

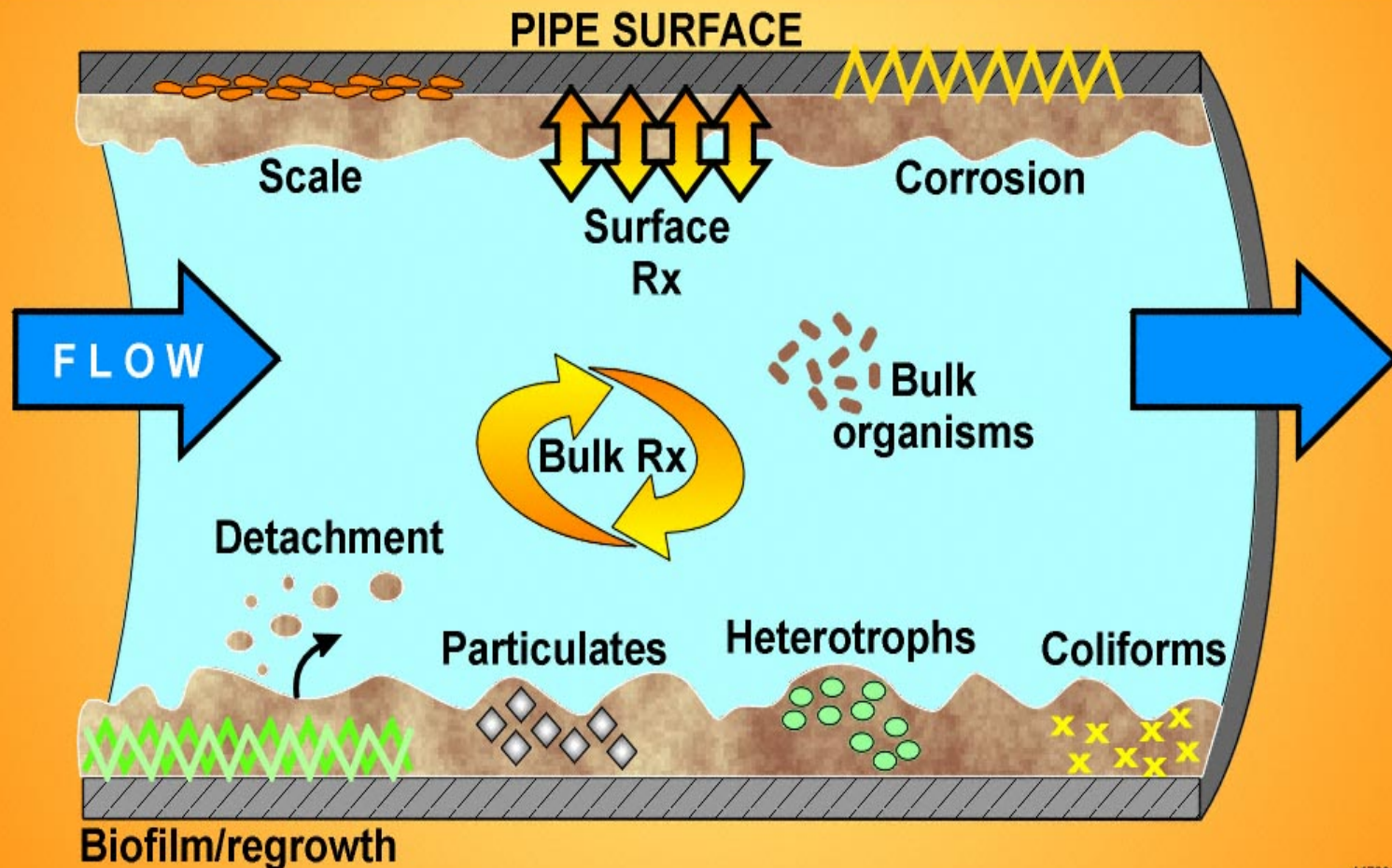
Balancing Distribution System Corrosion Control and Treatment for Simultaneous Compliance

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The Distribution System as Reactor



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Distribution System Materials

- **Iron corrosion**
 - **Materials preservation**
 - **“Red Water”/aesthetics**
 - **Hydraulic efficiency/energy costs**
- **Cementitious materials**
 - **Materials preservation**
 - **Water quality deterioration**
 - **pH increases**
 - **Turbid water & other aesthetics**

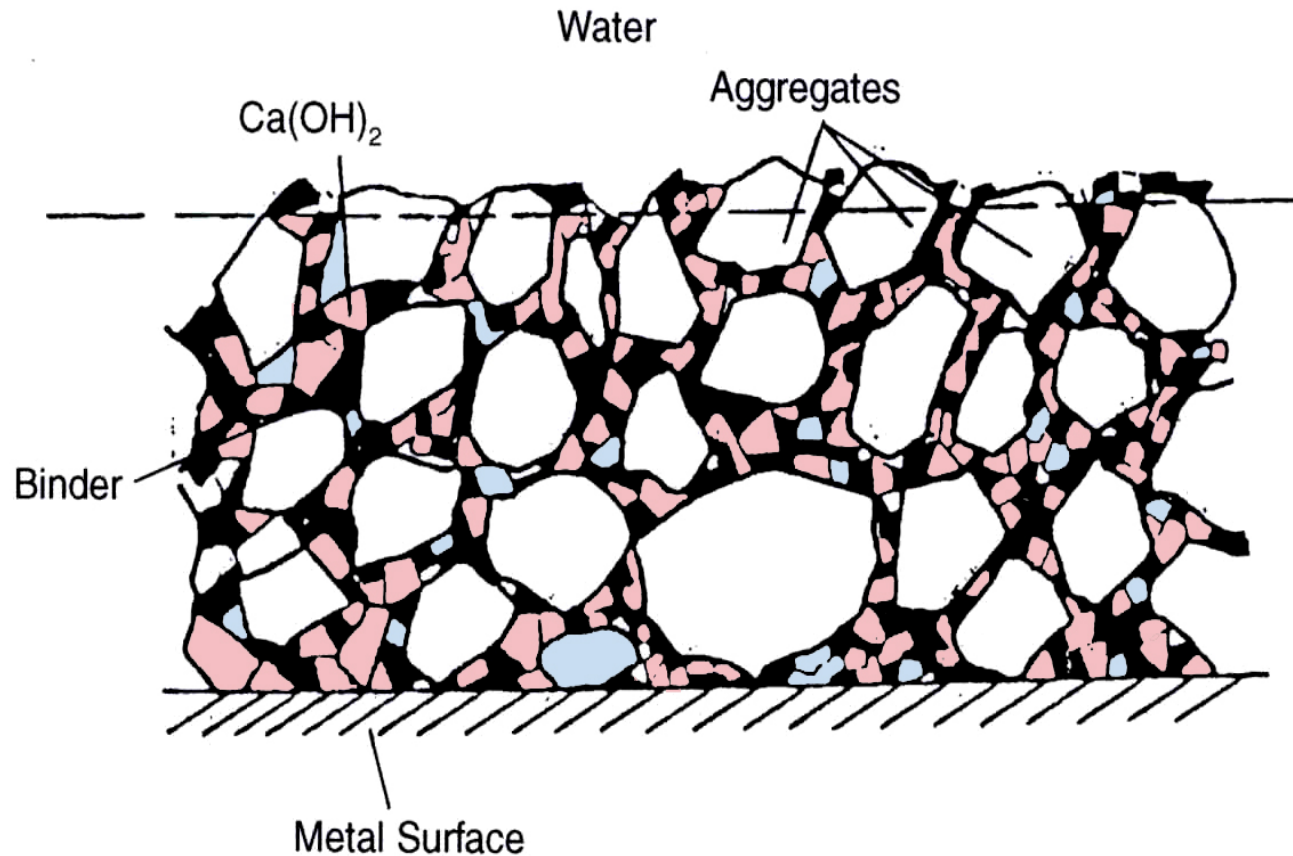
General Nature of Pipe Surfaces

- **Metallic**
 - Oxides, hydroxides, hydroxycarbonates, carbonates, hydroxysulfates, etc. from corrosion
 - Similar compounds from deposition or post-precipitation (particularly Fe, Mn, Al), may include silicates
 - Phosphates from corrosion control
 - All may be mixed with NOM

