maine Water Utilities Association

April 13, 2017

Agenda

- US EPA Lead and Copper Rule
- Corrosion Definition
- Chemical Factors Influencing Corrosion and Corrosion Control
- Factors to Reduce Corrosion
- Phosphates in Water Treatment
- Chemical Inhibitors
- Dosage Rates
- Selection of Phosphates/Benefits of Phosphates
- Case Studies
- Monitoring Corrosion Control Success

June 7, 1991 EPA Document in Effect

	Current Action Level	1991 MCLG
Lead	0.015 mg/L	0 mg/L
Copper	1.30 mg/L	1.30 mg/L

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

Copper: Gastrointestinal/liver/kidney problems

90th 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.

Sampling of “First Draw”

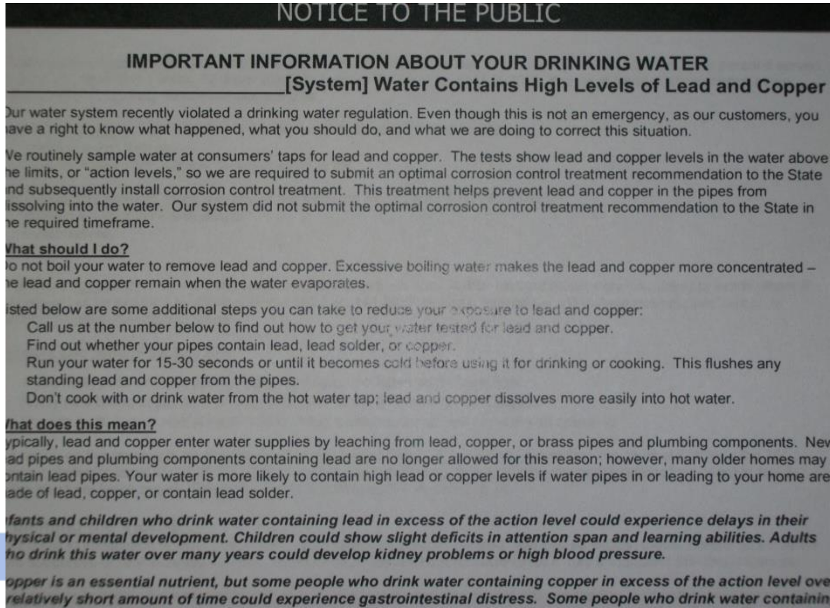
- 1-Liter of water from a cold water tap that has not been used for at least 6 hours.
- No upper limit on stagnation time.

2016 Recommendations

- No pre-flush
- Use wide mouth bottles
  - Higher flow rate
- Don’t remove faucet aerators

<u>Actions Required</u> 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



NOTICE TO THE PUBLIC

IMPORTANT INFORMATION ABOUT YOUR DRINKING WATER

____________________[System] Water Contains High Levels of Lead and Copper

Our water system recently violated a drinking water regulation. Even though this is not an emergency, as our customers, you have a right to know what happened, what you should do, and what we are doing to correct this situation.

We routinely sample water at consumers' taps for lead and copper. The tests show lead and copper levels in the water above the limits, or "action levels," so we are required to submit an optimal corrosion control treatment recommendation to the State and subsequently install corrosion control treatment. This treatment helps prevent lead and copper in the pipes from dissolving into the water. Our system did not submit the optimal corrosion control treatment recommendation to the State in the required timeframe.

<u>What should I do?</u>

Do not boil your water to remove lead and copper. Excessive boiling water makes the lead and copper more concentrated – the lead and copper remain when the water evaporates.

Listed below are some additional steps you can take to reduce your exposure to lead and copper:

- Call us at the number below to find out how to get your water tested for lead and copper.
- Find out whether your pipes contain lead, lead solder, or copper.
- Run your water for 15-30 seconds or until it becomes cold before using it for drinking or cooking. This flushes any standing lead and copper from the pipes.
- Don't cook with or drink water from the hot water tap; lead and copper dissolves more easily into hot water.

<u>What does this mean?</u>

Typically, lead and copper enter water supplies by leaching from lead, copper, or brass pipes and plumbing components. New lead pipes and plumbing components containing lead are no longer allowed for this reason; however, many older homes may contain lead pipes. Your water is more likely to contain high lead or copper levels if water pipes in or leading to your home are made of lead, copper, or contain lead solder.

Infants and children who drink water containing lead in excess of the action level could experience delays in their physical or mental development. Children could show slight deficits in attention span and learning abilities. Adults who drink this water over many years could develop kidney problems or high blood pressure.

Copper is an essential nutrient, but some people who drink water containing copper in excess of the action level over a relatively short amount of time could experience gastrointestinal distress. Some people who drink water containin

Lead and Copper Rule - References

- Lead and Copper Rule
  - https://www.epa.gov/dwreginfo/lead-and-copper-rule
- Water Research Foundation – Fact Sheet – Dist. Syst. Mgmt. – "Impacts from Lead and Copper Corrosion"
  - http://www.waterrf.org/knowledge/distribution-system-management/FactSheets/DistributionSystemMgmt_LeadCopper_FactSheet.pdf
- Optimal Corrosion Control Treatment Evaluation Technical Recommendations for Primacy Agency and Public Water Systems – March 2016
  - https://www.epa.gov/sites/production/files/2016-03/documents/occtmarch2016.pdf

Corrosion

Destructive attack of a material by a chemical or electrochemical reaction with its environment.

- Electrochemical
- Chemical
- Microbiological

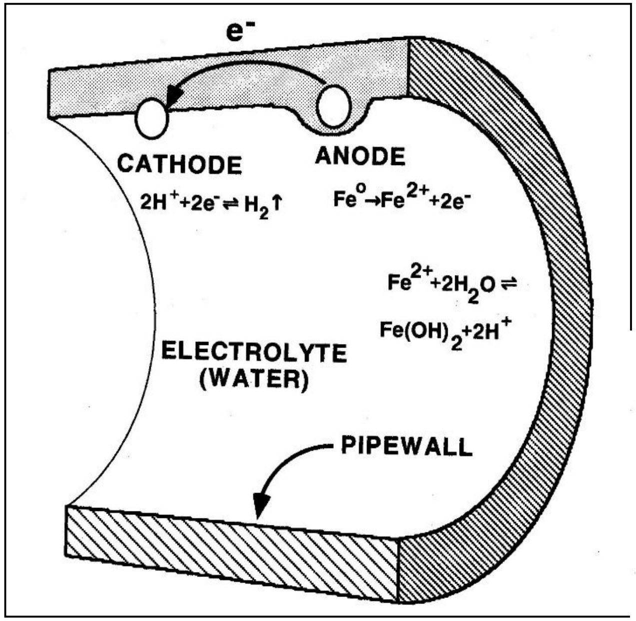
Electrochemical Corrosion
Galvanic Series

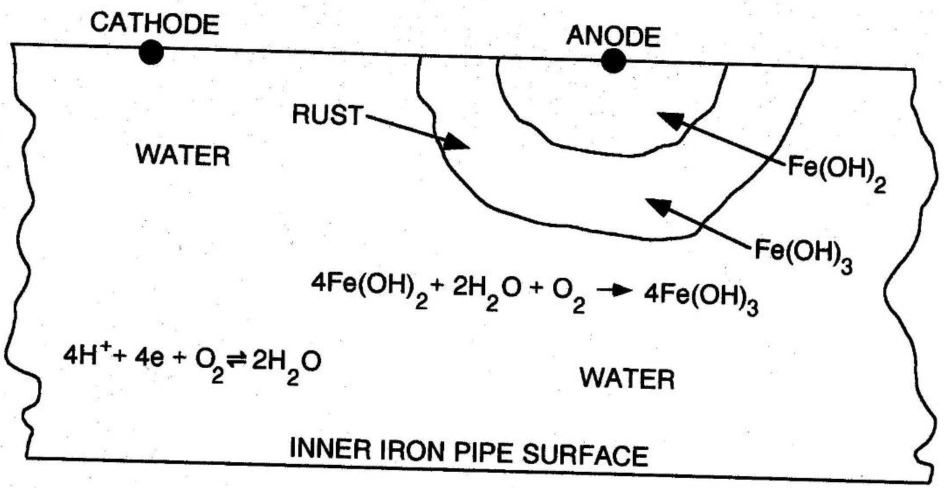
Anode (Most Active)

Magnesium (Base Metals)
Zinc
Aluminum
Steel
Cast Iron
Lead - Tin Solder
Lead
Nickel
Brass
Copper
Stainless Steel
Silver
Gold

Cathode (Least Active) (Noble Metals)

