Chemistry of Lead Corrosion and Release

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US EPA Office of Research and Development (ORD)

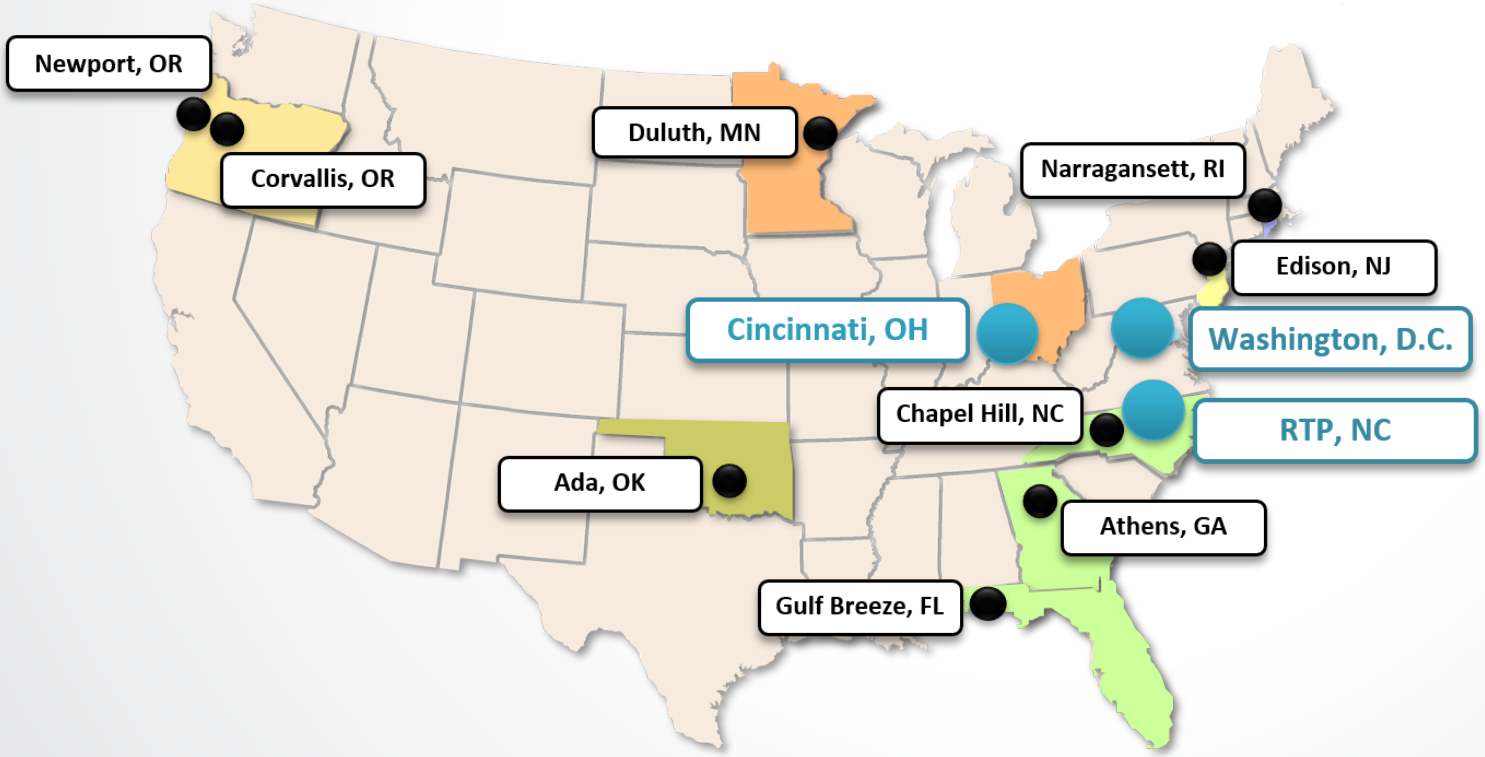
ORD/OW Small Drinking Water Systems Webinar:
Lead and Copper

February 23, 2021

What we do

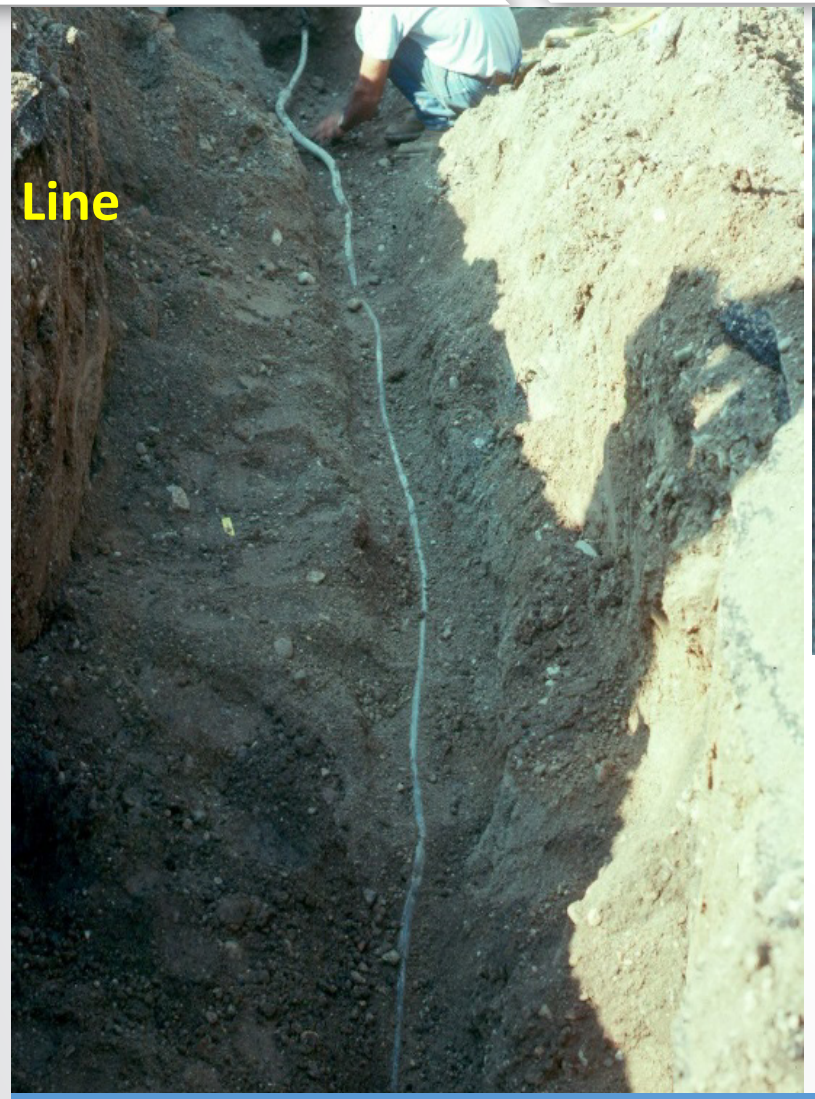
ORD provides the data, tools and information that form the sound scientific foundation the Agency relies on to fulfill its mission to protect the environment and safeguard public health.

