Hot Research Topics in Lead Control

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Topics to be Covered

- Sampling Issues
- Importance of ORP/oxidants in lead solubility and release
- Results vs. Predictions: Fundamental pH-DIC relationships
- PbO_2 occurrence and implications
- Optimizing orthophosphate dosage factors
- Dissimilar scale materials on Pb surfaces
- Unusual lead minerals comprising bulk of scale
- Stagnation behavior of Pb
- Water quality monitoring & simultaneous compliance

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Known Issues with Sampling

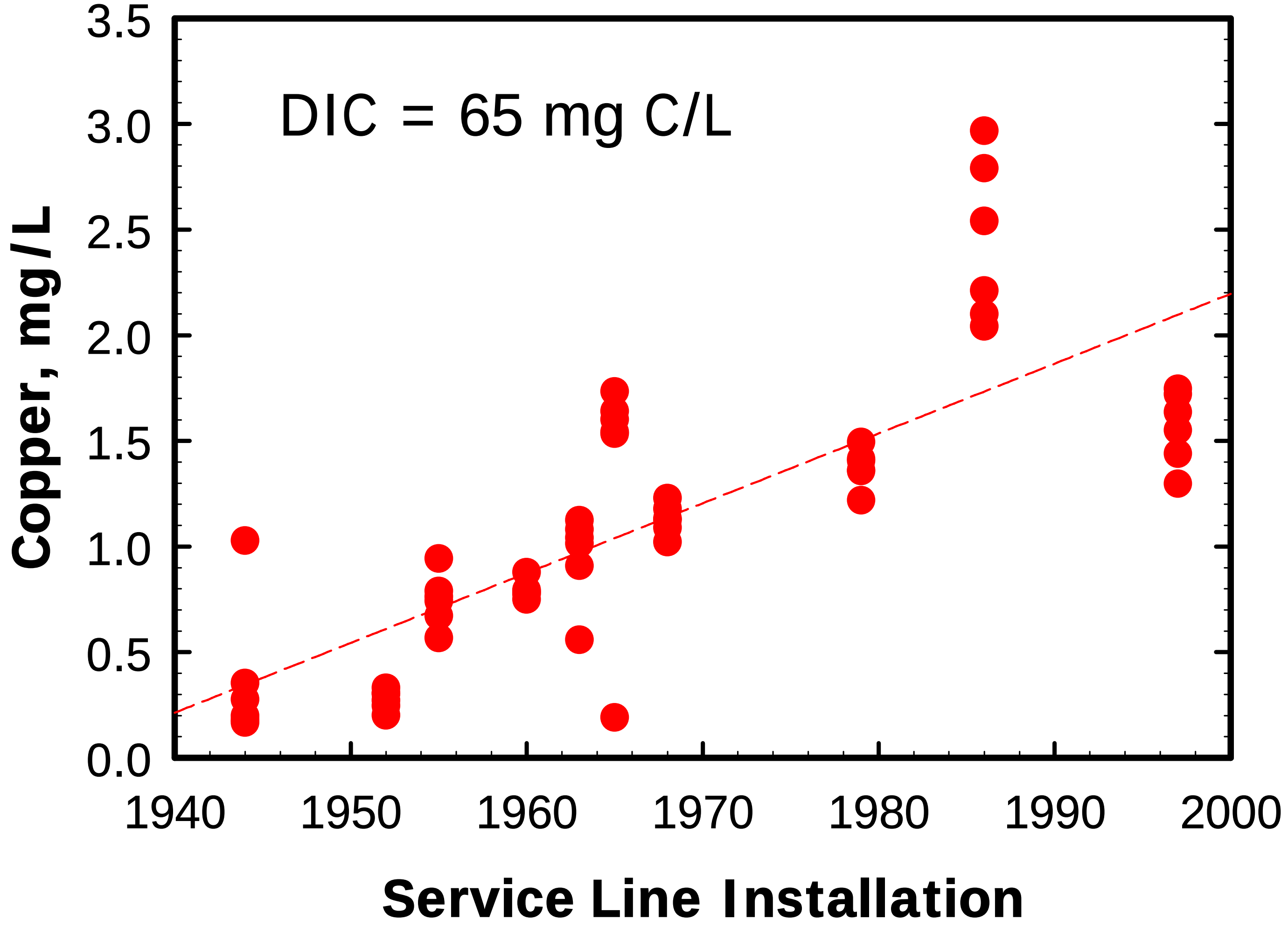
- First-draw protocol may miss peak Pb concentrations in LSL locations
- The contribution of faucets and soldered joints to first-draw remains uncertain
  - Probably age and water-quality dependent
  - Many water systems without LSLs exceed AL
  - Degree of improvement in Pb release from Proposition 65 and NSF 61 Section 8 & 9 devices not systematically investigated
  - Enforcement through plumbing codes and voluntary 3rd party certification leaves many consumer coverage gaps

Known Issues with Sampling (cont'd)

- After LSLs, what is *really* the worst-case?
  - Soldered-joints containing Pb (current)?
  - Lead pig-tails?
  - Old faucets/valves?
  - New faucets/valves?
  - Brass in-line devices?
- Research clearly shows high Cu values systematically missed by current targeting

Cu vs. Age, Midwest Groundwater

Representative Example of Many Systems (no PO_4)