General Nature of Pipe Surfaces

- **Cement (A-C, CML, Concrete)**
 - **Metallic oxides, hydroxides, hydroxycarbonates, carbonates, hydroxysulfates, silicates, etc. from deposition or post-precipitation**
 - **Aluminosilicates, hydroxides, hydroxycarbonates from “corrosion”**
 - **May be mixed with NOM**

Schematic Anatomy of Cement Lining



A-C Pipes and CMLs Aren't Inert



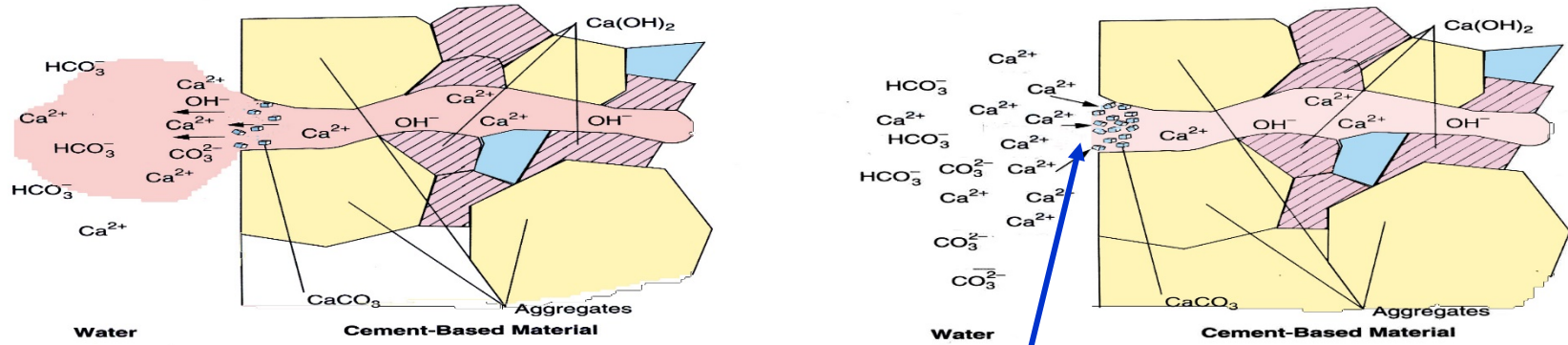
Badly deteriorated from soft water



Accidentally protected, represents good CCT

Lime leached from cement lasts years, can put orthophosphate in bad pH range, and accelerate THM formation

Protection of A-C and CML Pipes with CaCO_3 or Zn Dosing



Formation of CaCO_3 or other solid to plug porosity

- Zn silicate minerals harder than zinc hydroxide or hydroxycarbonate minerals
- Deposition of Zn, not PO_4 , in lab tests
- Initial Zn deposition from water is fast and occurs without significant silica in the water
- Deposits widespread across surface, liberated carbonate may help fill pores

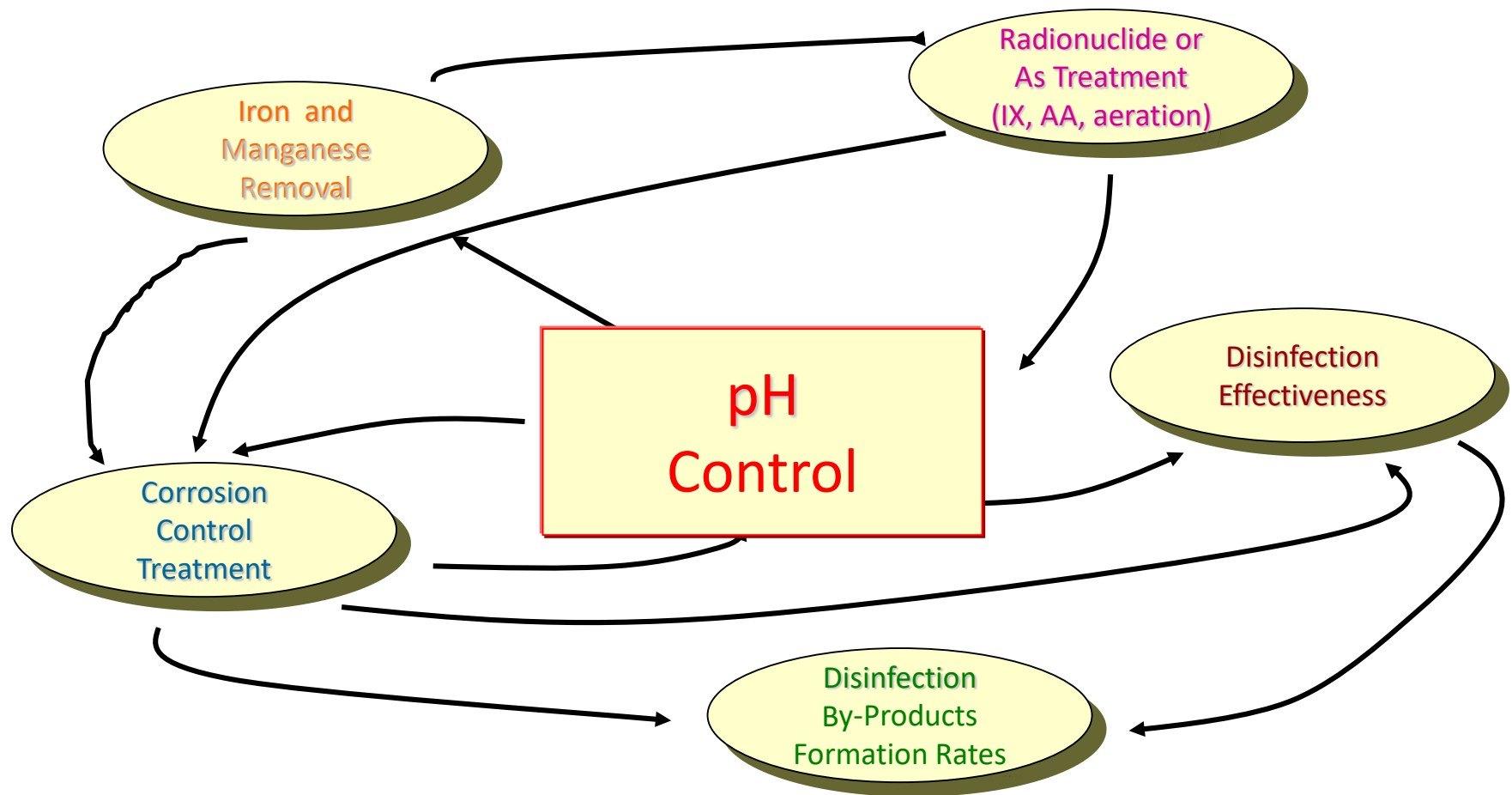
General Nature of Pipe Surfaces

- **Plastics**
 - **Metallic oxides, hydroxides, hydroxycarbonates, carbonates, hydroxysulfates, silicates, etc. from deposition or post-precipitation**
 - **May be mixed with NOM**