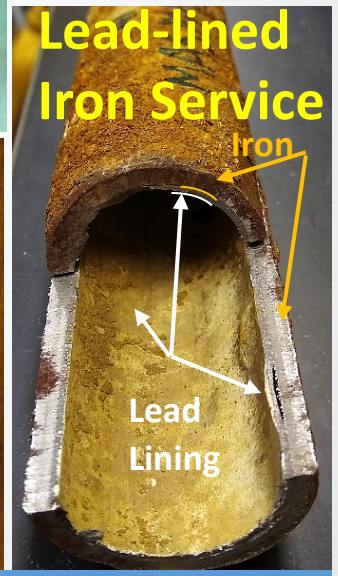
ORD at a Glance



Center for Environmental Solutions & Emergency Response (CESER) in Cincinnati:
We conduct applied stakeholder-driven **research** and provide **technical support** to help solve the Nation's environmental challenges

Lead (Pb) Sources

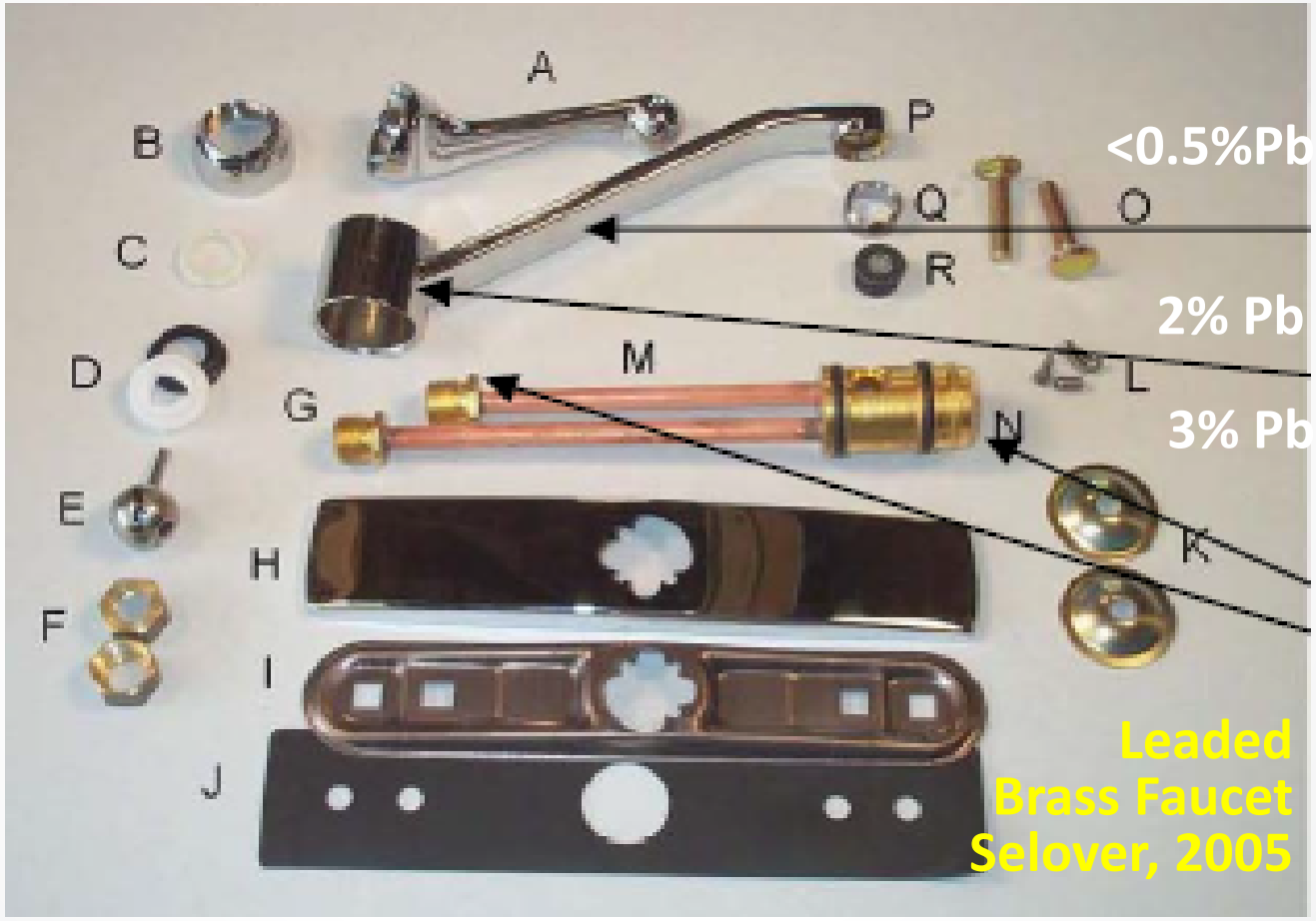




Triantafyllidou et al., 2020

Materials inventory is critical to understand where and what lead sources still exist

Pb Sources



Diverse legacy leaded materials may undergo different corrosion reactions and impact water quality differently