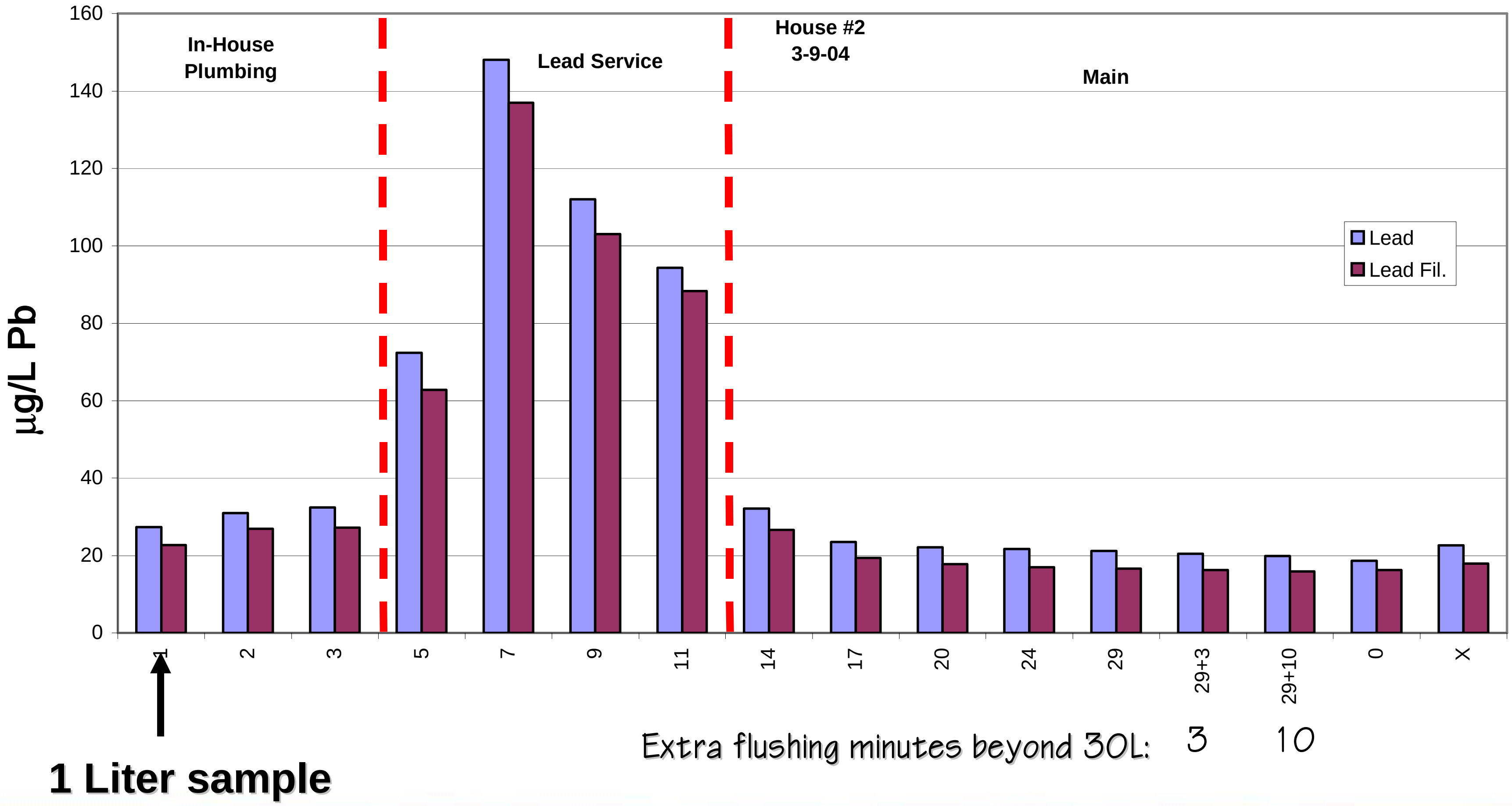


Summary of First-draw Issues

- Gives closer representation of worst-case slugs of lead that typify domestic plumbing situations than flushed samples
- Discomfort with consumer-collected samples remains
- Ability to detect/predict high exposures becomes reduced as corrosivity is reduced
- Multitude of plumbing configurations makes specifically capturing LSL contribution difficult
- Instead of 1st draw, modification can use 3rd, 4th or 5th or other sequential draw to get farther back into plumbing system to capture LSL
- Ongoing research in UK on random daytime sampling (large number of samples)

First Draw May Not Reach Pb Contamination

Need to "Profile" Sites for Public Education Flushing Guidance



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Treatment Influences on ORP in Drinking Water

- Disinfection
- Pre-oxidation (O_3, H_2O_2, ClO_2, $KMnO_4$)
- Oxidative metal removal (eg. As, Fe, Mn)
- Ammonia removal
- Aeration (corrosion control, VOC, Rn, H_2S removal)
- Taste and odor control

Notes on ORP Significance

- Most disinfecting agents or other oxidants have pH-dependent ORP relationship
- ORP affected by pipe and bulk water interactions
  - Reduced metals on pipe surfaces, such as Fe
  - NOM
  - Sulfide, ammonia, etc.
- ORP affects Pb & Cu solubility in opposite directions
- ORP affects post-treatment deposition & stability
  - Fe
  - Mn

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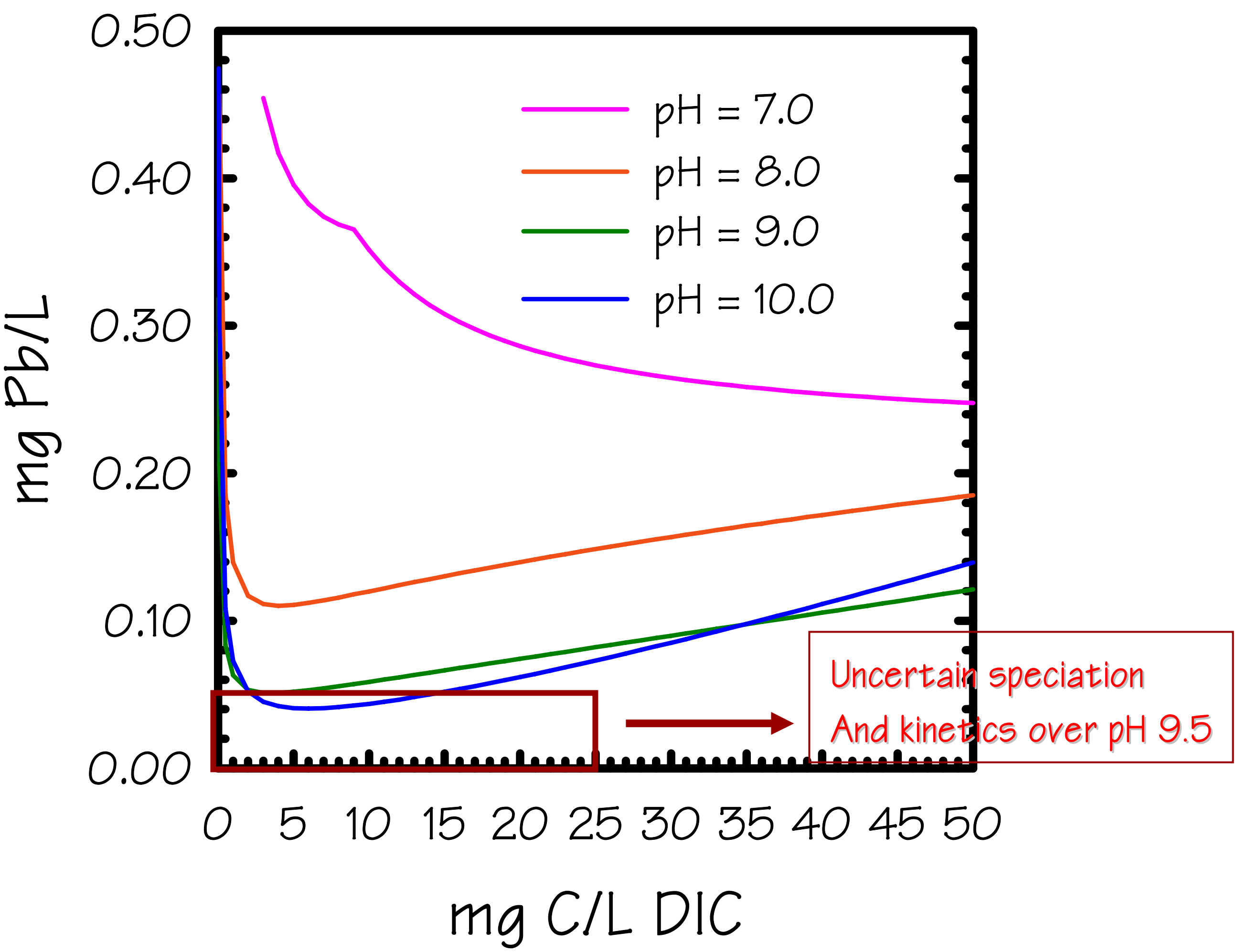
How Well Solubility Models Predict Pb and Cu

- Pb generally follows traditional models well, except
  - When PbO_2 is significant
  - At pH's over about 9.6
  - Substantial non-Pb mineral surface deposits
- US cities with large number of LSLs have needed to
  - Keep pH over 9 in distribution system (low alkalinity & lime softened)
  - Sufficient orthophosphate dosing in proper pH range (approx. 7.2-7.8)
- Cities without LSLs can sometimes use pH's in 8-9 range, if there is sufficient buffering.