Cast Iron Pipe Corrosion





Corrosion – Tuberculation

Corrosion

- Oxidation

$$Fe \longrightarrow Fe^{++} + 2e^-$$

$$Cu \longrightarrow Cu^{++} + 2e^-$$

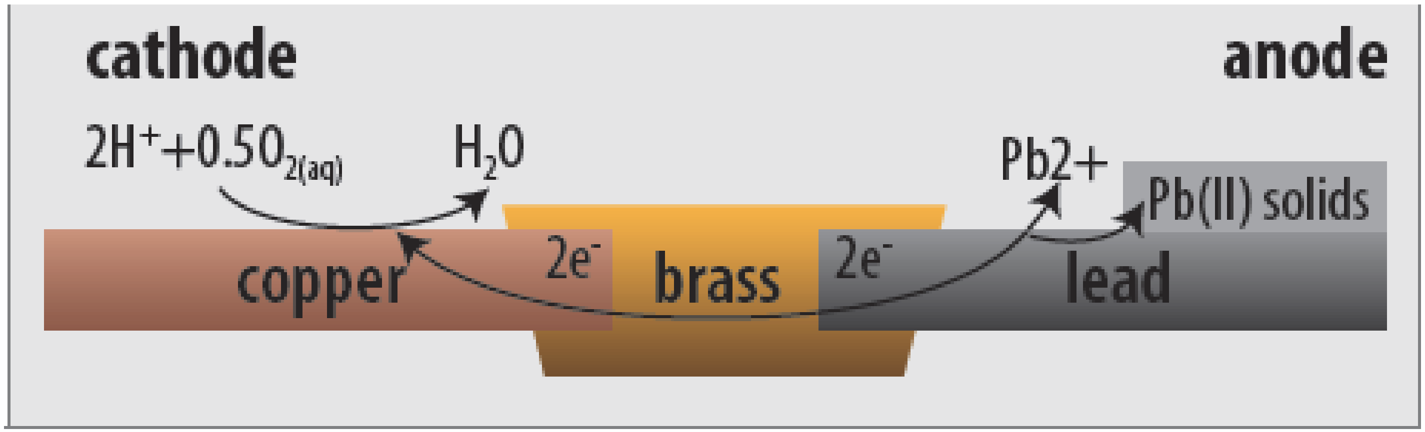
$$Pb \longrightarrow Pb^{++} + 2e^-$$

- Reduction

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

Electrochemical Corrosion

- Is an electrochemical process in which electrons flow from one site on the metal pipe surface to another
- Metal is oxidized to form positive ions (cations) while other chemical species either in the pipe or water are reduced.



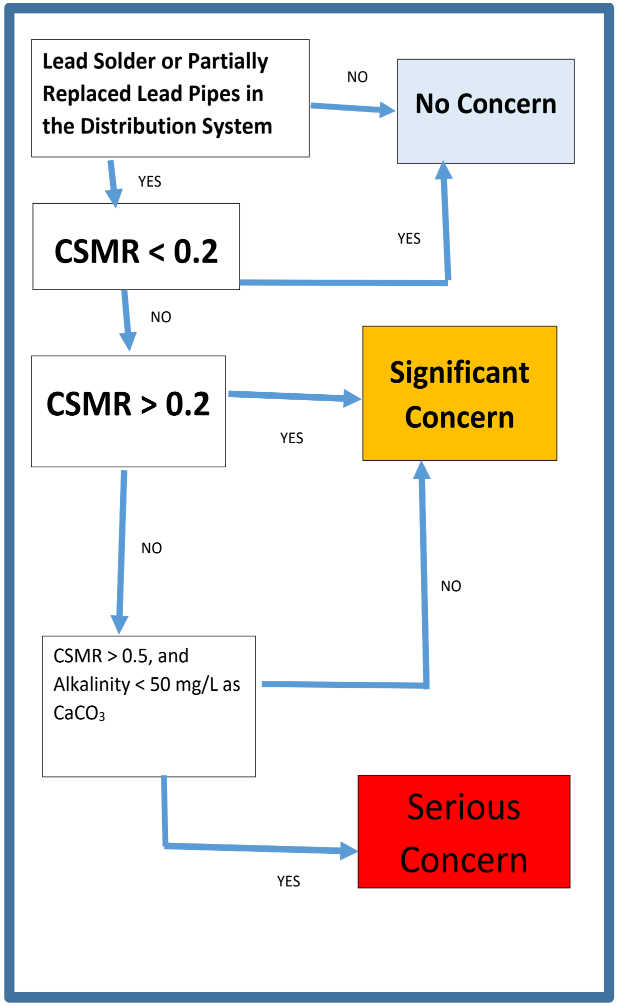
(source: Wellter et al. 2013)

- The anode is the place where the oxidation occurs (electrons lost)
- The cathode is where the reduction occurs (electrons accepted)

Chemical factors influencing corrosion and corrosion control

Factor	Effect
pH	Low pH increase corrosion, High pH protects
Alkalinity	Help form protective $CaCO_3$ coating, controls pH
D.O.	Increases rate of corrosion
Chlorine residual	Increases metallic corrosion
TDS	High TDS increases conductivity and corrosion
Hardness	Ca may precipitate as $CaCO_3$ provide protection
Chloride, sulfate	High levels increase corrosion in iron, copper,and steel

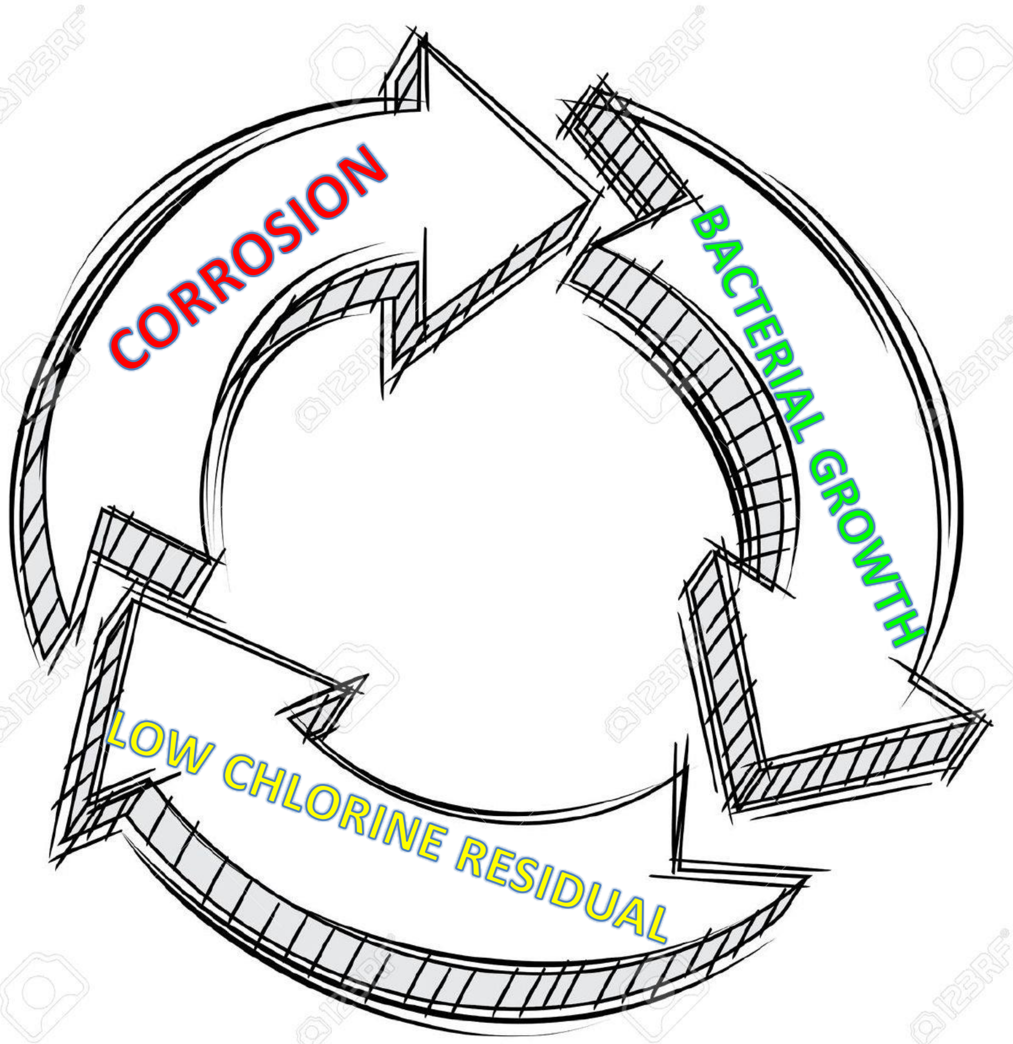
CSMR



Reference:

Chloride-to-Sulfate Mass Ratio and Lead Leaching to Water (PDF)
Author(s): Edwards, Marc; Triantafyllidou, Simoni
Publications: Journal - American Water Works Association
Issue Date: July 2007
Volume / Number: 99, Number 7

Corrosion Effects



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

Factors to Reduce Corrosion

- pH Adjustment
- Passivation Techniques
  - Carbonate Adjustment
  - Calcium Adjustment
- Inhibitors – orthophosphate or blends
- Reduction of DIC
  - Aeration
  - Lime Softening
  - Ion Exchange

Stabilization

- An Increase in pH + Alkalinity can prevent corrosion
- Lime-Increases both and adds hardness

  Soda Ash- increase Alkalinity
- Both use for protective coatings
- DIC is a very important parameter,
- pH + ALK + DIC are better indicators of corrosion control effectiveness
- Reference: https://www.epa.gov/sites/production/files/2016-03/documents/occtmarch2016.pdf

pH-Alkalinity Contribution

Chemical	Feed Rate mg/L	Alkalinity Increase per mg/L
Lime-$Ca(OH)_2$	1-20 mg/L (8-170 lb/MG)	1.35 mg/L (adds calcium and hydroxide alkalinity)
Caustic Soda NaOH (50% sol)	1-30 mg/L (8-250 lb/MG)	1.25 mg/L (hydroxide alk)
Soda Ash Na_2CO_3	1-40 mg/L (8-330 lb/MG)	0.94 mg/L (carbonate alk depending on pH)
Sodium Bicarbonate $NaHCO_3$	5-30 mg/L (40-250 lb/MG)	0.59 mg/L (carbonate alk depending on pH)

Buffer Intensity

- Increasing the buffer intensity in low alkalinity waters stabilizes pH. A stable pH is an important factor for maintaining a low corrosion rate and low metal release.
- A stable pH is important in controlling lead solubility for the long term.

Calcium Carbonate Precipitation Potential

- The CCPP measures the amount of carbonate precipitation that will deposit on the pipes
- The optimal range for treatment is 5-10 mg/L
- Controlling Calcium Carbonate is difficult because ;

Calcium Carbonate films rarely adhere to lead and copper pipe walls and are not considered an effective form of corrosion control.

- (Schock and Lytle, 2011; Hill and Cantor, 2011).

Calcium Carbonate Precipitation

- Is Achieved by taking pH/AlK adjustment too far

CO_2 +$Ca(OH)_2$ ⟶ $2HCO_3$- + Ca^{2+}

LIME **BICARBONATE**

$Ca(HCO_3)$ + $Ca(OH)_2$ ⟶ $2CaCO_3$ + $2H_2O$

Calcium Carbonate

- **Caustic Soda**

CO_2 + NaOH ⟶ HCO^3- + Na+

$Ca(HCO_3)_2$ + NaOH ⟶ $CaCO_3$ + $2H_20$

Corrosion Inhibitor and Sequestering agents

- Used if water cannot achieve $CaCO_3$ coating
- Sequestering Agents - prevent scale formation, prevent red water and pprecipitation of (Fe, Mn, Ca) preventing corrosion by-products

Galvanic Corrosion Prevention

- Use of DIELECTRIC couplings
  - » Plastic
  - » Ceramic
  - » Non-conductive
- SACRIFICIAL ANODES
  - » Zinc
  - » Magnesium
- CORROSION INHIBITORS
  - » Slow the rate of corrosion

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

Chemical Inhibitors

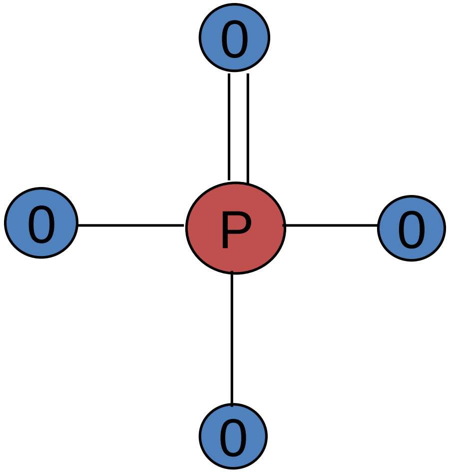
- Anodic film formers
  - orthophosphates
  - zinc **orthophosphates**
- Cathodic inhibitors
  - calcium carbonate
  - polyphosphates
  - **zinc** orthophosphate

Phosphate Classes

- Two distinct classes
  - Each has different properties
- Orthophosphate
  - Contains one PO_4 unit
- Condensed (poly) phosphate
  - Contains several PO_4 units "chained" together

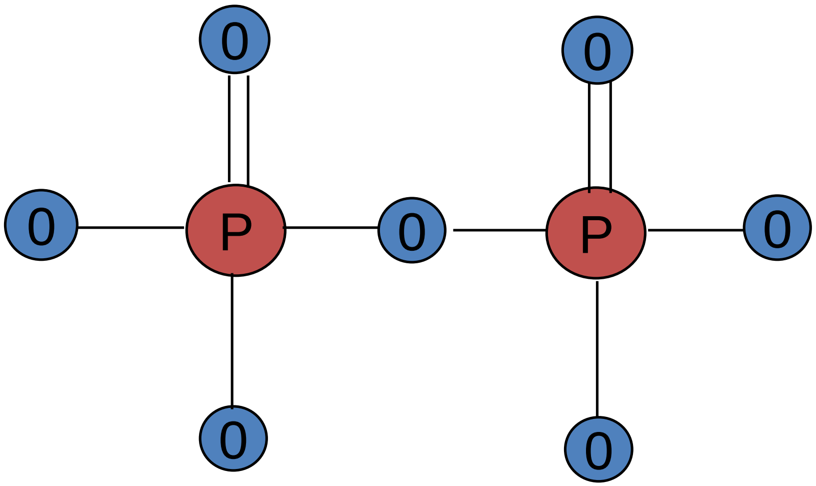
Orthophosphate

- Contains one PO_4 unit



Polyphosphate

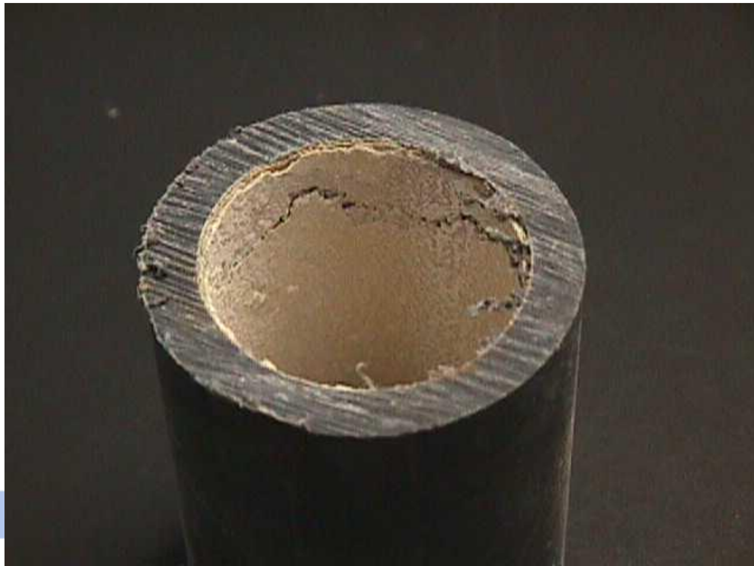
- Contains two or more PO_4 units



- 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
- <u>Microscopic Film</u>
  - ➢ Very insoluble compounds- phosphate salts
  - ➢ Mechanisms are still being researched



Orthophosphate Research

- Precipitates with 2+ valence metals
  - Ca, Mg, Pb, Fe, Mn, Cu [$Fe_3(P0_4)_2$* H_20]
- Formation of insoluble film (Schock, 1989 et al)
- $P0_4$ with two Fe^{3+} ions forming Fe-$P0_4$-Fe linkages (Stumm, 1996 et al)
- May bond directly with pipe or soluble ions (Vik, 1996 et al)
  - 0.5 –1.0 mg/L $P0_4$ reduced Fe release two-thirds
- Reduce corrosion in distribution system

Chemical Inhibitors - Orthophosphates

- Orthophosphate
  - Do not sequester
  - pH important - Ideal for lead control pH 7.2 -7.8
  - It is polyprotic acid - adds 3 H^+
  - DIC/Alkalinity important for its use
  - Anodic inhibitor
  - Applicable for lead control with pH adjustment