Corrosion is oxidation-reduction

Oxidation:
Lead metal losing electrons at anode

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

$$Pb \leftrightarrow Pb^{4+} + 4e^-$$

Reduction:
Oxidant gaining electrons at cathode

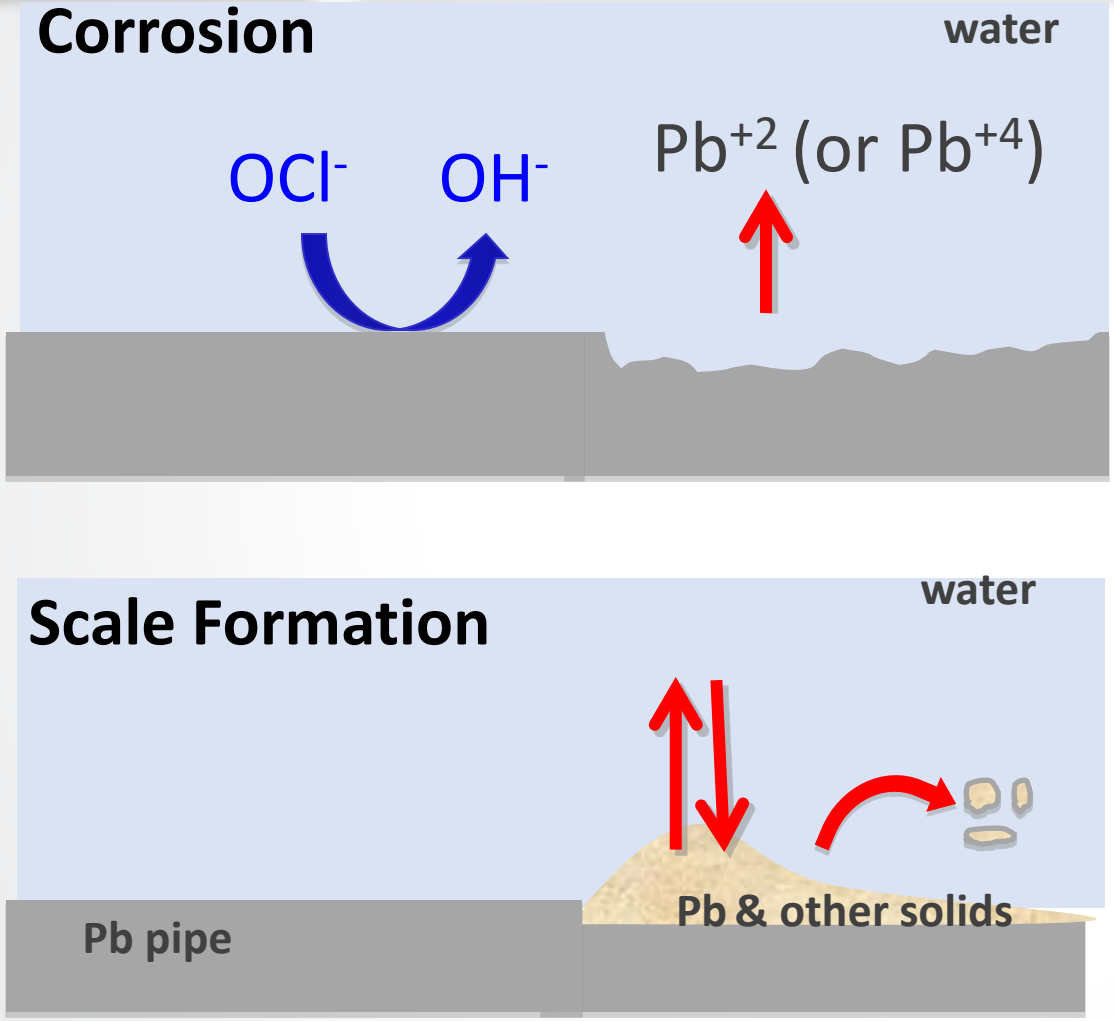
$$OCl^- + H^+ + 2e^- \leftrightarrow Cl^- + OH^-$$

$$2OCl^- + 2H+ + 4e^- \leftrightarrow 2Cl^- + 2OH^-$$

Oxidant is dissolved oxygen, free chlorine, chloramine, chlorine dioxide, etc.

There are two possible oxidation states for corroded lead: Pb^{+2} and Pb^{+4}

Corrosion and scale formation



Triantafyllidou et al., 2020

Corroded lead ions

Pb^{+2} ↕ Pb^{+4}

Idealized scenario of scale solids

Pb(+2) carbonates
Pb(+2) hydroxycarbonates
Pb(+2) orthophosphate

Pb(+4) oxide

Solubility of the scale is critically important because it controls Pb release

Scale can be very complex in practice

EPA ORD's Advanced Materials and Solids Analysis Research Core, 2021

Variety of scale coatings on lead service lines analyzed at EPA: heterogeneous, several layers, amorphous, many constituents

Al, Mn, Fe, P and Ca-rich coatings may interfere with orthophosphate, pH adjustment, or other corrosion control treatment (CCT)

Corrosion and metal release

- Pure corrosion (i.e., electrochemical oxidation-reduction reactions) becomes less important when the surface becomes covered with scale
- Metal solubility or destabilization of the scale at the water contact will be more important (if the scale is porous, corrosion may still occur at the base of the scale)
- Metal solubility varies by factor of 5 to 10 or more across drinking water systems

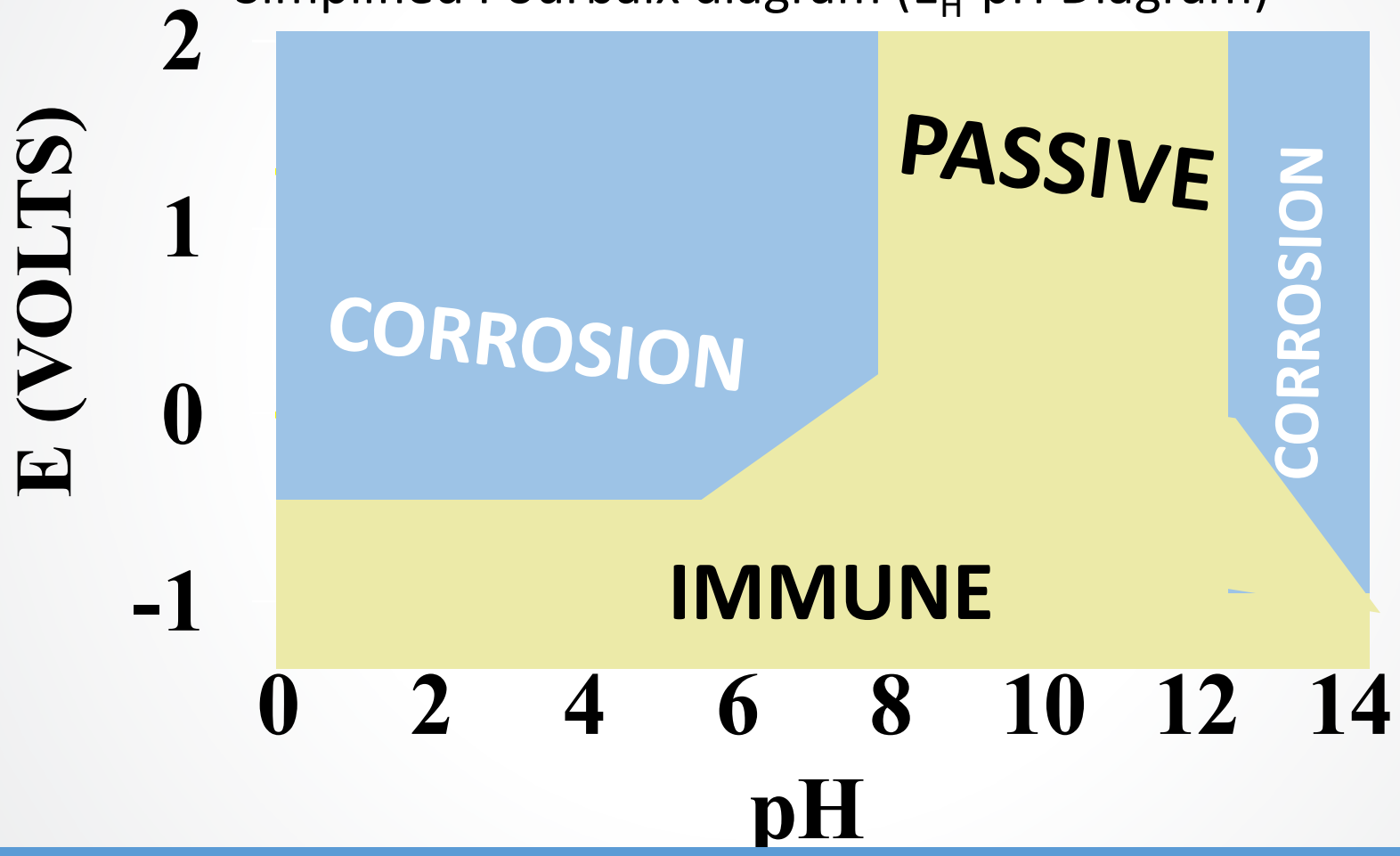
CCT includes control of pure corrosion and metal release from the pipe scale