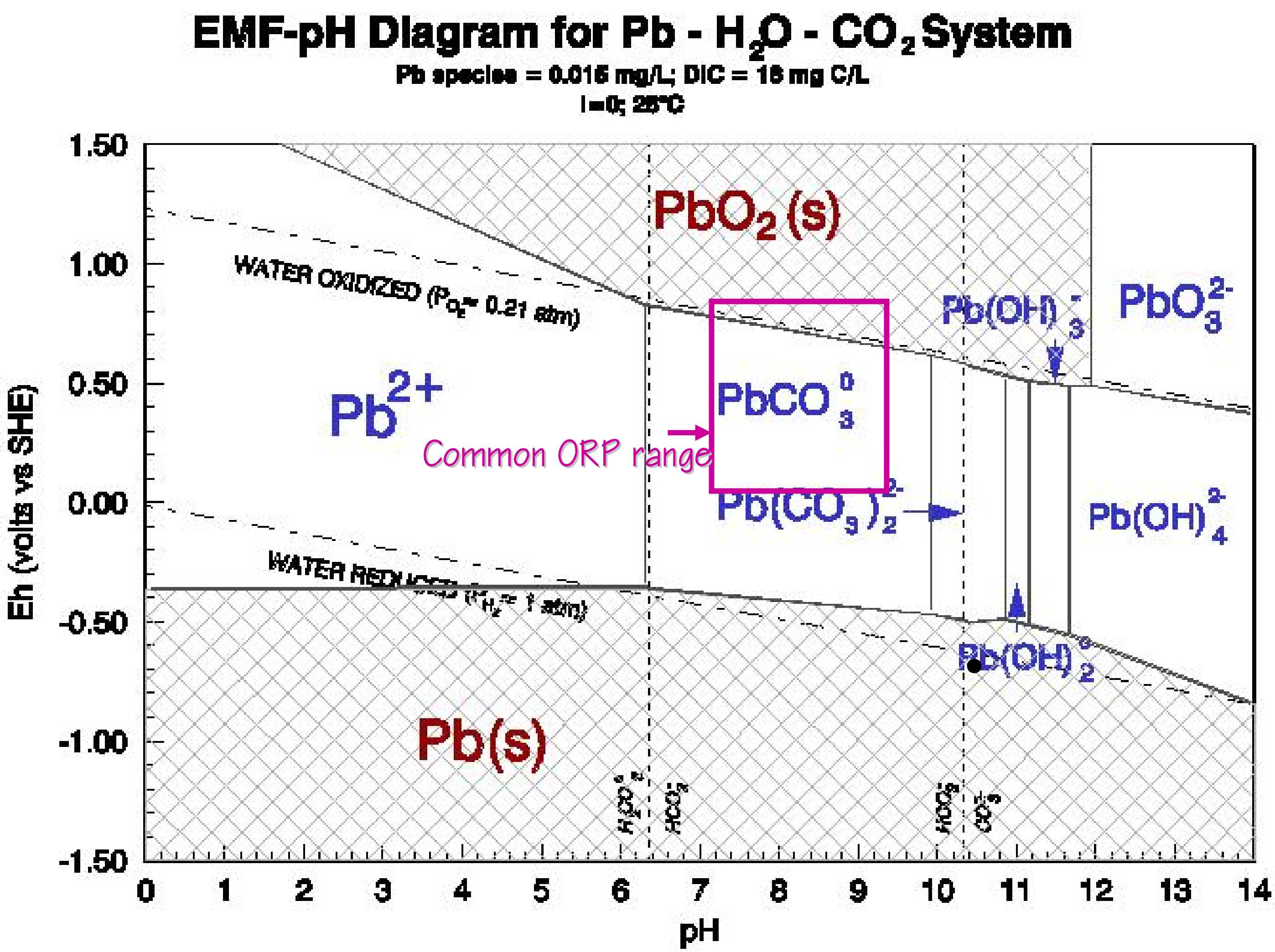
How Well Solubility Models Predict Pb and Cu

- Worst copper problems at low pH and high alkalinity
- Worst ability to keep stable pH: 8 to 8.5
- Copper follows solubility models well, provided that metastable phases (cupric hydroxide and aging) are taken into account
- Optimization of pH and DIC combination for best scale transformation kinetics is still a research issue

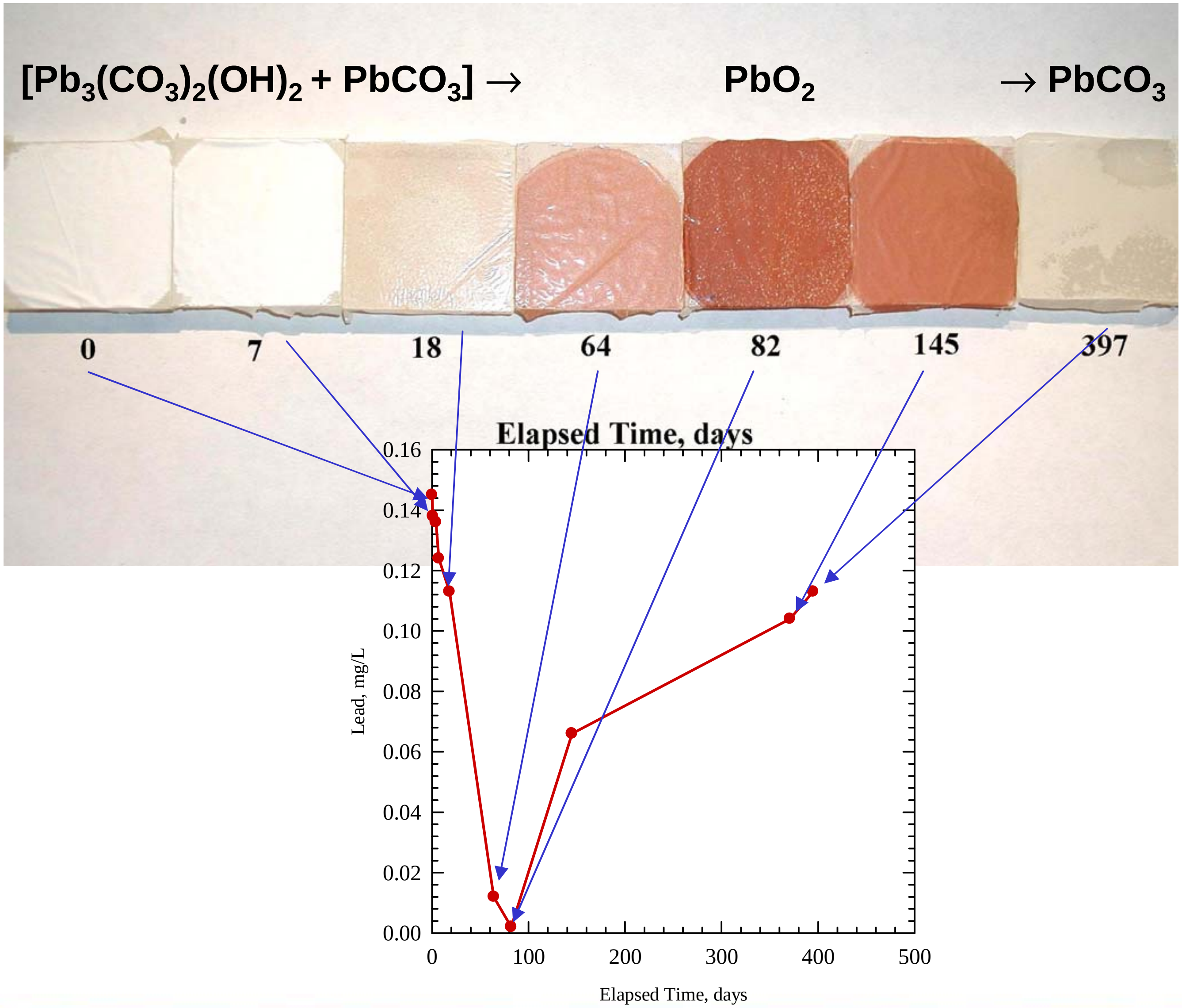
Pb(II) Solubility for $PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$