Interrelationships of Corrosion Control

pH Interactions with Treatment Processes



Parameters Strongly Affected by pH

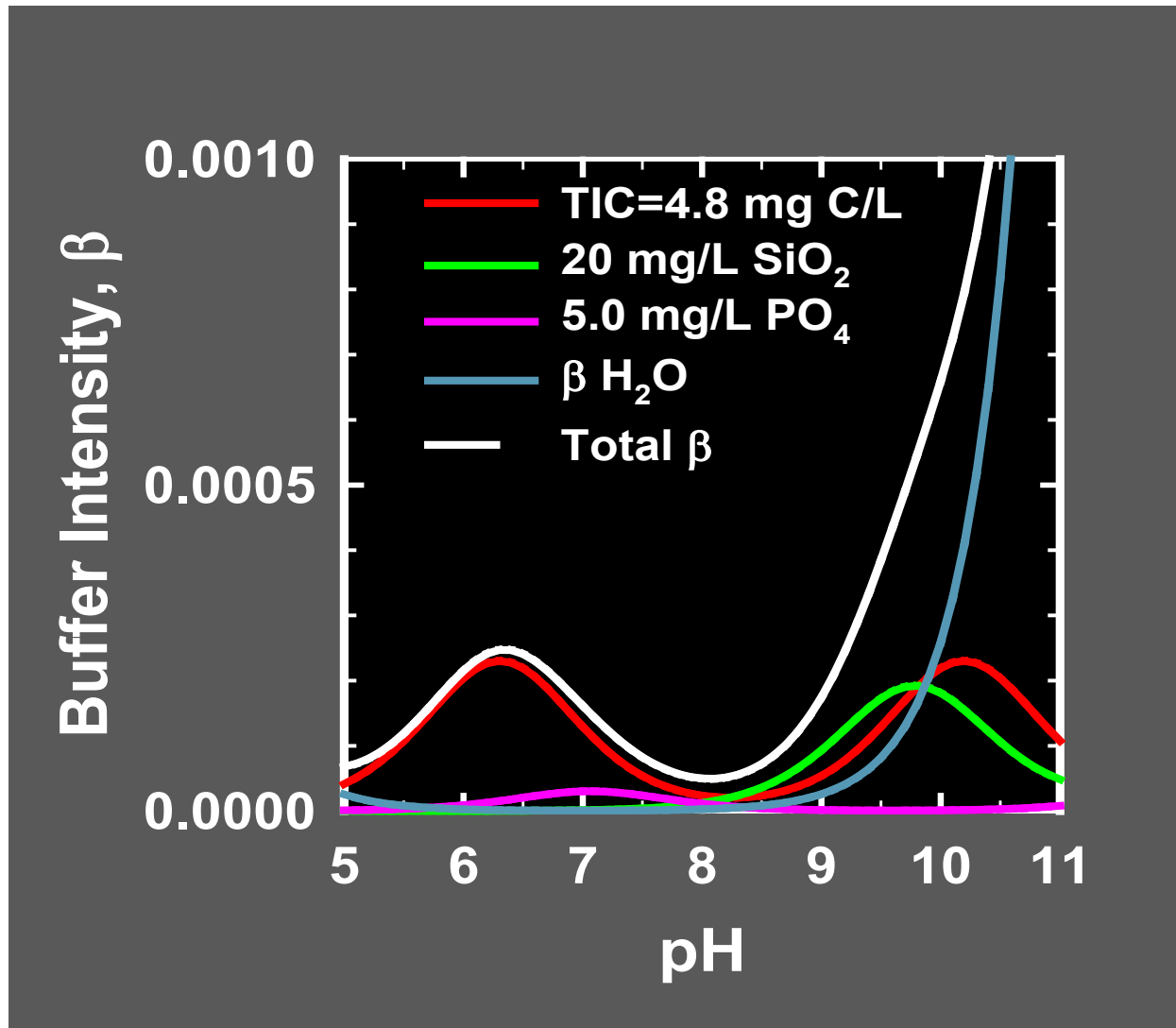
- **Metal solubility (eg. Fe, Pb, Cu, Mn)**
- **Scaling**
- **DBP formation rates**
- **Disinfection capacity and efficacy**
- **Taste and odor**
- **Biofilm growth**

Drinking Water Buffering

- **Usually, only carbonate system is of practical significance**
 - **Governed by DIC & pH if closed system**
 - **CO₂ gas also important if open system**
- **Temperature plays some role**
- **Surface solids may enhance buffering**

Why pH 8.2 Isn't Such a Great Idea

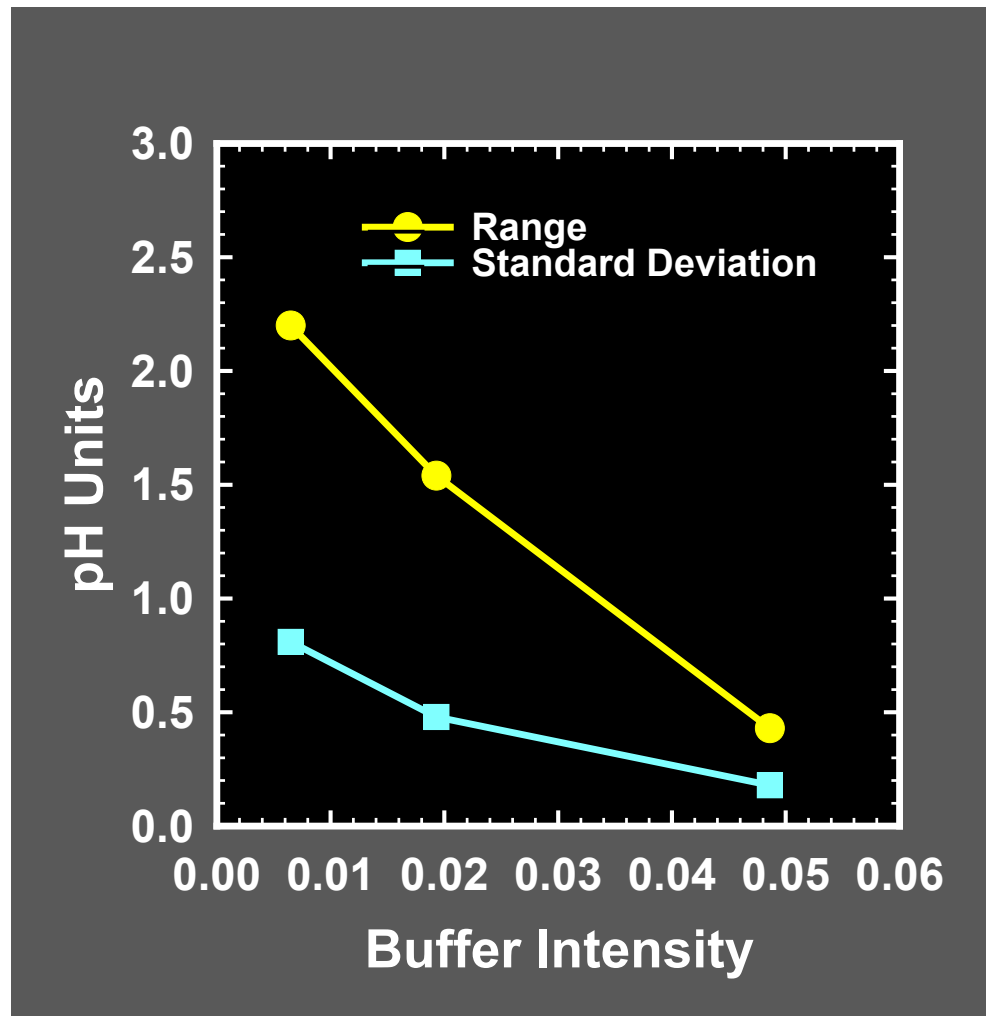
Carbonate, orthophosphate, plus silicate, $I=0.01$, 25°C



Iron corrosion also greatly benefits from better buffering and higher Ca and carbonate

Distribution System pH Variability as a Function of Buffer intensity

Concord, NH case study



**Dramatic reduction
in pH fluctuation by
increase in buffer
intensity.**



RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions



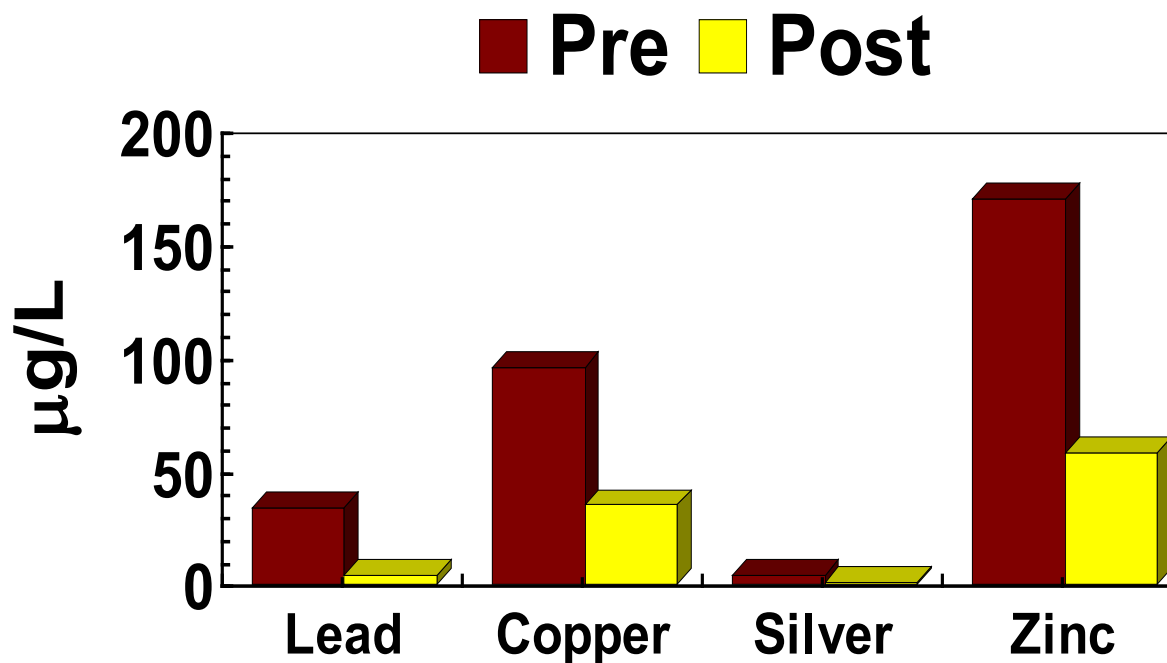
Basic Benefits of Good Corrosion Control