Important factors affecting corrosion and metal release

- pH and Alkalinity/Dissolved Inorganic Carbon
- Type and Concentration of Oxidants (chlorine species, dissolved oxygen, etc): Oxidation/Reduction Potential
- Corrosion Inhibitors
- Chloride and Sulfate

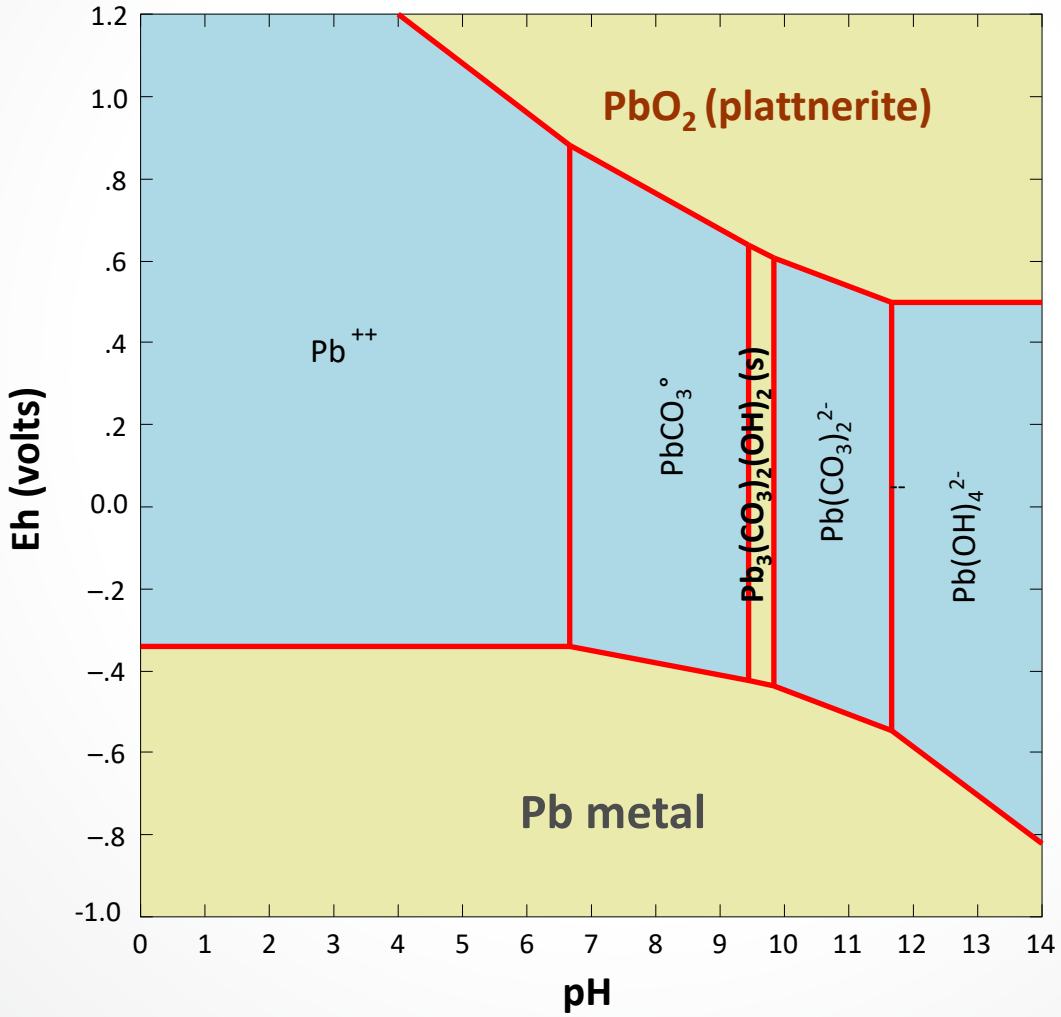
pH is master variable

Simplified Pourbaix diagram (E_H-pH Diagram)



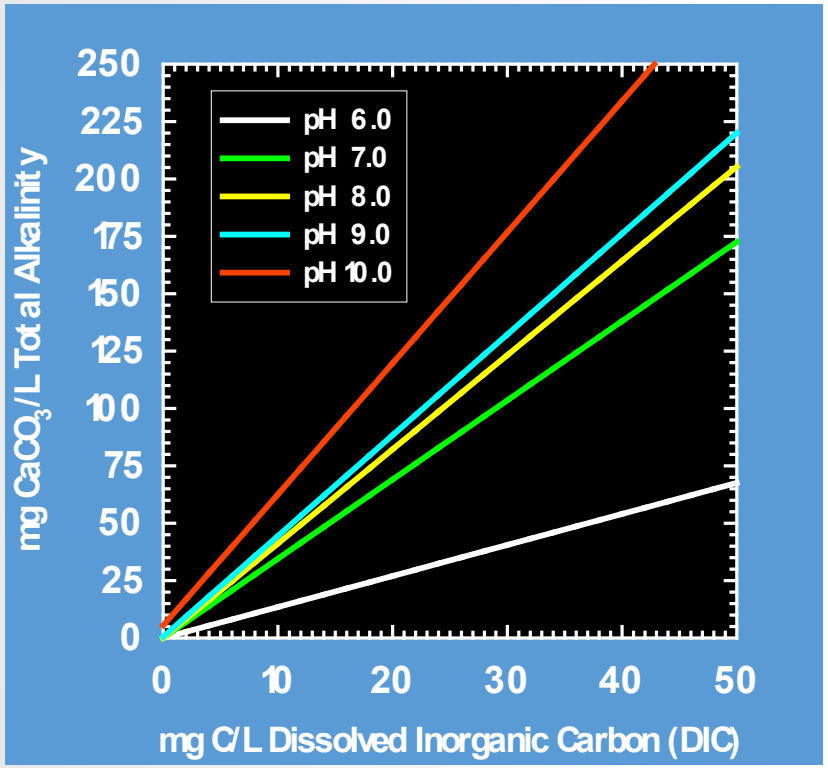
Desirable pH-E_H combinations allow passivation (i.e., formation of protective pipe scales)

pH is master variable



Illustrative modeling prediction example for assumed:
DIC = 18 mg C/L
Pb = 0.010 mg/L