Pb(II)-Pb(IV) Relationships



Pb(IV) Solubility, DIC=10, pH 7.9-8.2, 3 mg/L Cl_2



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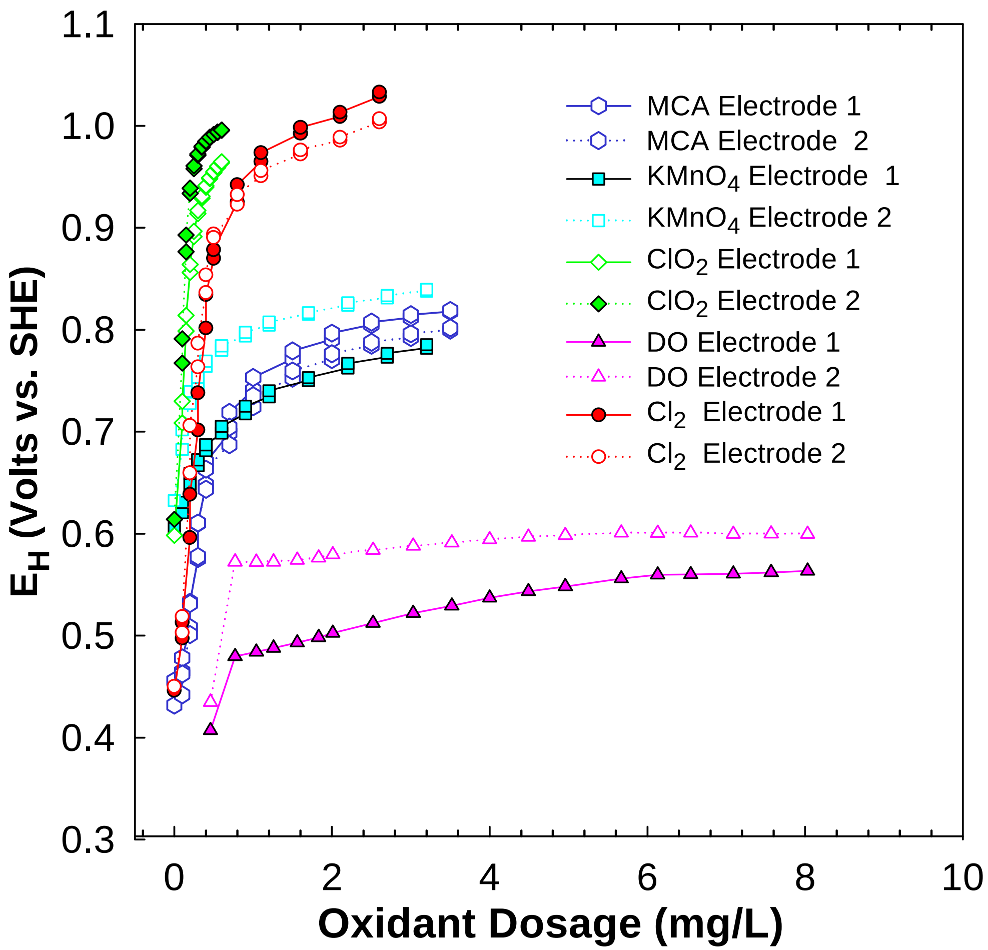
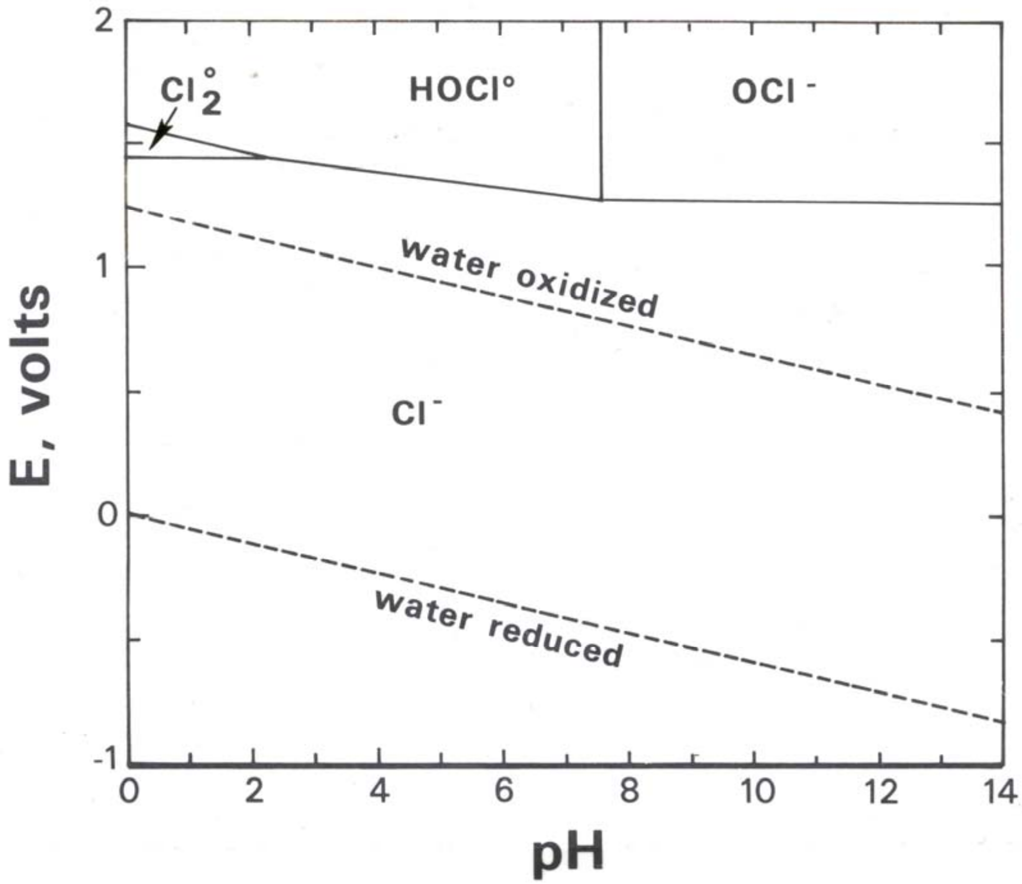
Redox Potential of Common Oxidants

(pH 7, 10 mg C/L, 25°C)



EMF-pH Diagram for Metastable Hypochlorite Species (1 mg/L as Cl_2)



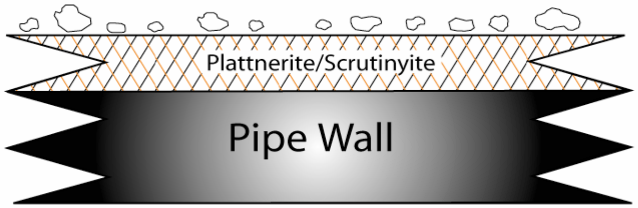
USEPA Pipe PbO_2 Occurrence Summary

- 190 Lead service line specimens analyzed
  - 38 different water systems
  - 15 states
- Samples from 13 systems: definitive PbO_2 (34%)
- Samples from 3 more systems have possible PbO_2
- Associated with low Pb levels in the water, regardless of pH

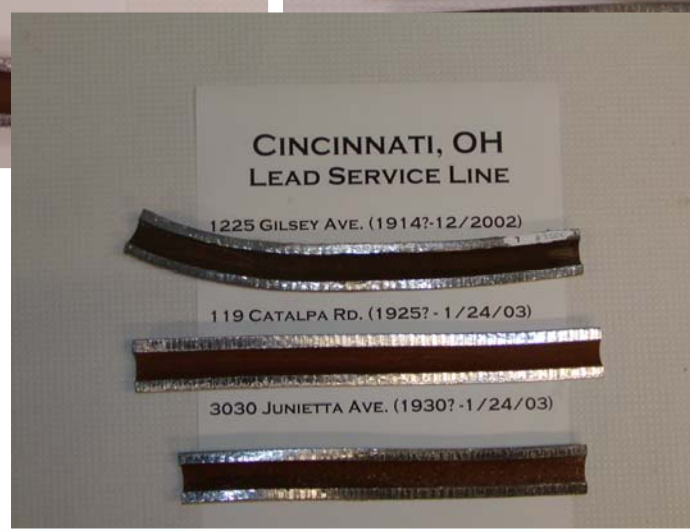
USEPA Pipe PbO_2 Occurrence Summary

- Major relationships of PbO_2 to treatment/WQ
  - High DS ORP: high free chlorine residual, ClO_2 use
  - Low oxidant demand
    - Oxidative pre-treatment like greensand
    - Non-corrosive to unlined iron mains
    - No NOM, ammonia, hydrogen sulfide, ferrous iron, etc.
- Some indications that rate of formation speeds up at pH's over 9
- Unlikely in systems
  - With low free chlorine residuals or chloramination
  - Dosing phosphate corrosion inhibitors

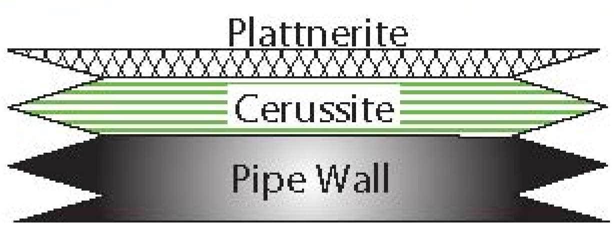
Nearly Uniform PbO_2 Scales: 60-90 mol %