Good Corrosion Control

- **Reduces metal load to wastewater plants**
- **Reduces disinfection & pumping costs**
- **Makes system more robust against disturbances**

Wastewater Discharge Metal Levels

Bellingham, WA Study



Optimal Corrosion and DBP Control

- **Removal of precursor material solves problems**
 - Reduces DBP formation and potential formation
 - Reduces nutrient material, starving biofilms
 - Reduces disinfectant demand and decay
- **Coupling with iron corrosion control is important**
- **Provides protection from copper not covered under the LCR**
 - Wilson's disease
 - Severe gastrointestinal upsets (often infants)
- **May protect against Ni, Cd**

Reduces Microbial Habitat & Nutrition

- Prevents growth of tubercles & rough surface
- Passivates surface to oxidation
- Reduces sorption of NOM
- Stabilizes pH
- Net Result
 - Disinfectant more persistent & effective
 - Removes biofilm support
 - Reduces shelters in tubercles
 - Reduces shelters, support in sediment

Predicting Corrosivity

- Different objectives for different materials
- THERE IS NO UNIVERSAL “INDEX” FOR MULTIPLE MATERIALS
- Only in rare cases is calcium carbonate an active inhibition mechanism
- “Langelier Index” predicts CaCO_3 SCALING, **not corrosion or metal release**

Predicting Scaling: LI versus CCPP

Same Langelier Index

| Concentration | Soft Water High pH | Hard Water Low pH |
|---|-----------------------|----------------------|
| Temp (°C) | 15 | 15 |
| Alkalinity (mg/L as CaCO ₃) | 25 | 350 |
| Calcium (mg/L) | 17 | 130 |
| TDS (mg/L) | 75 | 750 |
| pH (units) | 8.90 | 7.03 |
| LI (units) | 0.10 | 0.10 |
| CCPP (mg/L) | 0.40 | 15 |

Mixed deposits with hardness and carbonate are most likely in high CCPP



Langelier Index Limitations

- **Cannot predict CaCO_3 saturation state in presence of**
 - **Phosphate inhibitors**
 - **Silicate inhibitors**
 - **NOM that interferes with nucleation & growth**
 - **Trace metals that interfere with nucleation & growth**
- **Don't even try to do the calculations**
- **“Marble test” is more accurate for CaCO_3 saturation state**

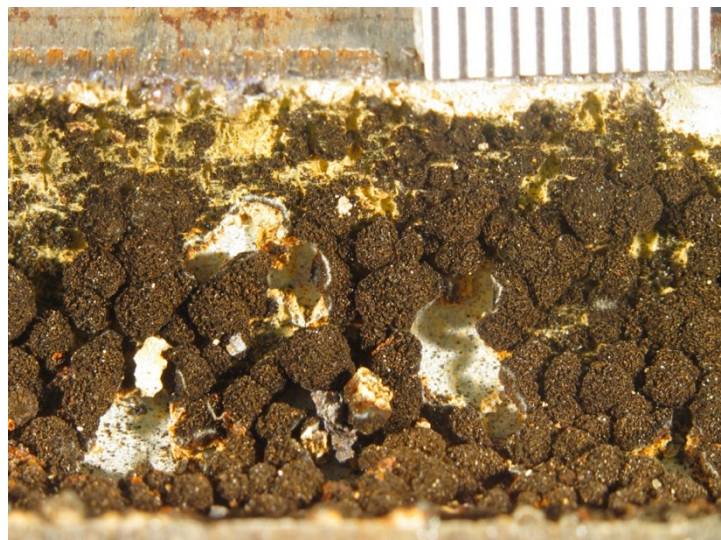


Effects of Different Metal Deposits

One man's corrosion deposit is
another man's removal media...



Mn-Rich Surface Material on Pb Pipe

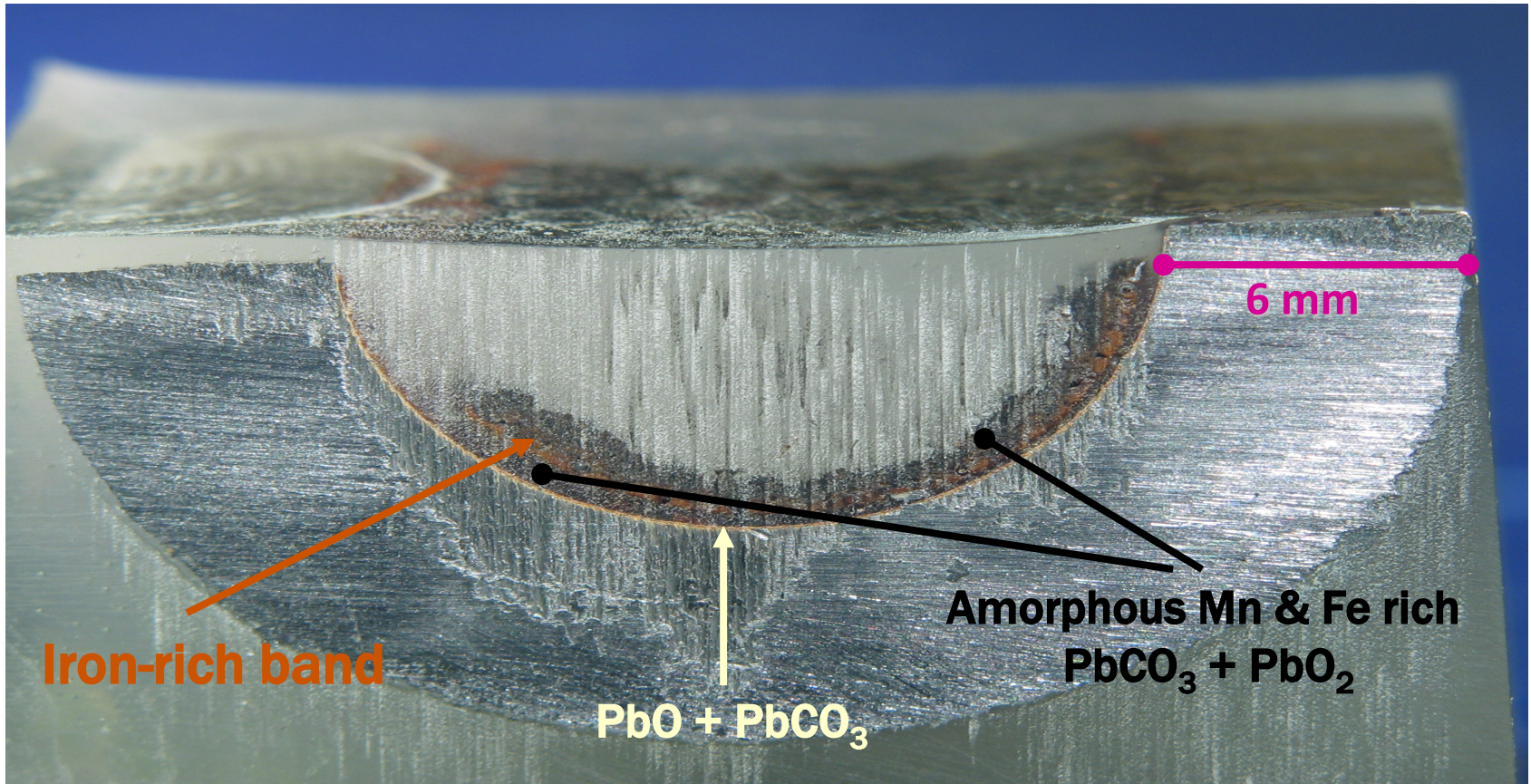


Often erratic Pb release associated with particulates, and poor efficiency of orthophosphate inhibition of lead release.