Dissolved Inorganic Carbon (DIC) and Total ALKalinity (TALK)



$$DIC = [CO_3^{2-}] + [H_2CO_3^*] + [HCO_3^-]$$

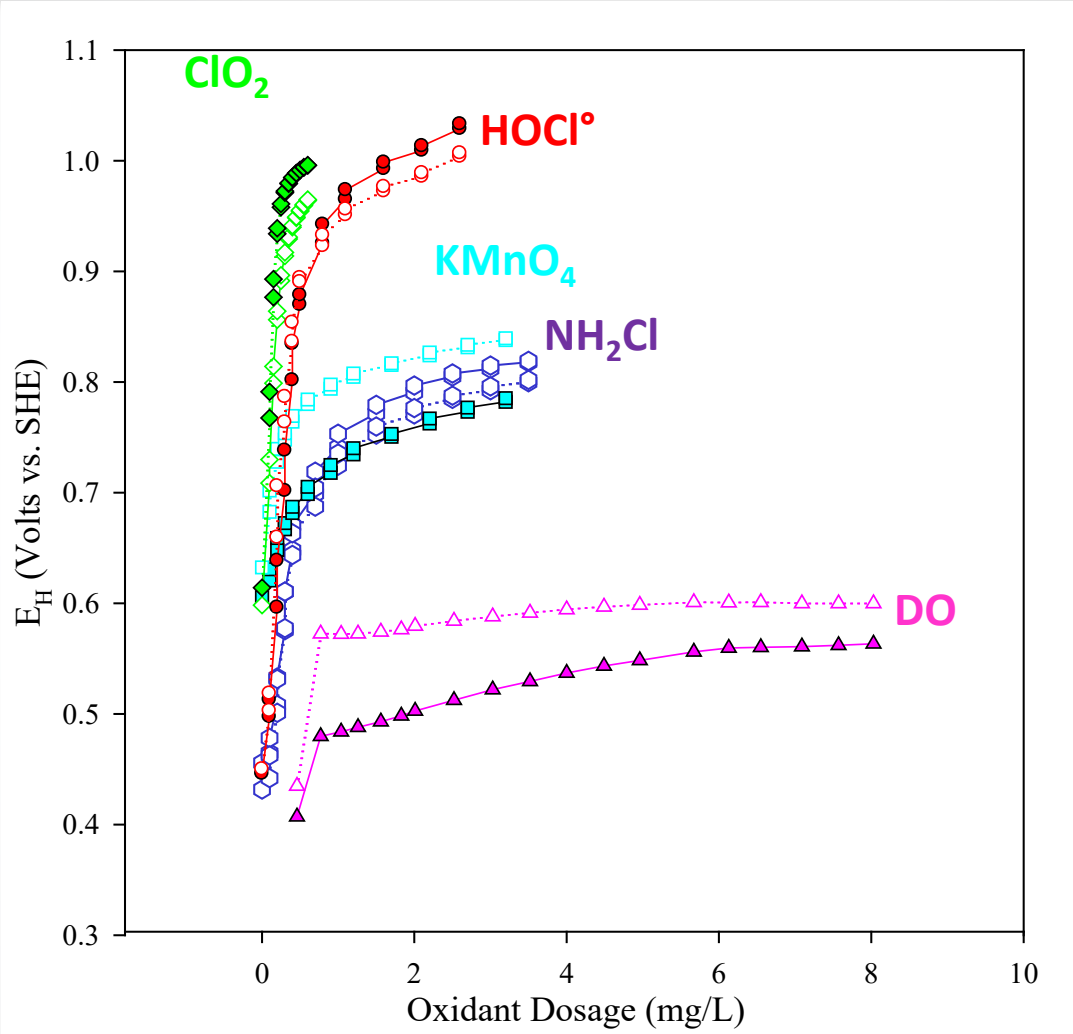
$$TALK = 2\,[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

- To understand corrosion, it is important to keep up with the carbonate system
- DIC and TALK have linear relationship but are not the same thing

Oxidants in drinking water

- Disinfection (Free chlorine, Chloramine, Chlorine dioxide)
- Pre-oxidation (O3, H2O2, ClO2, KMnO4)
- Oxidative metal removal (e.g., As, Fe, Mn)
- Ammonia removal
- Aeration (corrosion control, VOC/Rn/H_2S removal)
- Taste and odor control
- Dissolved oxygen