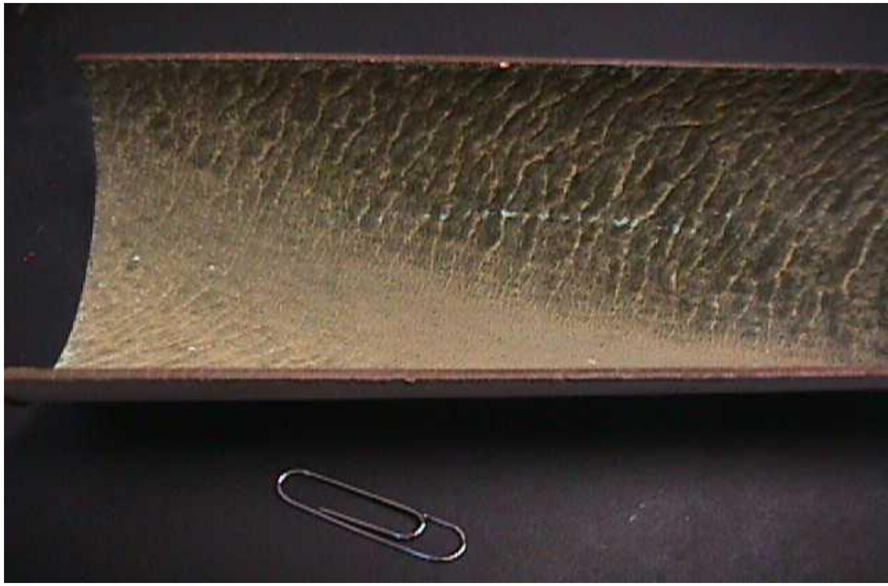
Chemical Inhibitors Phosphates

- Orthophosphate
  - Lead can form several orthophosphate solids that are less soluble than lead carbonates
  - Most likely form is hydroxypromorphite ($Pb_5[PO_4]_3OH$)
  - Other likely form is tertiary lead orthophosphate $Pb_3(PO_4)$

Optimal Orthophosphate

- Typically >0.5 mg/L PO_4 may reduce Pb solubility in pH range 7- 9
- Excess of 3 mg/L PO_4 yields little change
- Low DIC waters - even 1 mg/L is sufficient
- pH 7: Pb decreases with higher PO_4
- Maintenance levels typically >1.0 mg/L

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 $P0_4$
- Zinc loading limit in wastewater

Optimal Zinc Dose

- Typically >0.5 mg/L as Zinc
- Excess of 2 mg/L Zinc yields little change
- Low DIC waters - even 1 mg/L is sufficient
- pH 6.5 – 8.2 ideal range
- Maintenance levels typically 0.25 mg/L as Zinc

Poly/Ortho Blended Phosphate

- 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

Optimal Poly/Ortho Blended Phosphate Dosing

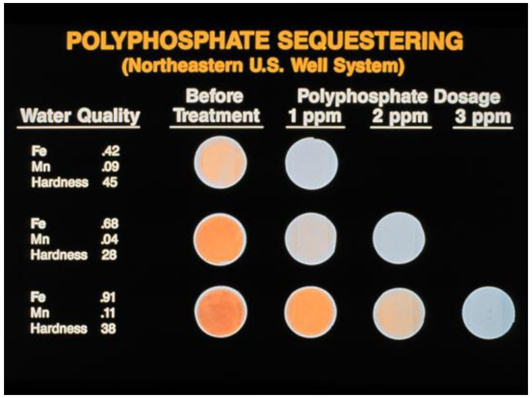
- Doses range: 0.20 to 1.50 mg/L as Ortho- $P0_4$
- Doses range: 0.50 to 4.00 mg/L as Total- $P0_4$
- Dose is dependent on water quality or equation
- Objective may also determine dosing
  - Sequestering: higher dose
  - Flushing: higher dose
  - Corrosion Control: lower dose

Iron & Manganese Sequestration

- "**Sequestering** is a chemical combination of a sequestrant and metal ions in which soluble complexes are formed… ... Sequestrants function as chelating agents, they donate electrons to form a "coordinate bond" with **iron and manganese** ions.

Sequestering Mechanism

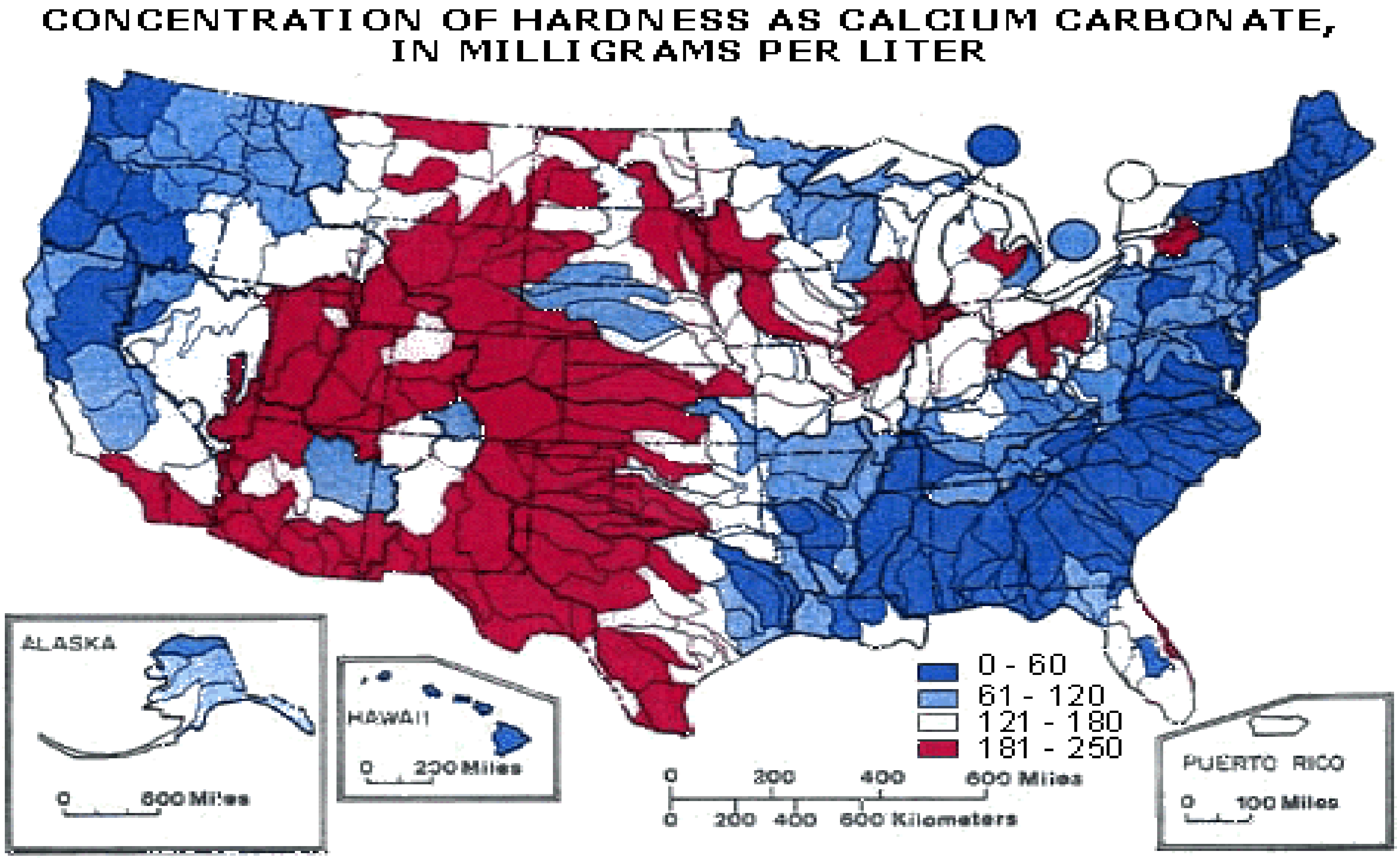
- Bonding of polyphosphate to metals
- Prevents chlorine from oxidizing metal
  - Typically, iron and manganese
- Result is clear water
  - Prior water was rusty orange (Fe^{3+})
  - Prior water was black or brown ($Mn0_2$)
- "Threshold Treatment"
  - calcium & bicarbonate ions-"ion-pairs"
  - phosphate attracted to these clusters
  - inhibit/retard crystal growth



Polyphosphate Research

- Sequestering of metals depends on water chemistry (Klueh & Robinson, 1988)
- Reduces apparent color and turbidity in Fe^{3+} colloids (Lytle, 2002)
- Polyphosphates improve disinfection (LeChevallier, 1990)
  - Application results in 1,000 fold decrease in biofilm counts
- Revert to ortho over time (Thilo, Chem, 1957)
  - Change to ortho as they age

Polyphosphate Sequestering Total Hardness



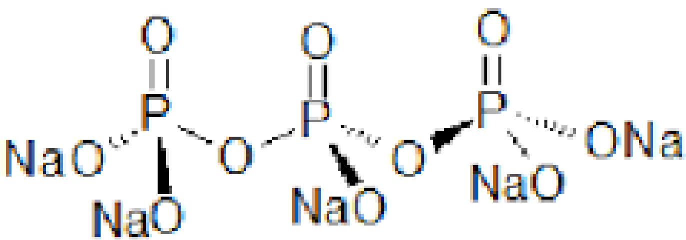
Mean hardness as calcium carbonate at USGS NASQAN stations during 1975 water year.