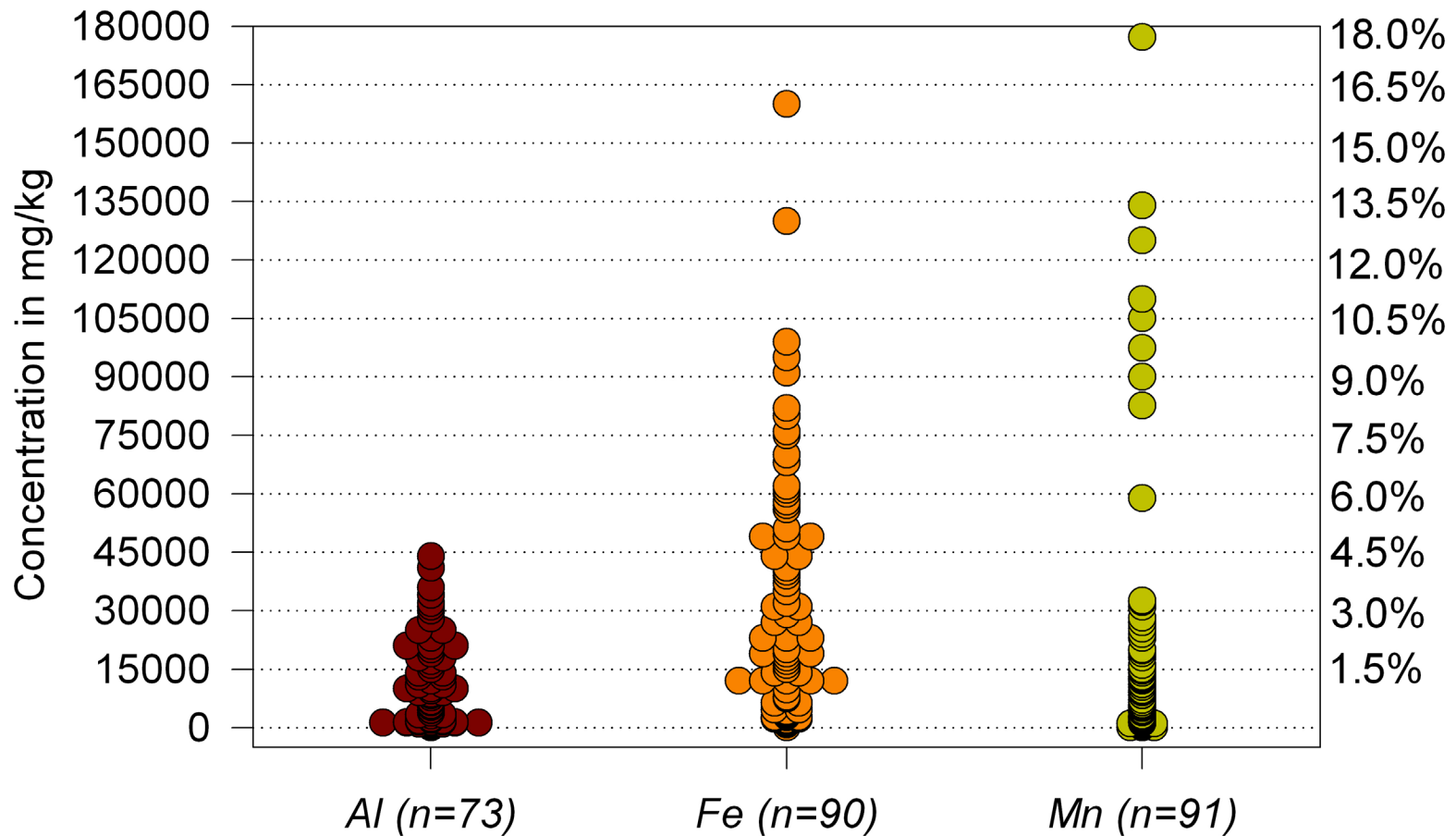
Effect of Surface Coatings

- **Greatly prolongs time it takes to reduce plumbosolvency (many years vs months to years)**
- **More prone to elevated Pb and particulate release**
- **Cu/Pb release indirectly controlled by treatment change impacts on coatings**
- **Requires much higher orthophosphate dosages to achieve equilibrium**
- **[reversibly] Scavenges trace metals and radionuclides that have detrimental health effects**
- **Stability of the coating affects accumulated metal release**