Oxidants in drinking water

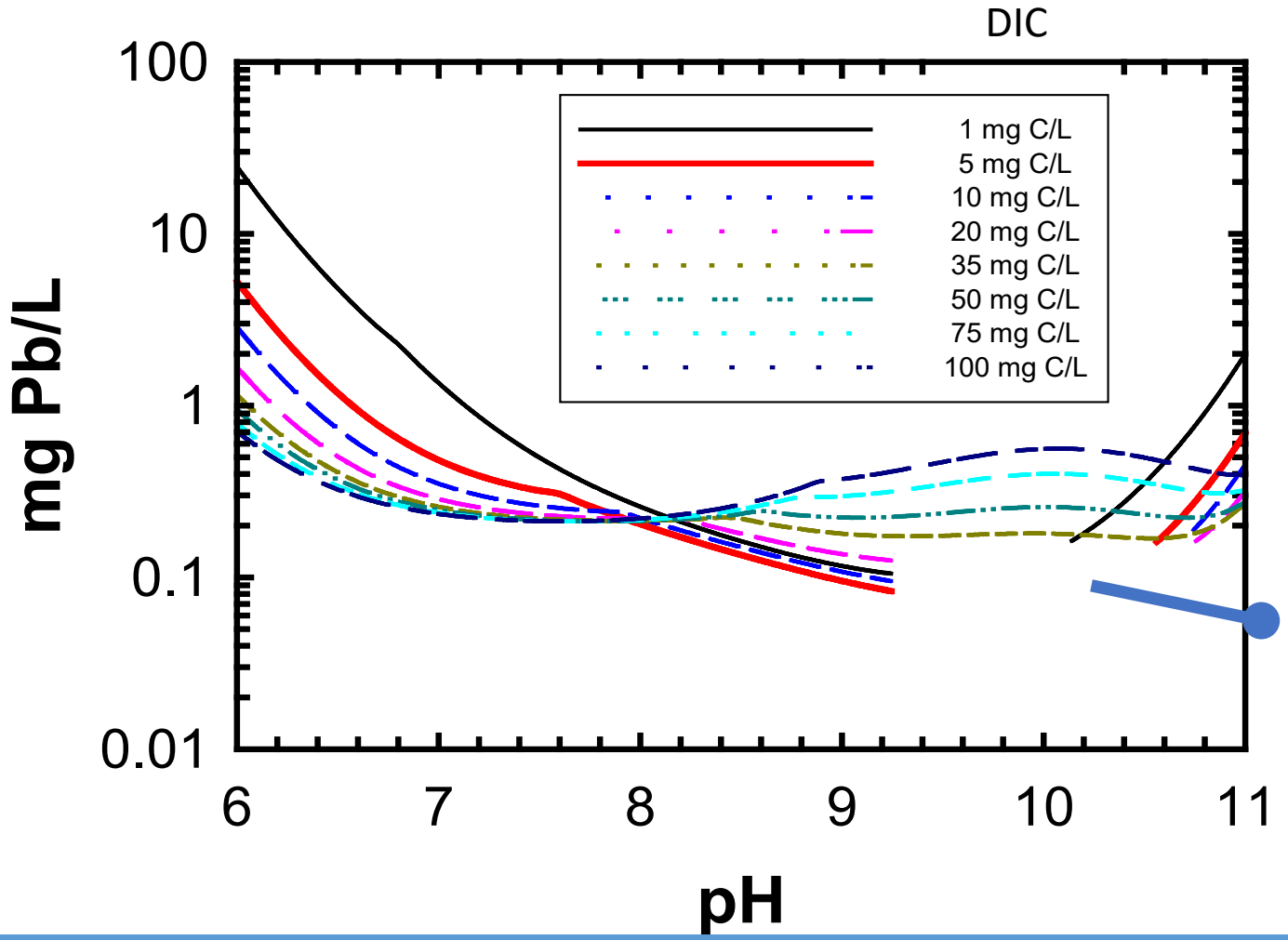


Oxidation-Reduction Potential of several disinfectants in experiment

James et al., 2004
(pH 7, 10 mg C/L, 25°C)

Different oxidants have different oxidizing power

"Classic" divalent Pb^{+2} solubility



Illustrative modeling for an assumed range of DIC and pH

Optimum pH/DIC range for lead service lines (LSLs)

- High pH is needed to minimize Pb solubility
- Optimum pH/DIC range is very narrow

Lead "Corrosion Inhibitors?"

- Phosphoric acid
- Alkalai-metal orthophosphate
- Zinc orthophosphate
- Blended ortho/polyphosphates*
- Polyphosphates*
- Sodium Silicate

*Polyphosphates are not corrosion inhibitors but rather sequestering agents

Efficiency depends on sufficient dose/concentration for the background pH and other reactive water quality constituents: what if the dose is too low to actually work?

Illustrative reactions of P in pipe

Orthophosphate (Ortho-P)

Precipitation (consumption of orthophosphate):

$3Pb^{+2} + 2PO_4^{-3} \text{ --> } Pb_3(PO_4)_2$ (solid)

<u>decreased Pb solubility</u>

Polyphosphates

- Partial Reversion (formation of orthophosphate):

$P_3O_{10}^{-5} \text{ ---> } P_2O_7^{-3} + PO_4^{-3}$

polymer --> monomers

- Complexation (soluble complexes):

$3Pb^{+2} + P_3O_{10}^{-5} \text{ --> } PbP_3O_{10}^{-2}$

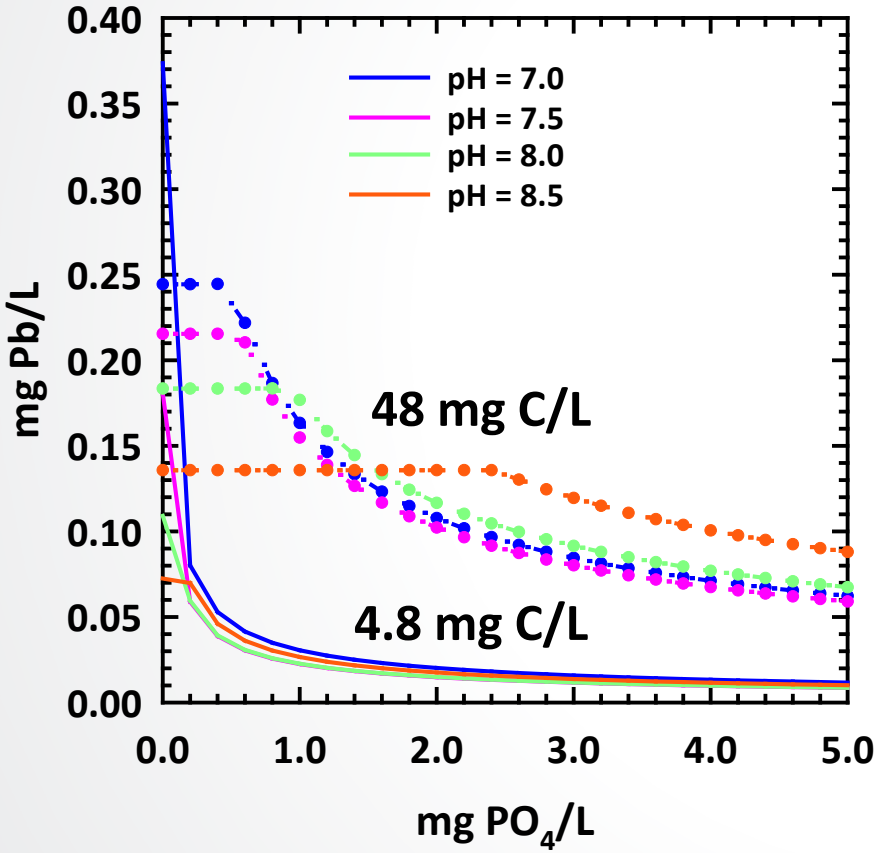
<u>increased Pb solubility</u>

Conceptual reactions credit: Marc Edwards

Conceptual simplified possible reactions. Actual reactants and products may be different. Polyphosphates cannot be easily quantified.