Photographs of Some PbO_2 Scales

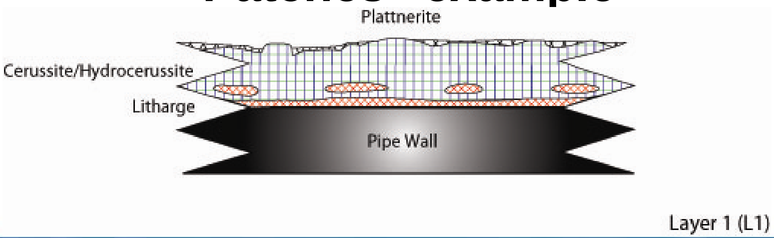


Distinctly Layered with PbO_2 on Top



PbO_2 in Patches or Intermingled

"Patches" example



What We DON'T Know about Pb(IV)

- What is the reaction pathway and product when PbO_2 breaks down?
  - Pb^{2+} ion?
  - PbO? (What crystal form?)
  - Surface reaction to form carbonate or hydroxycarbonate?
  - Direct surface reaction with other ligands, e.g. PO_4?
- How FAST are the competing reactions?
  - ORP-induced breakdown of PbO_2
  - Dissolution of product
  - Passivation/repassivation reaction
- What are important aqueous complexes of Pb^{4+} and what are their stability constants? (eg. PO_4, SO_4, Cl, OH)

What We DON'T Know about Pb(IV)?

- Does PbO_2 form from initial oxidation of lead-containing materials such as
  - Leaded-solder joints
  - Leaded brasses
- What is the rate and pathway of conversion of Pb(II) corrosion byproduct phases
  - $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$
  - $Pb_5(PO_4)_3OH$, $Pb_9(PO_4)_6$, $Pb_5(PO_4)_3(Cl,F)$, others

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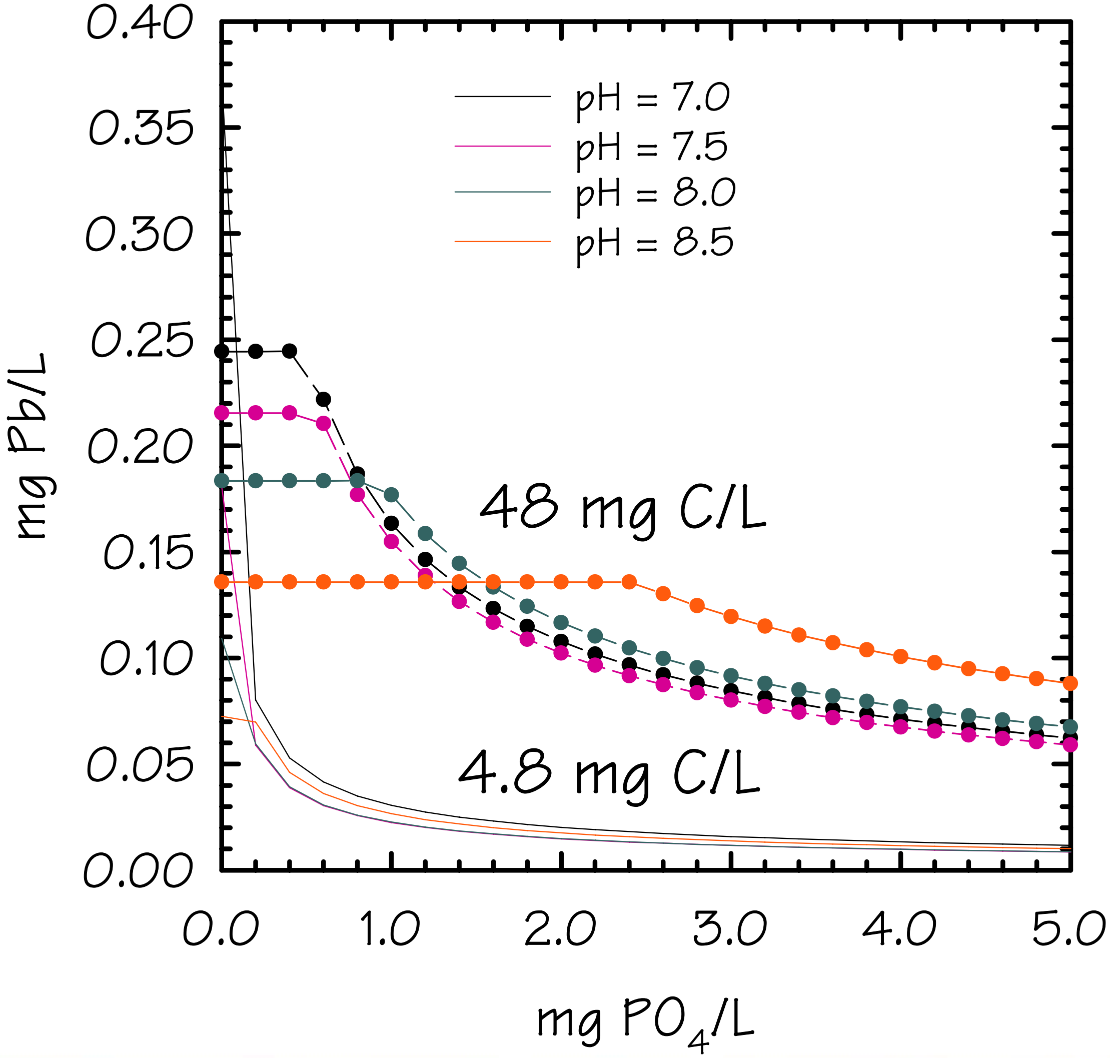
Phosphate Overview

- Orthophosphate is the active agent - avoid polyphosphates
- Analogous to chlorine residual, there is a "phosphate demand" to distribution system and premise plumbing materials
- To "recover" phosphate dose at ends of distribution system, months of exposure may be required
- Phosphate passivation requires constant dosage above the solubility threshold, which depends on pH, DIC, water quality background, and mineralogy of pipe scales
- Most systems see Pb levels decrease for years after sufficient dosage is maintained, due to slow scale conversion kinetics.
- Phosphate most effective on Pb(II) deposits and new copper

Under-dosing of PO_4 for Pb in High DIC Water



Dosage point of diminishing returns is higher in high alkalinity waters

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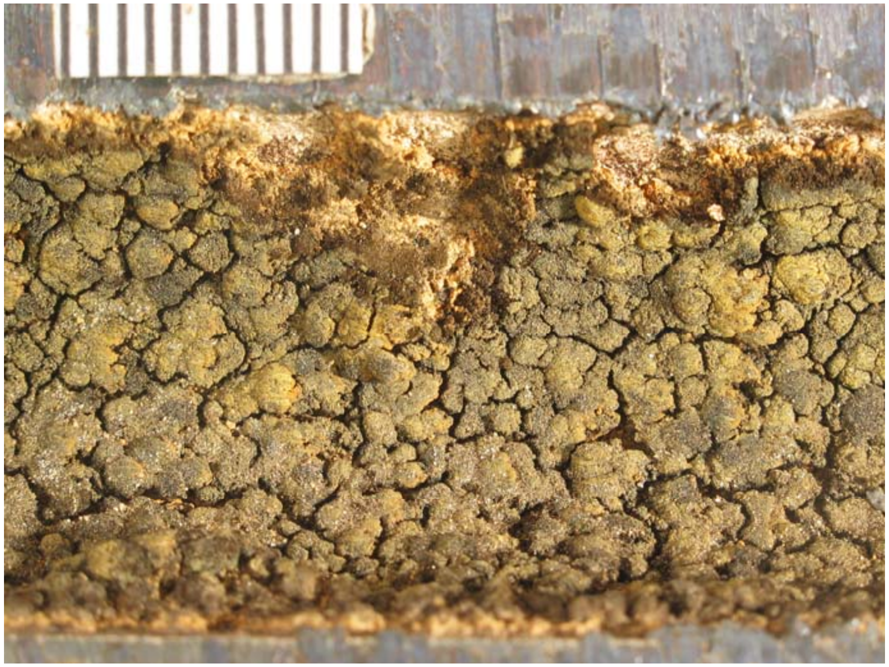
Iron, Manganese & Aluminum Deposits