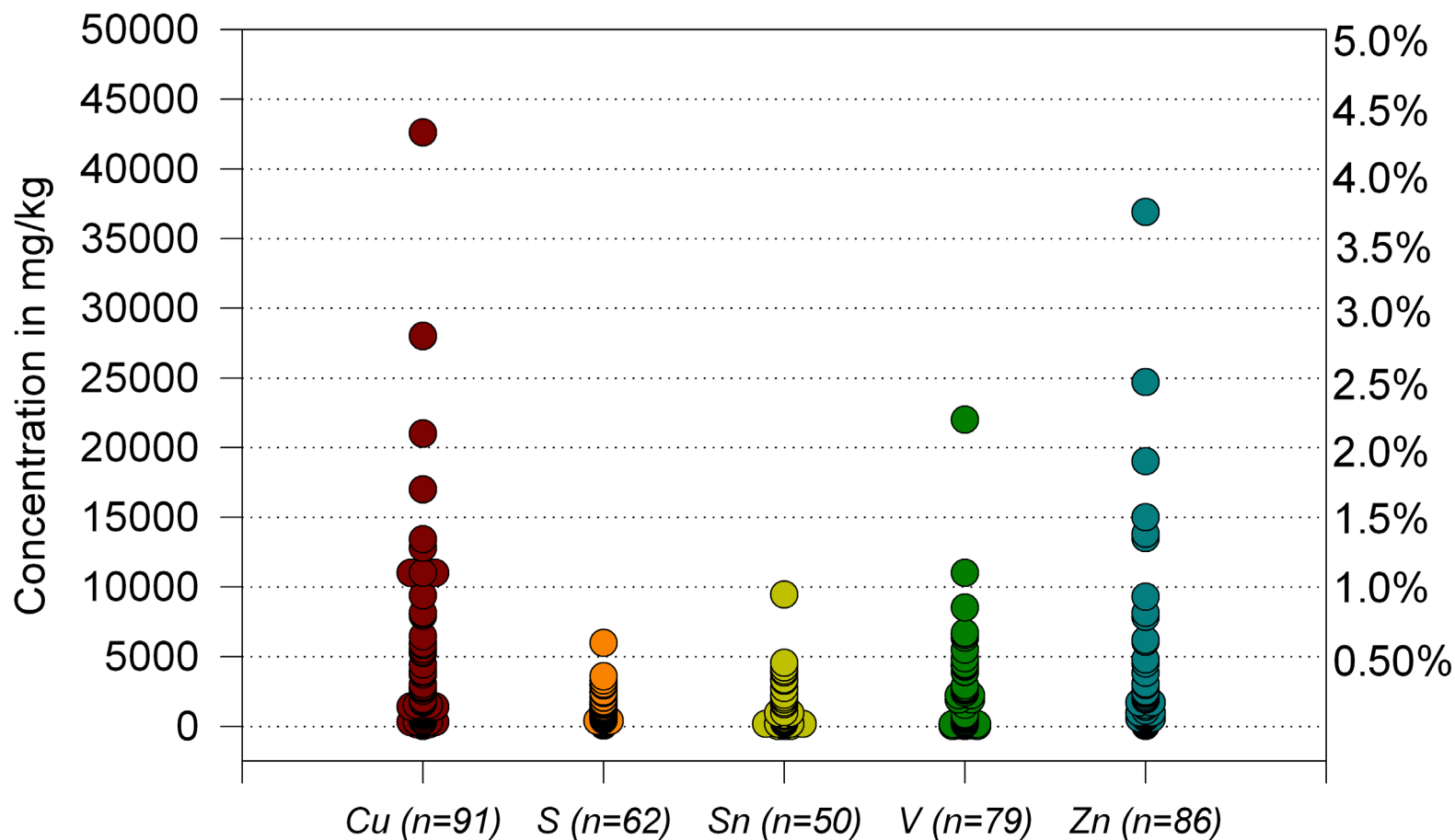
Layering from ORP-Induced Deposition



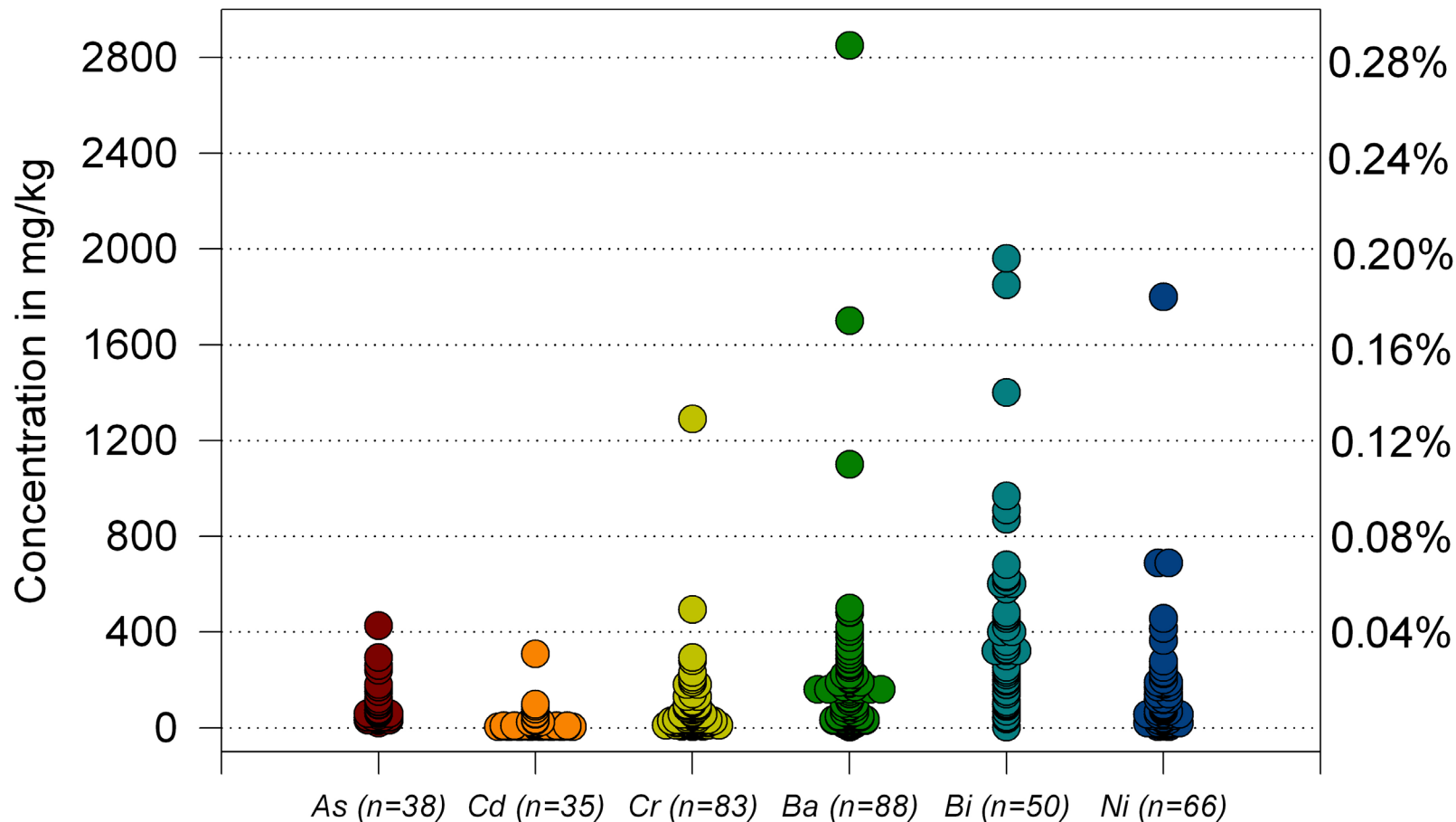
Pb Pipe Survey: Major Constituents



Pb Pipe Survey: Moderate Constituents

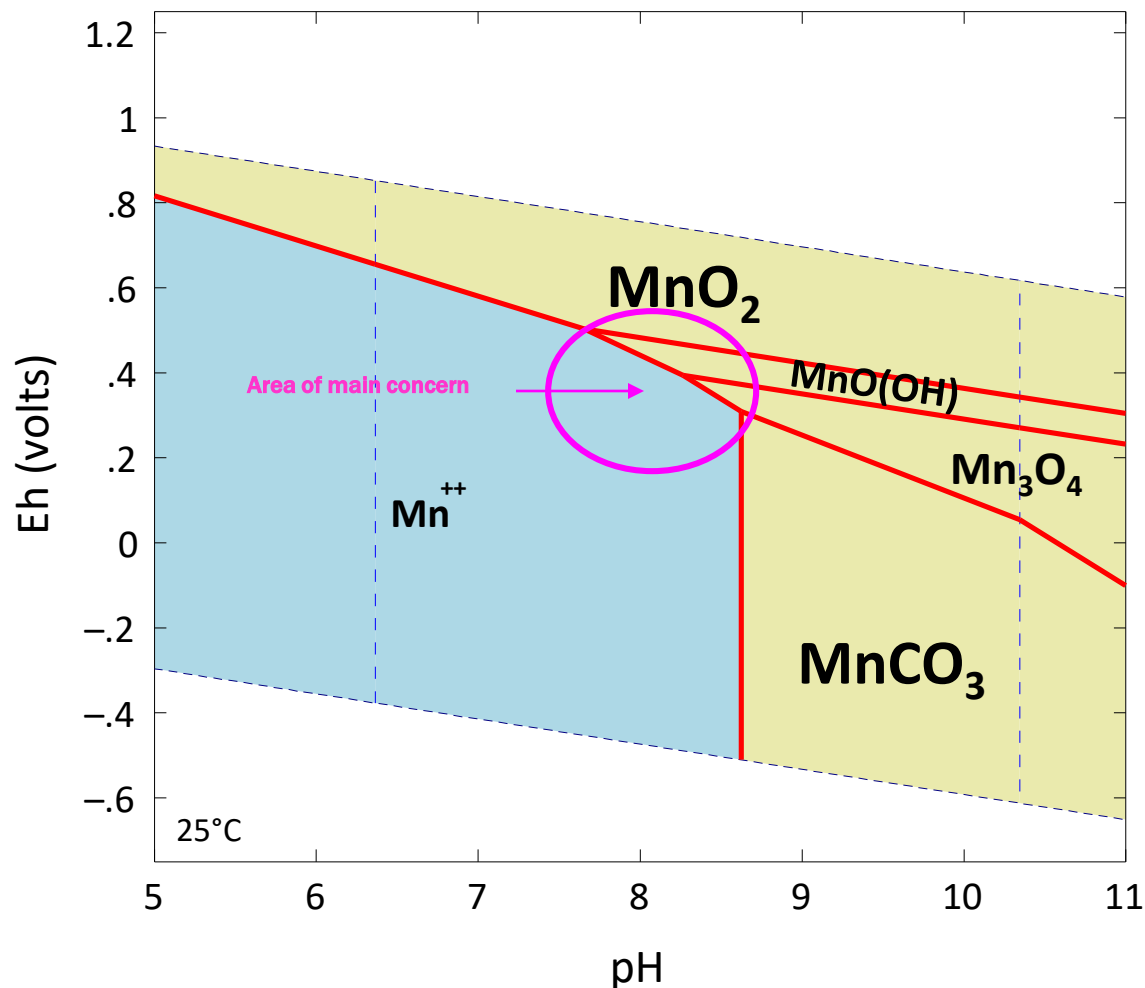


Pb Pipe Survey: Minimal and Minor Constituents



Importance of Speciation in Mn Mobility

Mn (0.05 mg/L) DIC = 18 mg C/L



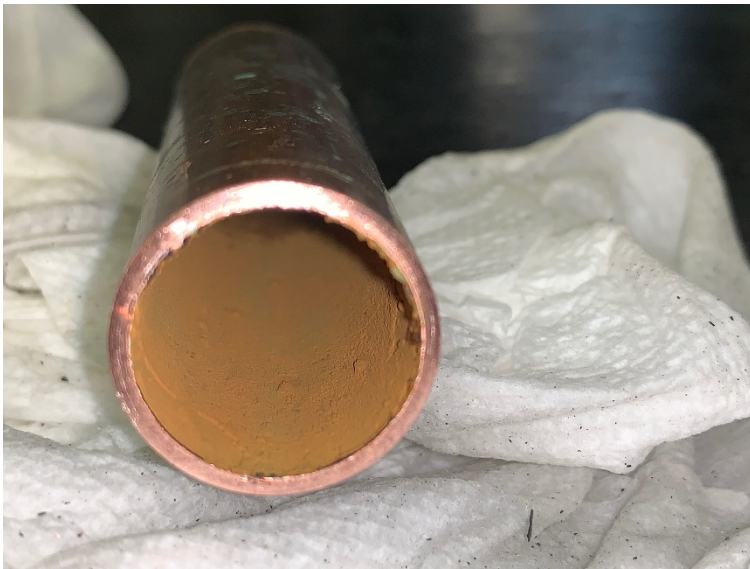
Simple Fact: Inorganics are NOT “Conservative” in DS