Chemical Inhibitors - Polyphosphates

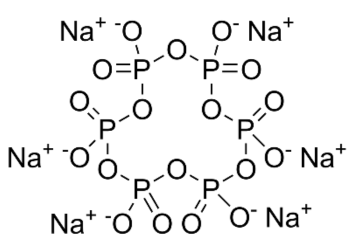
- Polyphosphates
  - In general strongest complexing agent for iron and manganese of the phosphates.
  - Sequester calcium
  - Cathodic inhibitor
  - Degrades to orthophosphate
  - Polyprotic acid (4 H^+) in water will become $P_2O_7^{-3}$
  - Wide pH range for it effective use

Iron & Manganese Sequestration

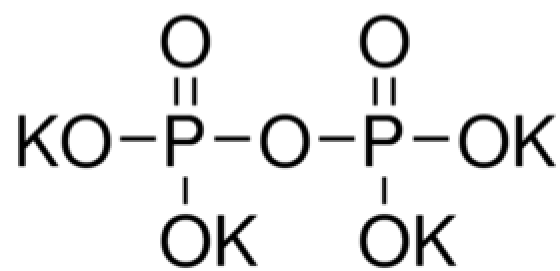
Polyphosphates – “Condensed Phosphates” – Threshold Treatment



Tripolyphosphate



SHMP

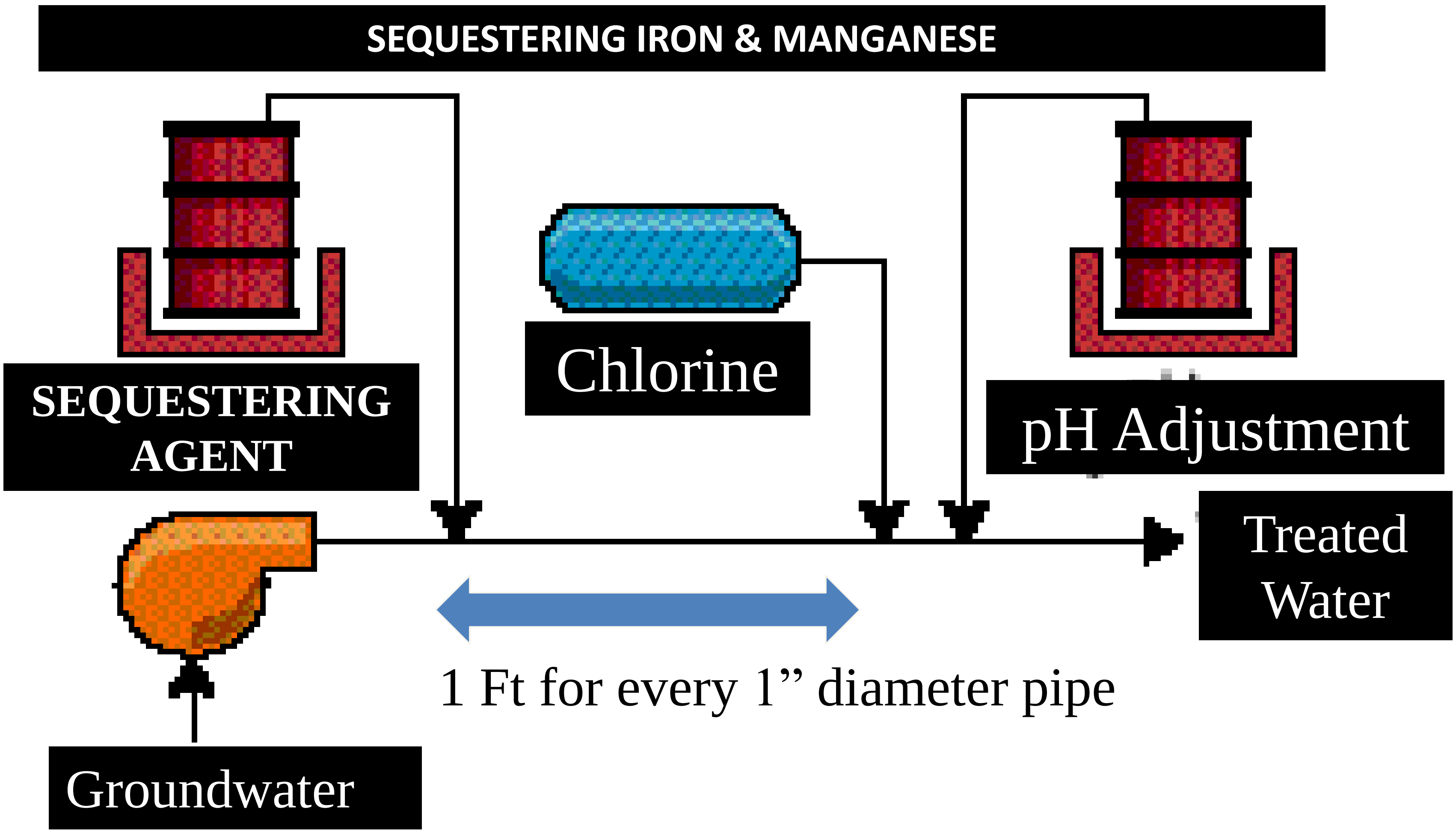


TKPP

Optimal Polyphosphate Dosing

- Doses range 0.50 to 4.00 mg/L as Total-$P0_4$
- Dose is dependent on soluble cations in water
- Objective may also determine dosing
  - Sequestering: higher dose
  - Flushing: higher dose