- Widely distributed
- Post-precipitation (such as Al-Ca-Fe-OH-PO_4) may actually coat surface and help Pb levels
  - Form diffusion barriers
  - Slow metal release rates into water
- Reacts with corrosion inhibitor residual: Can cause "mysterious" corrosion control failures
- Can cause erratic Pb levels in monitoring program
- Readily accumulates on all types of pipes
- Strong surface binding properties for metals, phosphate, and metals that form oxyanions
- Help entrain U, As, Cr, Co, V, Sn, Bi, Cd and other metals
- Could be hydraulic, aesthetic and contamination headache

High Fe, Mn & Al on Lead

$Pb_9(PO_4)_6$ + residual $PbCO_3$



$PbCO_3 + Pb_3(CO_3)_2(OH)_2$

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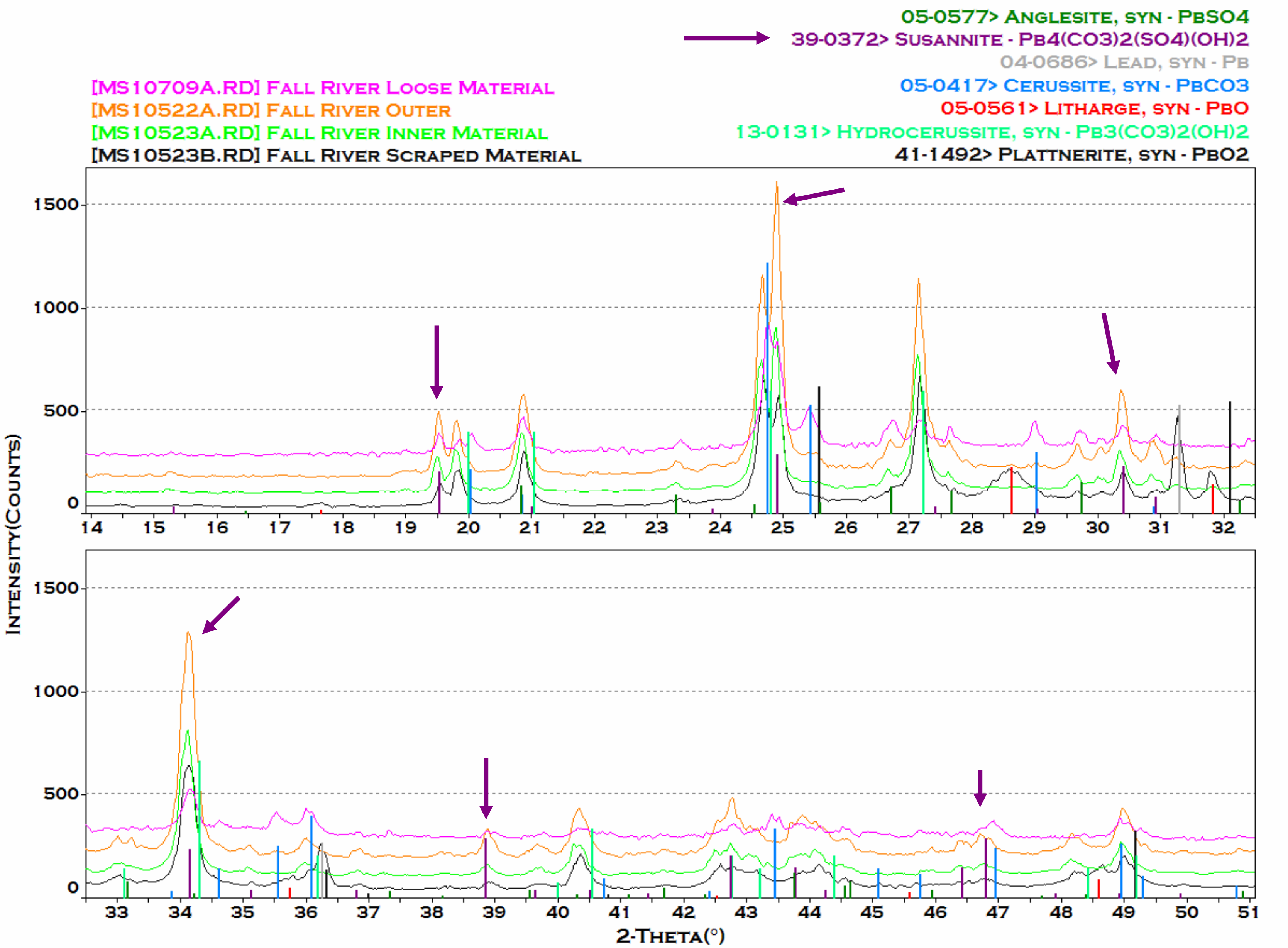
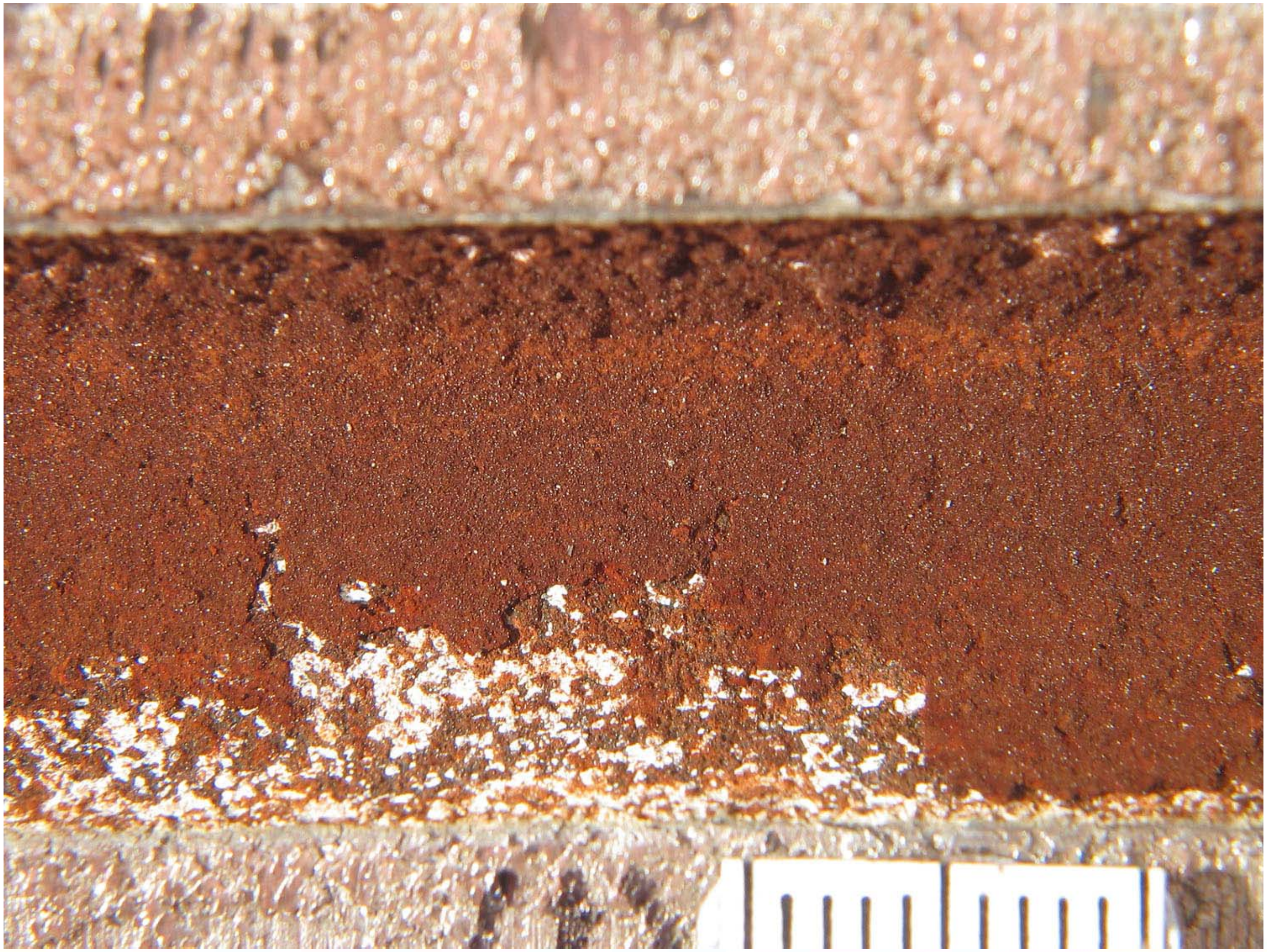
Initial situation: Inadequate pH control