- **Trace metals**
- **Radionuclides**
- **Nitrate, nitrite and ammonia**



Destabilization Example

- Hard, high alkalinity anoxic GW, with inadvertent chloramination
- Shift to soft surface water, pH 8.5: **Scales dissolve**
- About 1-2% Pb by weight in the scale
- No LSLs



(By permission from Cornwell Engineering)

Lead (II) Reaction Pathway Matters

(going back to 1996)

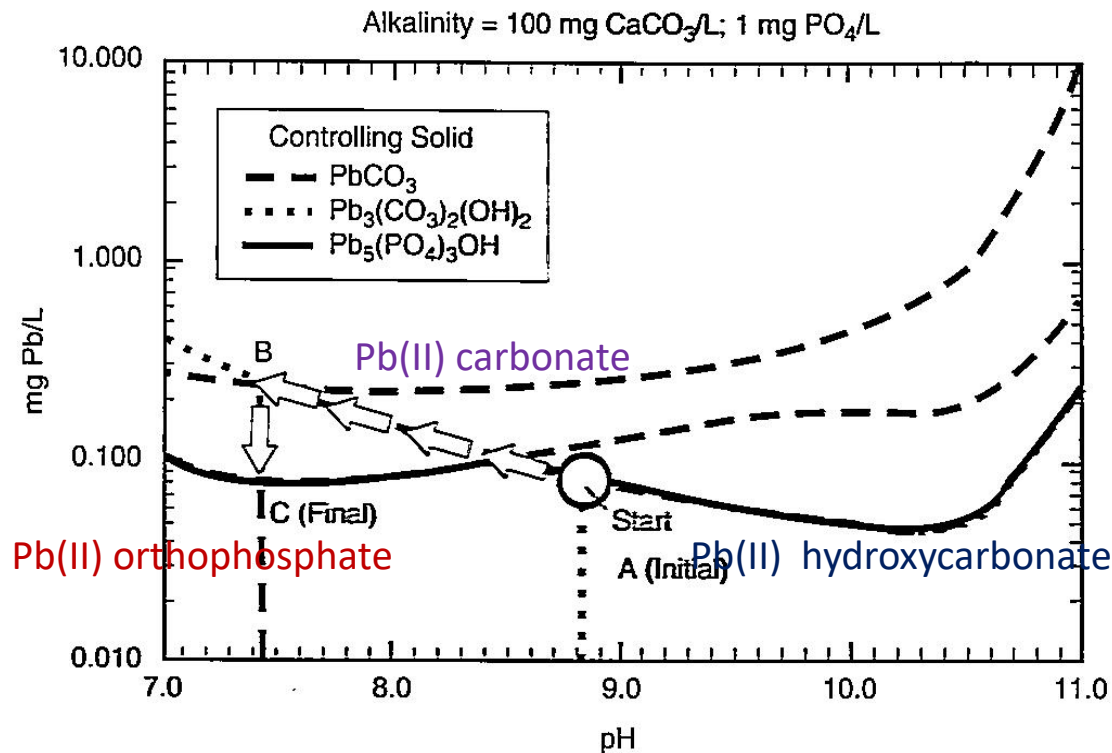
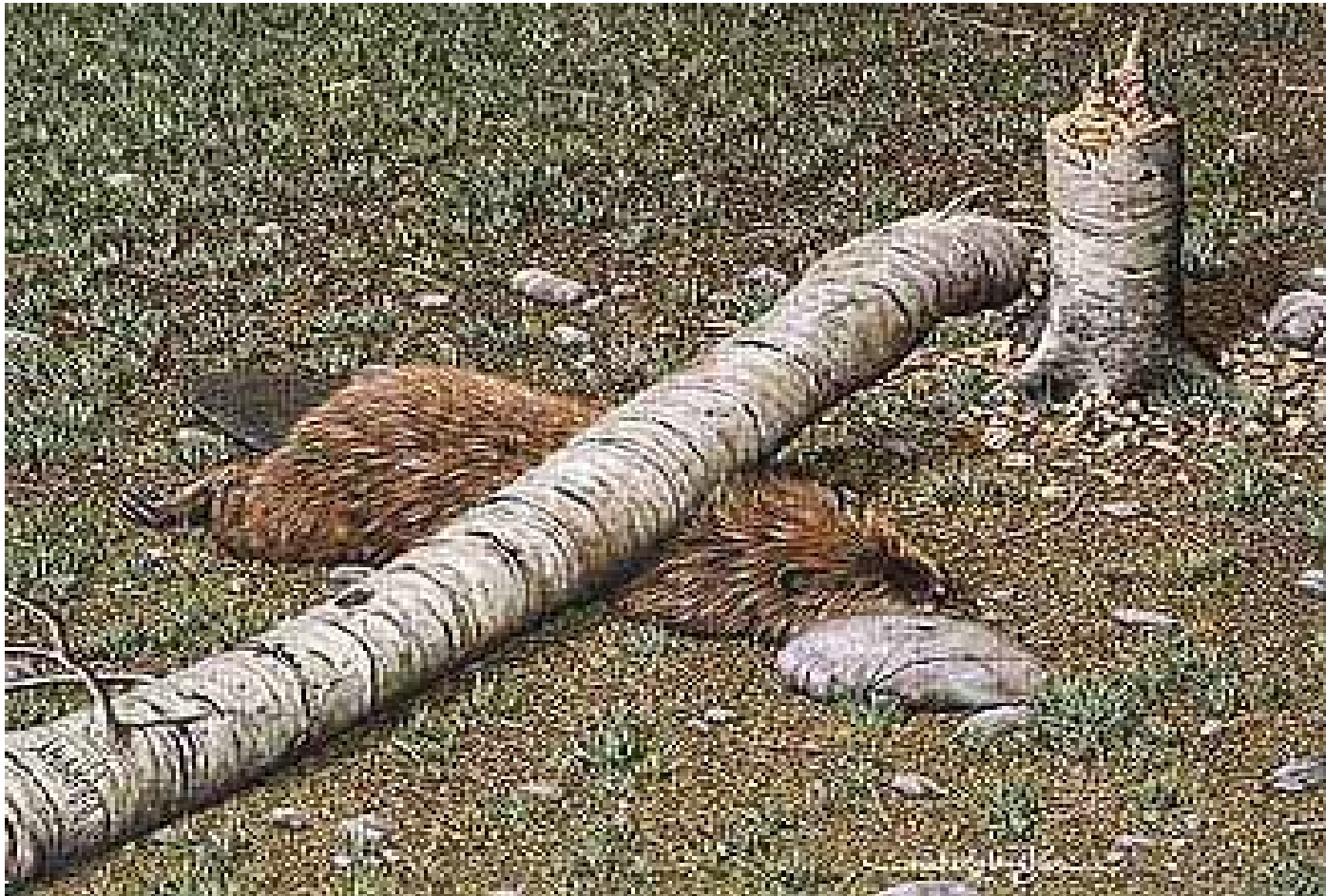


Figure 4-43 Hypothetical path of lead solubility in response to changing stability of passivation films for a water with alkalinity of 100 mg CaCO_3/L and orthophosphate dose of 1 mg PO_4/L after pH decrease

Why Do We Think This Is Important?