Typical Well Water Application



Flushing Process – Water Quality

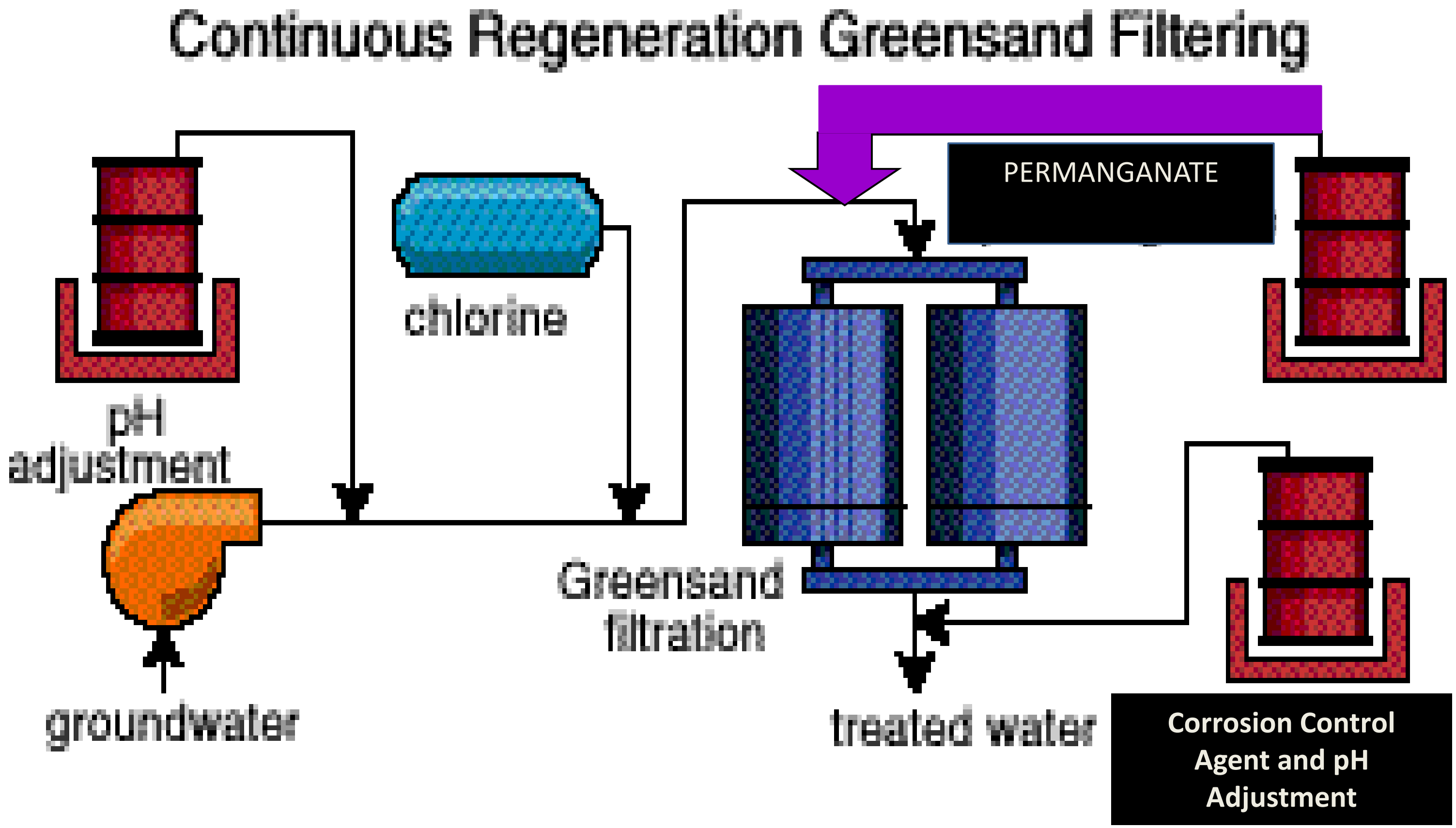
Flushing Process – Water Quality

SPRING & FALL - FLUSHING SEQUENCE TO REMOVE PARTICULATE MATTER

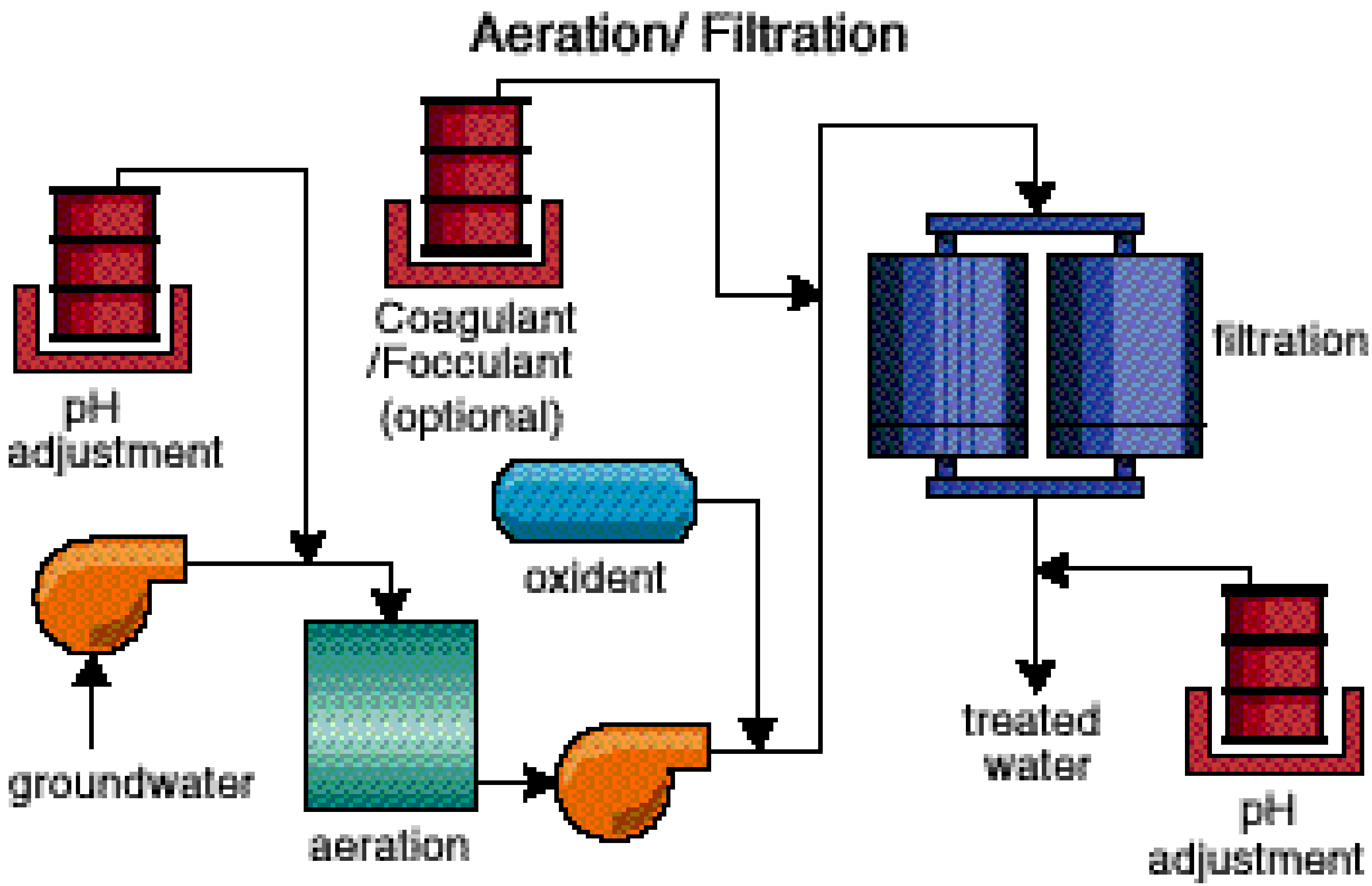
Iron & Manganese Oxidation

When iron and manganese are present in high concentrations the recommendation is Oxidation and Filtration.

Oxidation Process



Typical Well Water Application



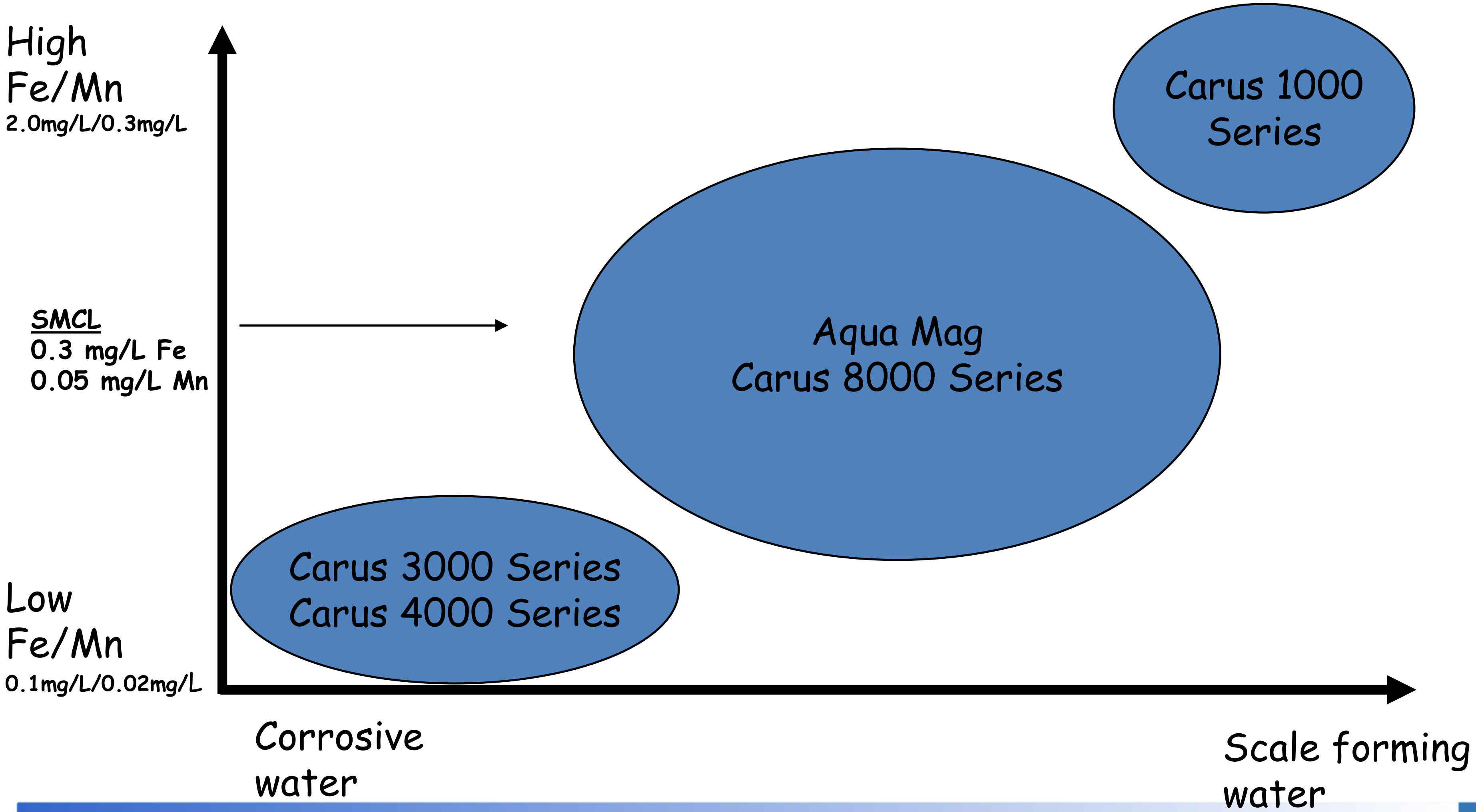
Choice of Phosphate

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

Product Selection & Dose

- 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



Case Study 1
Carus 4105

- Background:
  - Eliminate pH adjustment for corrosion control (soda ash combined with calcium chloride)
  - Eliminate bad taste caused by pH adjustment
  - Reduce periodic dirty water (red water)
  - Reduce lead and copper levels below action levels