Ortho-P Treatment for Pb^{+2}

Effectiveness Depends on Dose, DIC, pH and "Cleanliness" of Pipe Surface



- pH less critical at low DIC
- pH less critical at high PO_4
- Point of diminishing returns higher with high DIC
- Faster Pb reduction at high PO_4

Typical UK Dosages: 4-6 mg/L

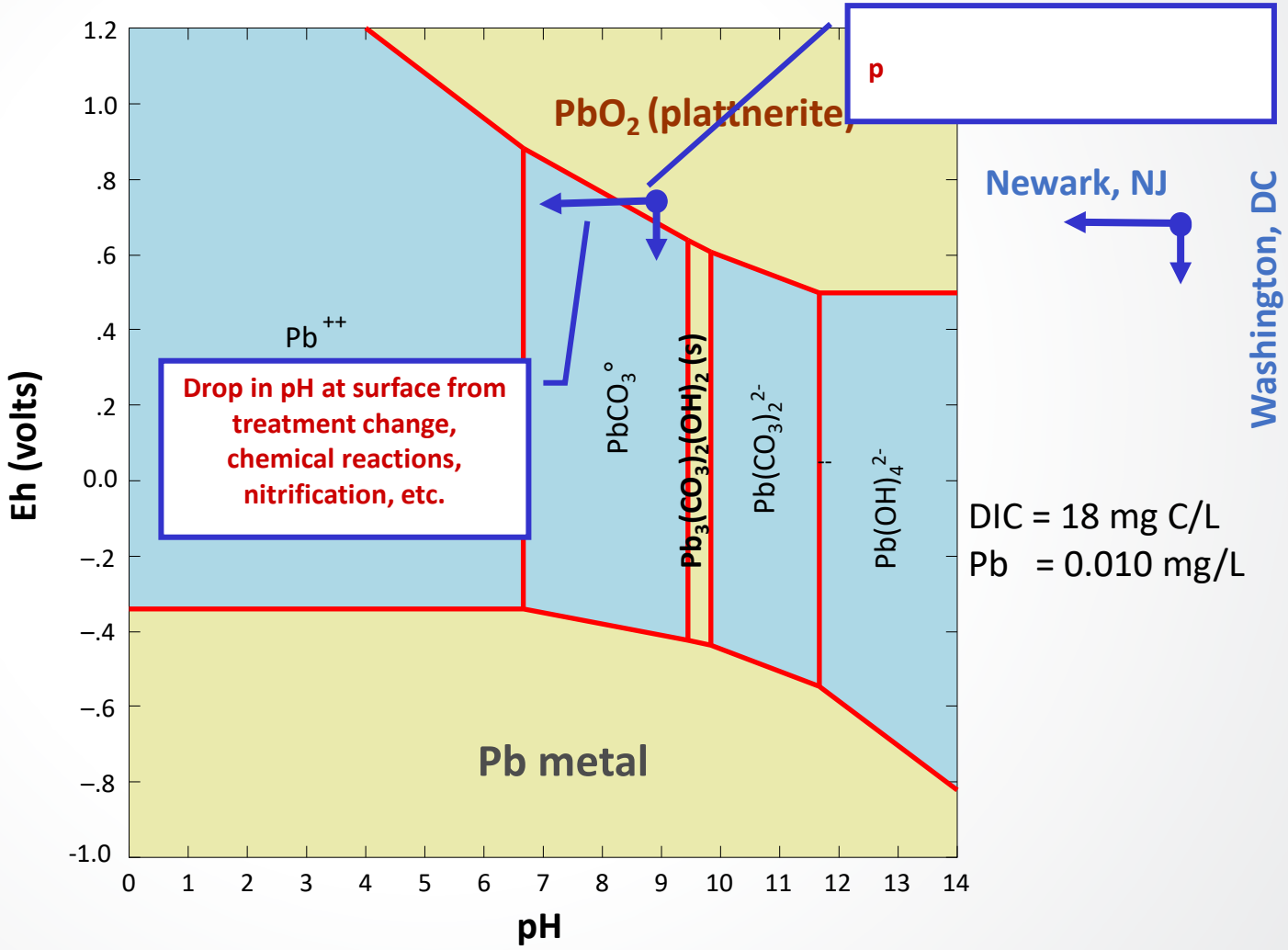
Most public water systems with LSLs do not have CCT that minimizes Pb release

Ortho-P point of diminishing returns

- Orthophosphate addition to where large increments result in small reductions in lead release
- Key to cost-effective lead release control and exposure reduction
- Becomes the ”maintenance” dosage unless the scale “ages”
- Background constituents such as aluminum, hardness ions, iron, manganese and others *interfere* with optimum reduction of lead release
- Varies with the background water chemistry from system to system

Chemical changes may reduce Pb^{+4} to Pb^{+2}

Disinfectant demand in distribution system (DS) must be controlled & enough free chlorine consistently maintained throughout LSL area to keep protective Pb^{+4} corrosion scales in place



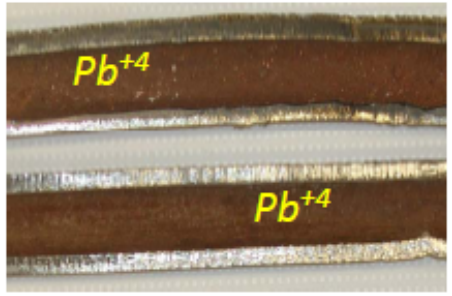
Switching disinfectants may reduce Pb^{+4} to Pb^{+2}

Chlorine Disinfectant

Strong Oxidant

$Pb^{0} \rightarrow Pb^{+2} \rightarrow Pb^{+4}$

Stable Corrosion Layer



Chloramine Disinfectant

Weak Oxidant

$Pb^{+4} \rightarrow Pb^{+2}$

Unstable Corrosion Layer

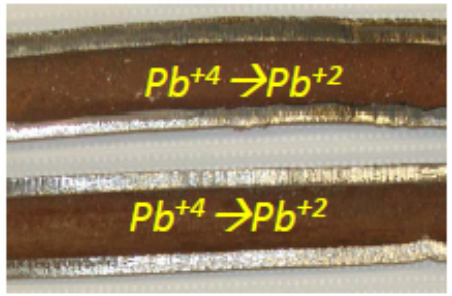


Photo of Cut Lead Service Line from M. Schock

Switch from chlorine to chloramine disinfectant dissolved lead from pipe scales during the Washington, DC "lead-in-water crisis" in 2001-2004

Chloride and sulfate

CSMR a factor controlling galvanic corrosion (Oliphant 1983, Gregory 1986):

$$\text{Chloride to Sulfate Mass Ratio (CSMR)} = \frac{[Cl^-]}{[SO_4^{-2}]} = \frac{12\ \text{mg/L}\ Cl^-}{20\ \text{mg/L}\ SO_4^{-2}} = 0.6$$