- “Discolored” water isn’t just aesthetic
- Coprecipitation and sorption are potentially *reversible* processes
- Dissolution is possible with favorable kinetics
- Growth in complexity of health-based water regulations (e.g. Pb, Cu, As, TCR, perchlorate, D/DBP) requires treatment changes
- Growth in water demand or deterioration in quality requires additional water sources, treatment plants, blending
- Changes in pressure and flow velocity/direction easily mobilizes sediment and microparticles

Some Thoughts on Vulnerability to Unintended or Unwanted Side-Effects



Vulnerabilities to Disinfectant Change Problems

- **Lead service lines and history of very low Pb levels**
 - Ground waters not previously disinfected
 - Surface waters without phosphate inhibitors
 - Possible PbO₂ scales
 - High chlorine residuals or oxidizing treatments?
- **Mn deposits in distribution system and service line piping**
- **Nitrite already present in the water**
- **pH is 7-8.5, optimum for nitrification**
- **Accumulated tuberculation and sediments that could be mobilized (phosphate, pH change)**
- **NOM providing nutrient for biofilm**
- **Poor buffer intensity**

Imbalancing Processes

- **Softening processes**
 - Lime softening change to IX
 - Lime softening to RO
- **Tight membrane processes**
- **Optimum or enhanced coagulation**
 - Changes in type of coagulant
 - Changes in coagulant dosage
- **Polyphosphate sequestration**
- **Major changes to pH, Ca, Alkalinity (DIC)**
- **Changes in levels of oxidants through introducing disinfection (GWR)**
- **Anion exchange treatment that can affect bicarbonate concentration and pH**

Polyphosphate Sequestration

- **Competes with carbonate and orthophosphate ions trying to form passivating films on pipes**
- **More aggressive in solubilizing Pb and Cu in soft waters without competition from Ca**
- **Reduces effectiveness of existing Ca, HCO_3^-**
- **Attacks calcareous cement minerals**
- **Prevents Ca-supported passivation**
- **Frequently causes post-deposition of Mn and Fe, hindering health (Mn) and effective corrosion control**

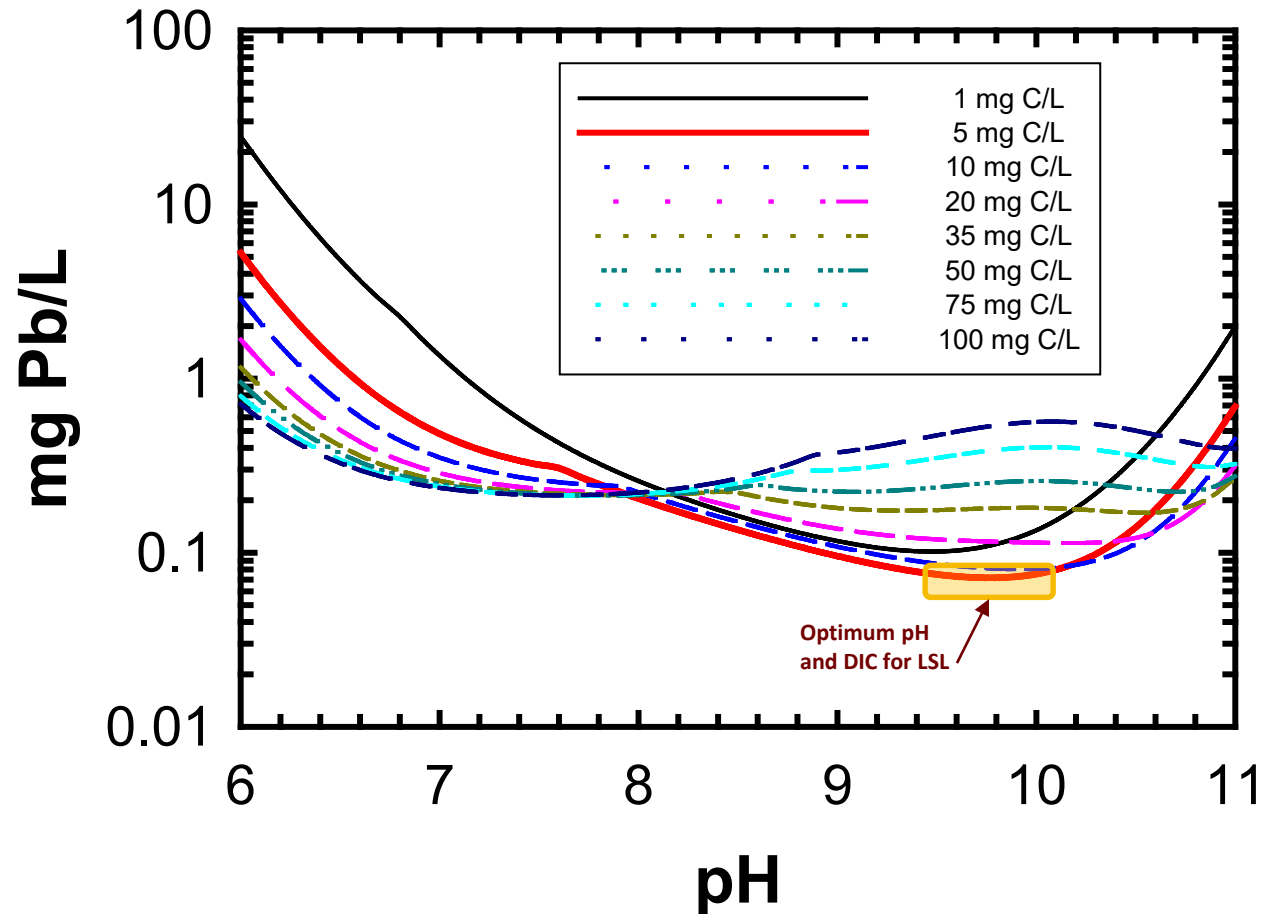
Minimize Water Quality Changes

- **Well-buffered water**
 - Reduces general corrosion
 - Reduces tuberculation of iron
 - Deters nitrification
 - Holds quality with storage
 - Facilitates action of phosphates
- **Balance of hardness, DIC, pH--Why?**
 - Unlined iron
 - Cement linings
 - Asbestos-cement
- **Dissolution of existing scale that can release accumulated metals**
- **Cyclic precipitation and dissolution of scale minerals (especially PbO_2)**

Optimal Corrosion and DBP Control

- **Removal of precursor material solves problems**
 - Reduces DBP formation and potential formation
 - Reduces nutrient material, starving biofilms
 - Reduces disinfectant demand and decay
- **Removal of source Fe, Mn and NOM removes CCT potential conflicts**
- **Coupling with iron corrosion control is important**
 - Reduces demand, hence dosage, hence DBPs
 - Reduces microbe habitat, less disinfectant needed

Classic Pb(II) Solubility W/O PO_4



- The first formed solids with major treatment change.
- It is only possible to nearly minimize Pb levels at $pH > 9$. Can only work in “soft” waters.
- Likely never as good as PbO_2 or orthophosphate

Do NOT Forget Basic Solubility

- **LCR sampling does not capture LSL**
- **LCR sampling does not target high risk copper**
- **If pH < 9-10, suspect lead levels are high in LSL water, regardless of 90th percentile results**
- **If Pb levels are low in LSL water in free chlorine system, suspect PbO₂ scale**
- **If alkalinity > 200, check for high copper in areas of new construction/rehab with copper pipe**

Obsolete Practices Persist: Examples

- **Still widespread use of LSI for Pb and Cu corrosion control in spite of last 30+ years of research to the contrary**
 - pH is a shared factor
 - Alkalinity increase can increase corrosivity
- **State(s) still enforcing Secondary MCL for pH at 8.5**

Need to Revisit Old Research

This is, after all, a RESEARCH symposium)

- What water chemistry factors favor or prevent tuberculation?
- What are the roles of pH, hardness, chloride and alkalinity on improving unlined CI and DI performance, balanced with CML, AC, etc.
- Role of pH, alkalinity, hardness, orthophosphate and chloride on galvanically-driven corrosion
- Benefits of zinc orthophosphate for galvanically-driven corrosion, freshly-relined with cement, and existing CML and AC pipes
- Potential benefits of orthophosphate on iron and lead at high pH



Questions?

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