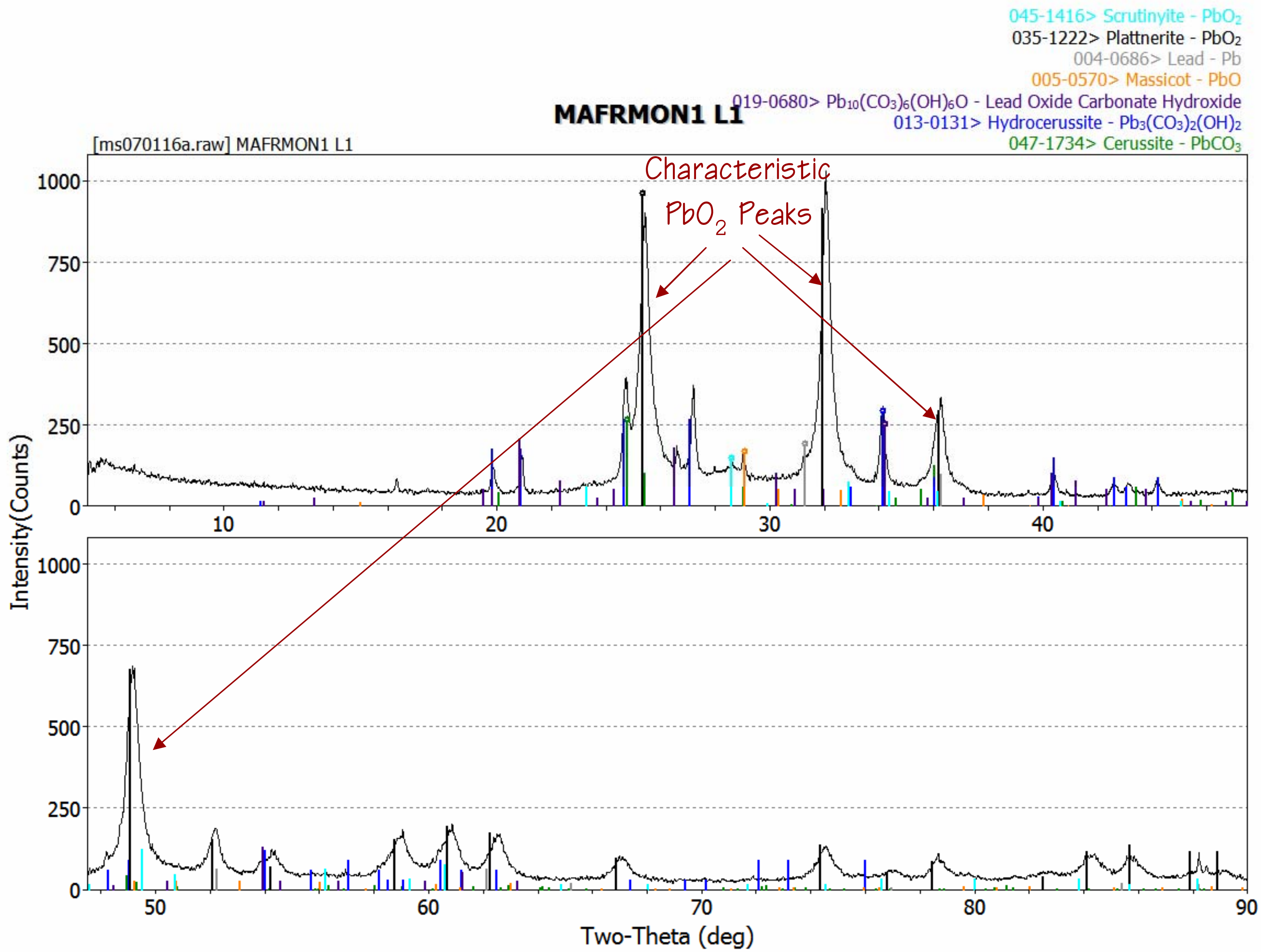
Pitted surface from aggressive attack revealed after scraping


05-0577> Anglesite, syn - PbSO4
39-0372> Susannite - Pb4(CO3)2(SO4)(OH)2
04-0686> Lead, syn - Pb
05-0417> Cerussite, syn - PbCO3
05-0561> Litharge, syn - PbO
13-0131> Hydrocerussite, syn - Pb3(CO3)2(OH)2
41-1492> Plattnerite, syn - PbO2
[MS10709A.RD] Fall River Loose Material
[MS10522A.RD] Fall River Outer
[MS10523A.RD] Fall River Inner Material
[MS10523B.RD] Fall River Scraped Material
Intensity(Counts)
2-Theta(°)

MAFREMA 1- Today PbO_2 is Forming

MAFREMA 1 Detail (bars are mm)





045-1416> Scrutinyite - PbO2
035-1222> Plattnerite - PbO2
004-0686> Lead - Pb
005-0570> Massicot - PbO
019-0680> Pb10(CO3)6(OH)6O - Lead Oxide Carbonate Hydroxide
013-0131> Hydrocerussite - Pb3(CO3)2(OH)2
047-1734> Cerussite - PbCO3
MAFRMON1 L1
[ms070116a.raw] MAFRMON1 L1
Characteristic
PbO2 Peaks
Intensity(Counts)
Two-Theta (deg)

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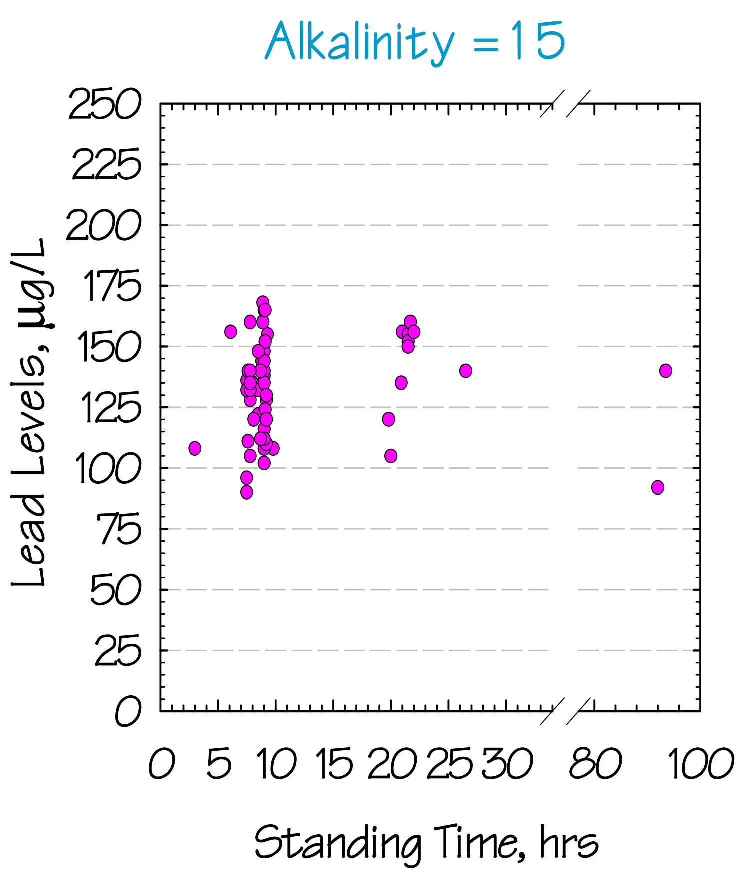
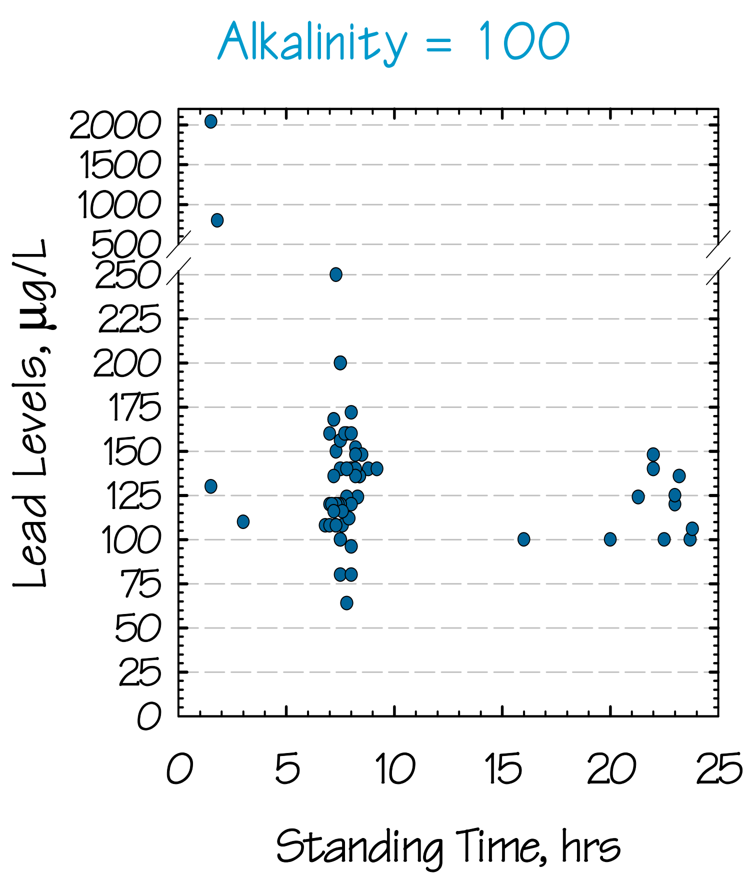
Pb Achieves Saturation Equilibrium