Case Study 1
Carus 4105

- Plant Operation
  - Ground Water Filtration Plant
  - 1.5 MGD
- Water Quality

Fe	0.04 mg/L	TDS	200 mg/L
Mn	0.01 mg/L	Alkalinity	68 mg/L
pH	8.40	Hardness	24 mg/L

- Treatment
  - 100% Orthophosphate
  - Dosage: 1.0 mg/L as Ortho-PO_4
  - Feed Rate: 23 lbs per MGD
- Results
  - Improved Taste
  - Reduced pH to 7.5 saved 37% in soda ash costs
  - Replaced calcium chloride saved 50% in costs
  - Lead Levels < 2 ppb
  - Copper Levels < 0.05 mg/L (after 2 yrs)

Case Study 2
Carus 8500 Blended Phosphate

- Background:
  - Reduce Lead Below Action Level
    - ➢Current Action Level of 22 ppb
  - Reduce Discoloration in Households
  - Reduce Long Hydrant Flushing Times
    - ➢Greater than 30 minutes

Case Study 2
Carus 8500 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	280-340 mg/L	Alkalinity	288 mg/L

Case Study 2
Carus 8500 Blended Phosphate

- Treatment
  - Blended Phosphate (50/50 Ratio Poly/Ortho)
  - Dosage: 1.5 mg/L as Total PO_4
  - 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 3
Aqua Mag Blended Phosphate

- Background:
  - Heavy Tuberculation
  - Reduced Flows
  - Periodic Dirty Water (Red Water)
  - 90^{th} Percentile Copper Levels: 2.25 mg/L

Case Study 3
Aqua Mag Blended Phosphate

- Plant Operation
  - Iron Removal (aeration), Gravity Filtration
  - 2.5 MGD
- Water Quality

Fe	0.1 –0.3 mg/L	TDS	350 mg/L
Mn	0.01 mg/L	Alkalinity	340 mg/L
pH	7.6 – 7.9	Hardness	180 mg/L

Case Study 3
Aqua Mag Blended Phosphate

- Treatment
  - Blended Phosphate (70/30 Ratio Poly/Ortho)
  - Dosage: 1.50 mg/L as Total PO_4
  - Feed Rate: 38 lbs per MGD
- Results
  - Average Flow Improvement by 10-40%
  - Reduced Customer Complaints
  - Copper Levels Decreased 65% to 0.79 mg/L

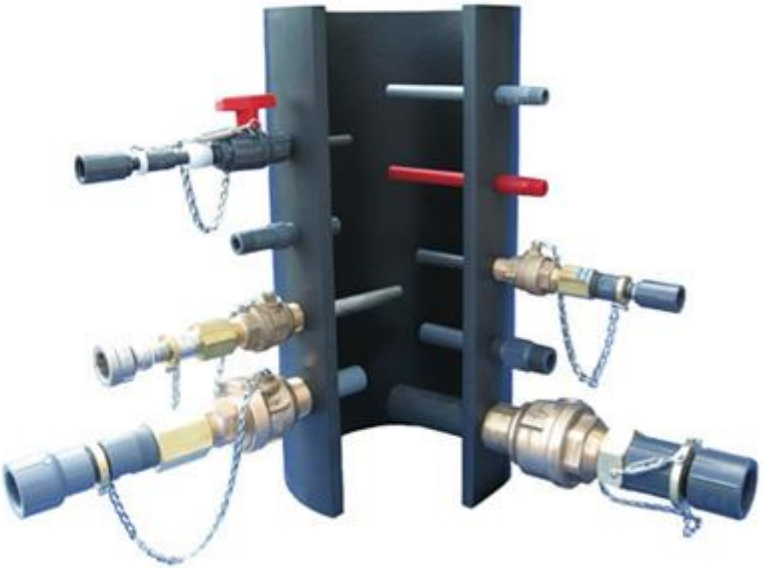
Phosphate Injection Applications

- 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

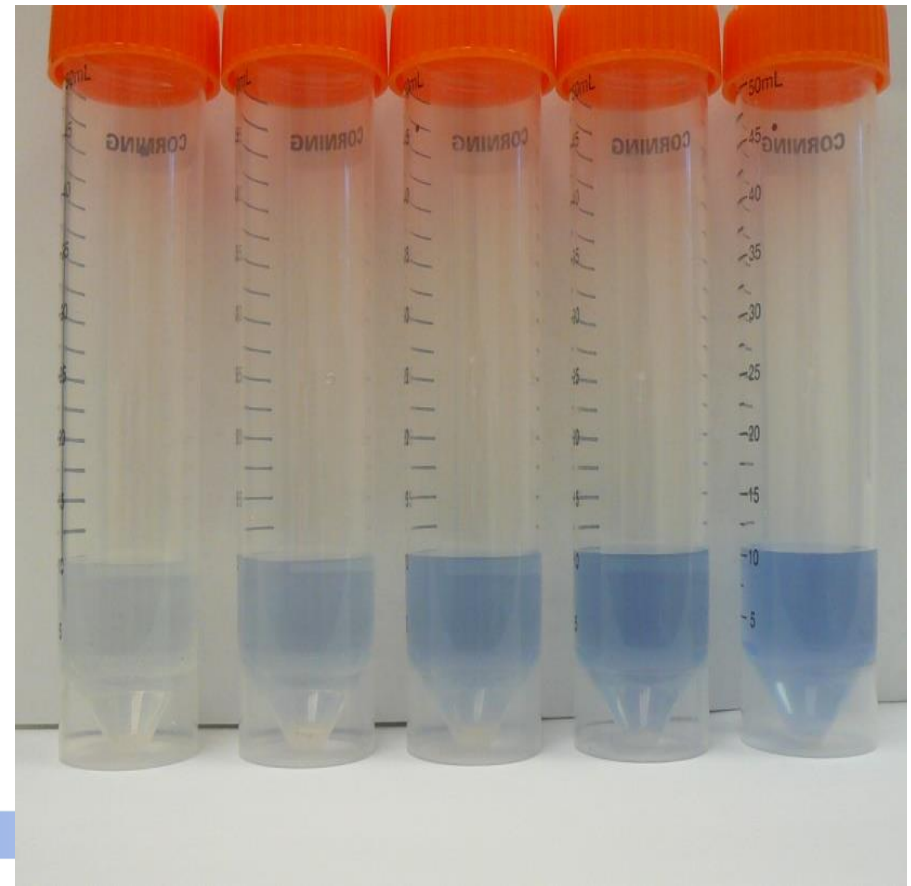


Phosphate Injection Applications

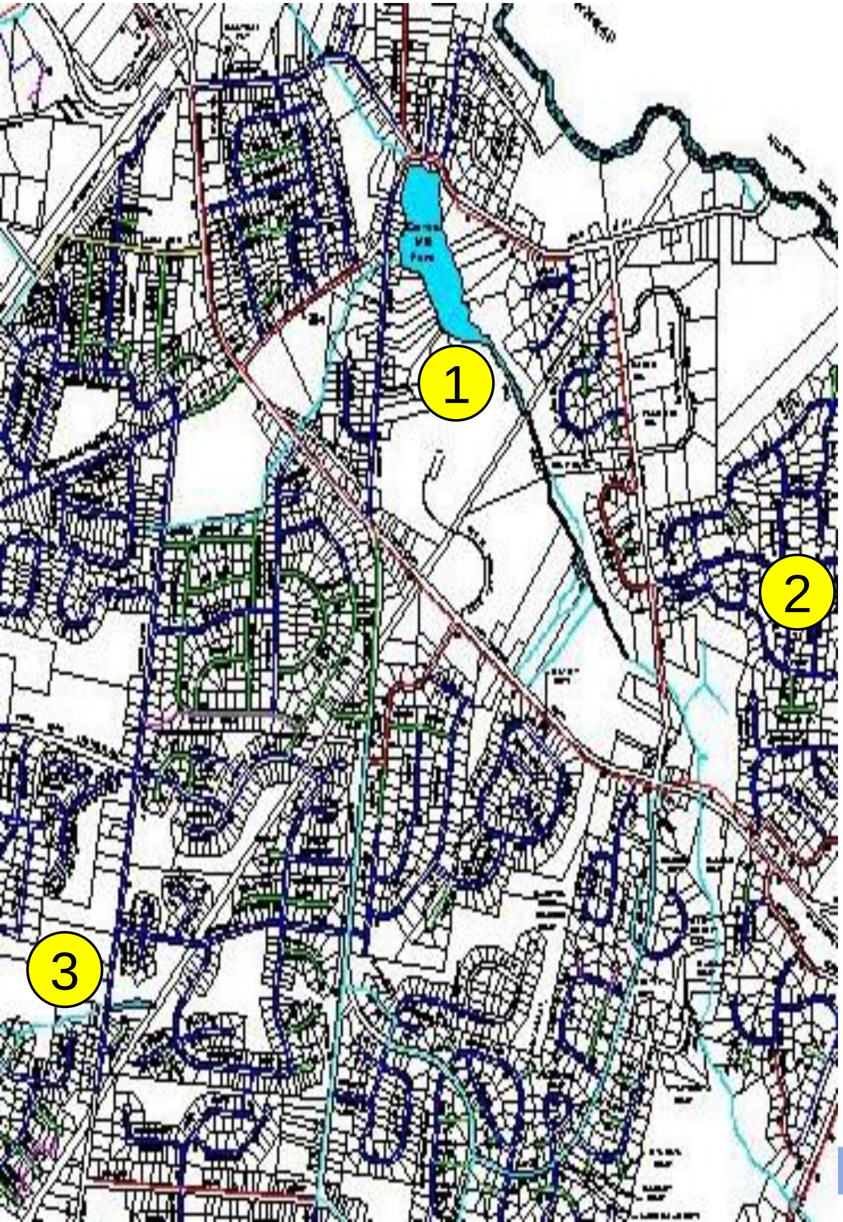
- Typical Phosphate Feed Rate Measurements
  - Calibration of Metering Pump (mLs/min or gals/hr)
  - Weigh Scale for Day Tank (pounds used per day)
  - Level Indicator for Day Tank (gallons used per day)

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?

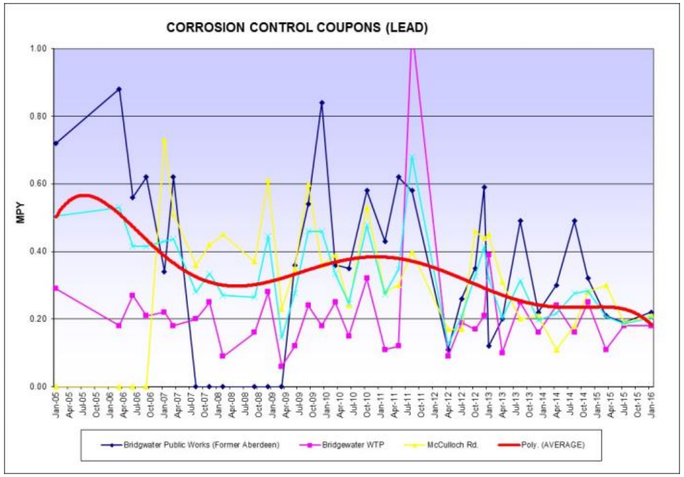


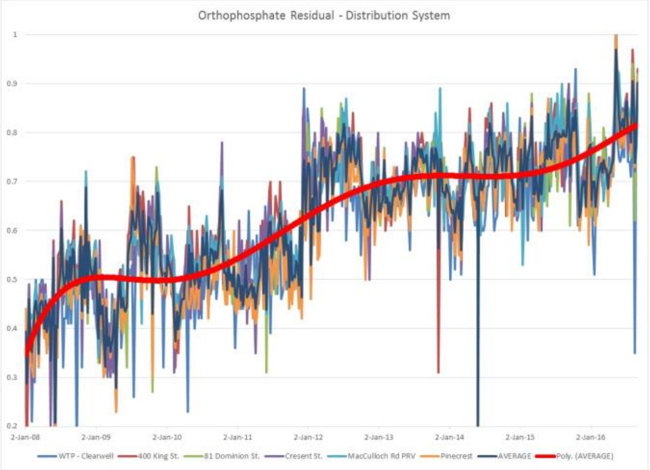
- Test at Finished Water Tap, Distribution System, & Dead Ends
- Results should be at or above the target level throughout the distribution system

Coupon Testing Design

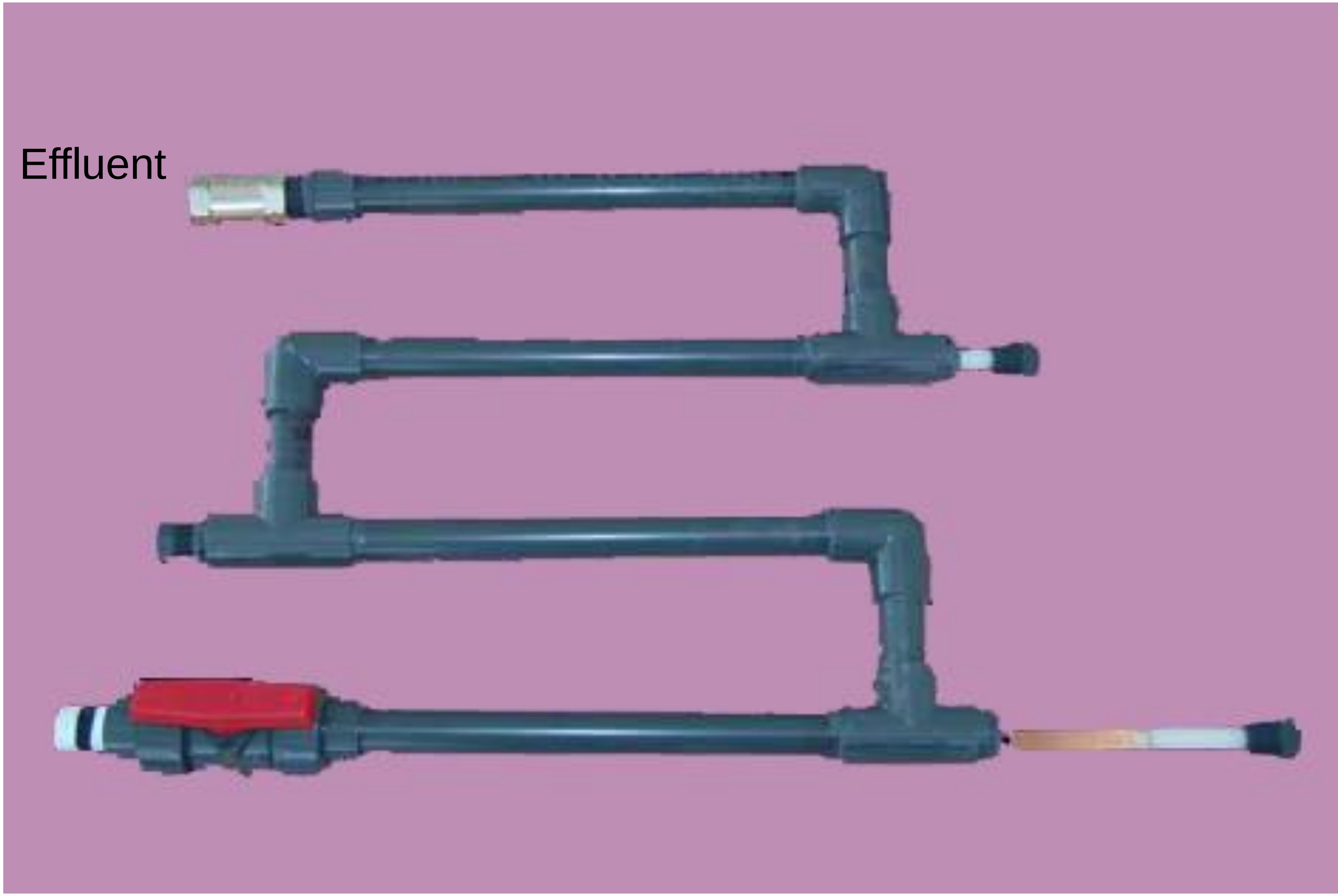
- Coupon Based Monitoring (NACE Protocol)
- Test Exposed Coupons for MPY

  “Mils penetration per year”
- Test Duration (90 days exposed)
- Need non-treated, treated and distribution loops
- Focus on “trend of data” not numerical data





Coupon Testing Rack



Effluent

Influent

Coupon Testing Results

Coupon Exposure:
90 Days

Matrix:
Surface Water

No Treatment

50:50 Blend Treated

Personal Protection Equipment (PPE)

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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