Chlorine + DO, Initial pH = 8.3-8.5



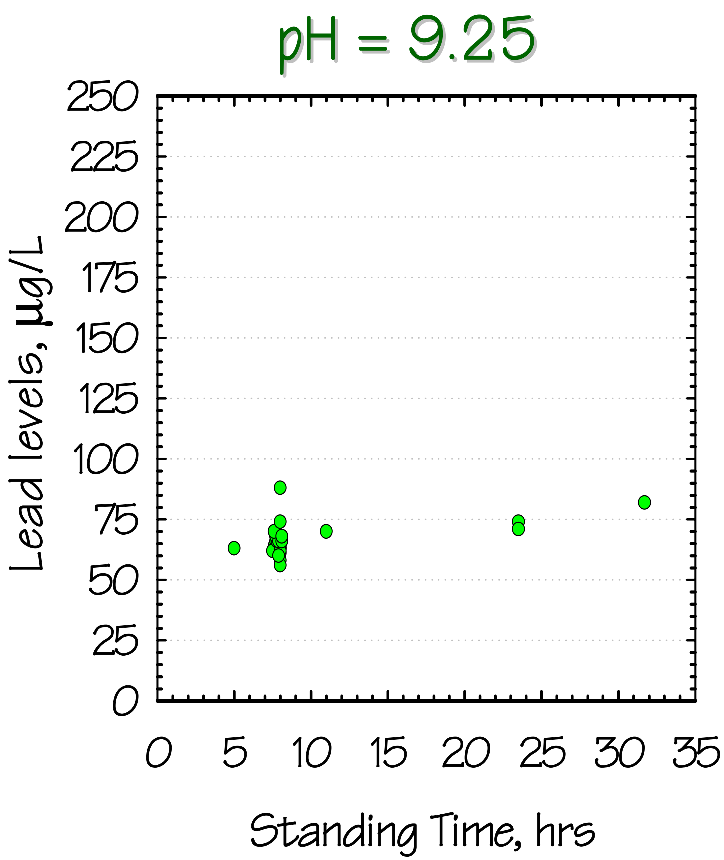


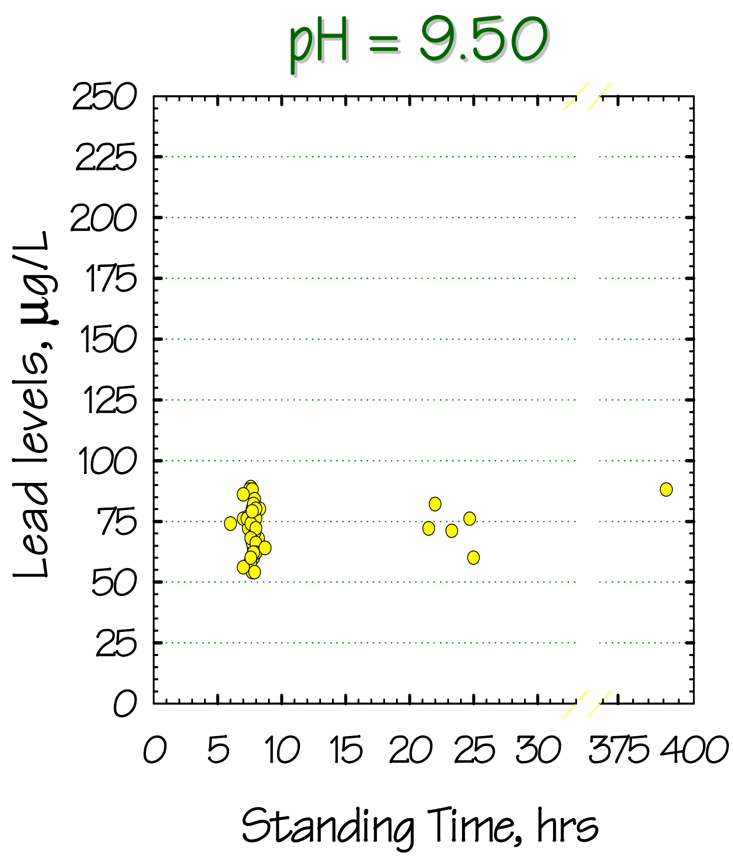
RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

Pb Pipe, Chlorine + DO

Initial Alkalinity ≈ 25-30





Stagnation Summary

- Lead follows diffusion-based model, but more shallow slope depending on water chemistry and pipe deposits
- Lead generally hits plateau around 8 hours or more
- Copper levels rise more slowly and for much longer time, as long as oxidants persist
- With persistent oxidants, Cu equilibrium at 8 hours would be rare
- Copper level increases vs time decrease with age
- Copper levels can go back down when oxidants are depleted

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Supplemental Water Quality Monitoring

- To diagnose problems
- To understand treatment success or failure
- To assure proper chemistry conditions in DS are maintained between compliance monitoring periods
- To build database of water chemistry characteristics and contaminant occurrence to make sound future treatment change decisions

Critical Parameters @ Different Frequencies

- Constant monitoring and synchronize with Pb/Cu samples
  - pH
  - Alkalinity or DIC
  - ORP, disinfectant residual
  - Corrosion inhibitor residual
  - Temperature
- Periodic monitoring
  - Sulfate, chloride, silicate (metal release kinetics)
  - Iron, aluminum, manganese (scale and ORP demand)
  - Trace metals/radionuclides (for scale accumulation)
  - Nitrite (for chloraminated systems)

Most Common Treatment Conflicts for LCR Among Regulations

- Small systems with multiple contaminants (U, As, Rn) using anion-exchange
- High THM levels, especially consecutive systems & high pH
- Addition of oxygen or chlorine to high alkalinity ground water with low natural ORP
  - Fe, Mn, hydrogen sulfide, ammonia removal
  - Disinfection
- Low pH from coagulation in poorly-buffered waters
- Coagulant change (may be kinetic effect of added chloride)
- Replacing lime softening with IX softening or membranes
- Overdosing of polyphosphate to prevent post-deposition of calcium carbonate
- Change from free chlorine to chloramine (check pipes)

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- Darren Lytle, USEPA
- USEPA, Region 1
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Questions?

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