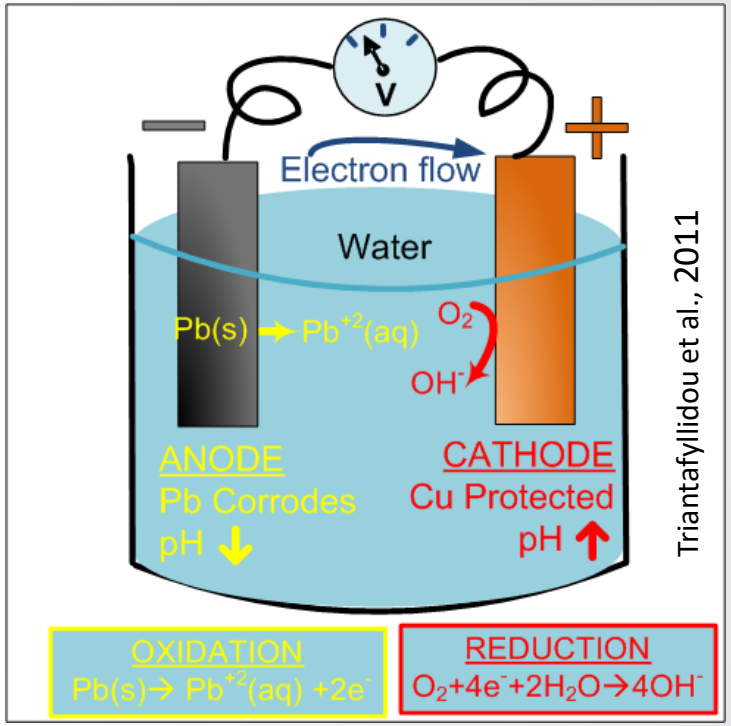
- Case studies of US water utilities
(Dodrill and Edwards, 1995; Edwards and Triantafyllidou 2007)
  - High CSMR > 0.5-0.6 more lead leaching
  - Low CSMR < 0.5-0.6 less lead leaching

- Important in experiments with fresh galvanic Pb junctions (e.g., Wang et al. 2013; Triantafyllidou et al 2011; *Nguyen* et al 2010, 2011) and in excavated galvanic Pb junction mineralogy (DeSantis et al, 2019)

- Contributed to the Flint water Pb crisis:

parameter	before[32] 2014	after[33] Dec. 2014
phosphate (mg/L as P)	1.07 (0.67–1.69)	absent[21]
chloride (mg/L)	11.4 (4.2–39.8)	80 (74–87)
sulfate (mg/L)	25.2 (11.9–33.9)	39.2 (24.3–45.0)[b]
CSMR[c]	0.45	2.04

(Pieper et al., 2017)



Triantafyllidou et al., 2011

Chloride and sulfate

- Increasing chloride and sulfate concentrations at a constant CSMR of 1 increased total lead concentrations in galvanic corrosion experiments (Ng & Lin, 2016)

- Absolute concentrations of chloride and sulfate important; chloride considered particularly detrimental to galvanic Pb corrosion

- High CSMR ratio proven empirically important in aggravating galvanic lead corrosion (verified by experiments and modeling)
- Water source or treatment changes that affect the CSMR must be evaluated prior to change
- Absolute concentrations also important, particularly for chloride

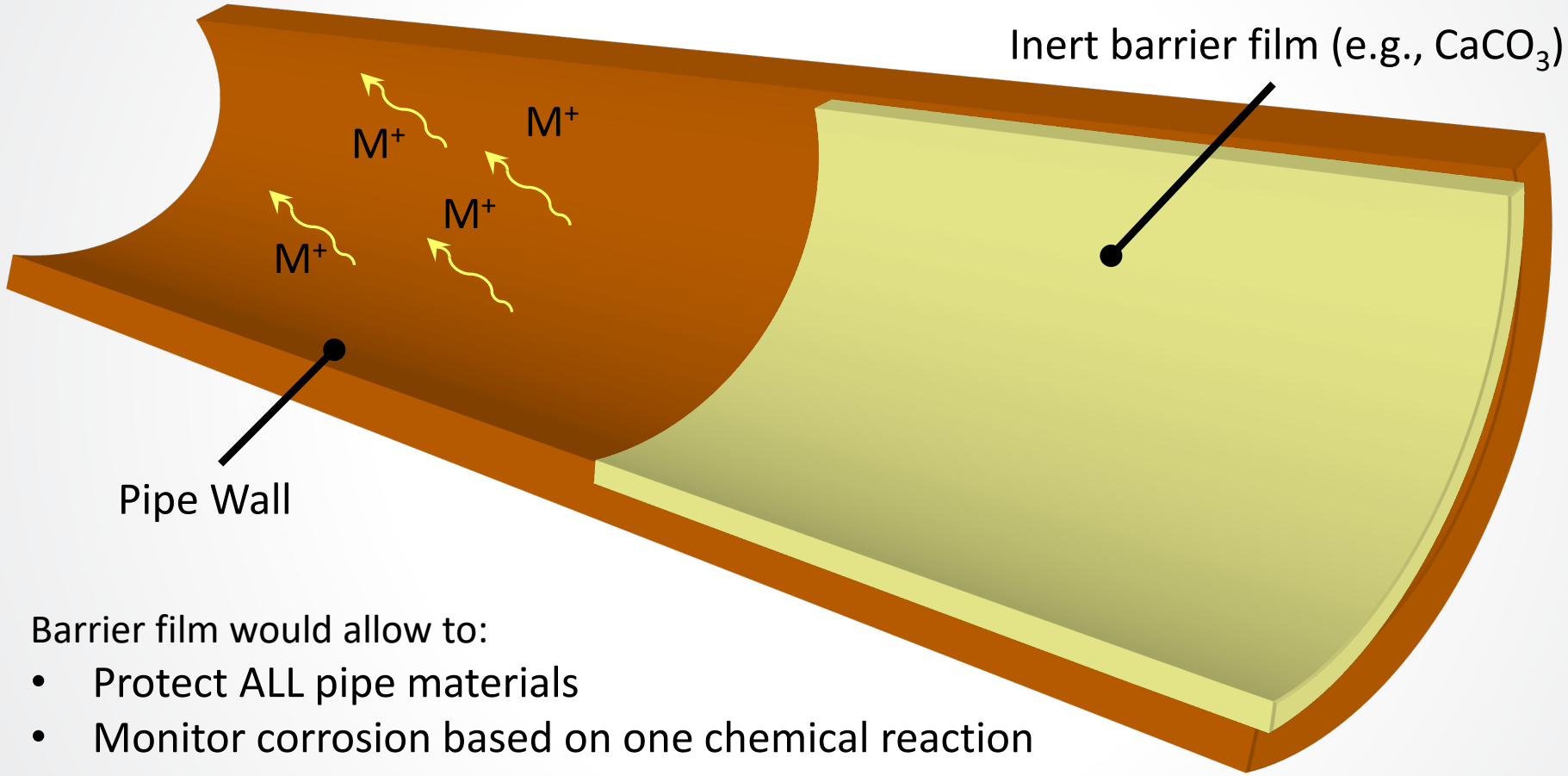
More water parameters affect metal release

- **pH & Alkalinity/DIC**
- **Concentration and type of oxidants (disinfectants, dissolved oxygen)**
- **ORP/corrosion potential**
- **Corrosion Inhibitors**
- **Chloride**
- **Sulfate**

- Manganese
- Iron (deposition and corrosion)
- Calcium
- Aluminum
- Natural organic material (NOM) (type, amount)
- Ammonia
- Hydrogen Sulfide
- Microbial activity (nitrification & other)

CCT is intertwined with all treatments affecting water chemistry

Corrosion barrier film hypothesis



Schematic: Marc Edwards

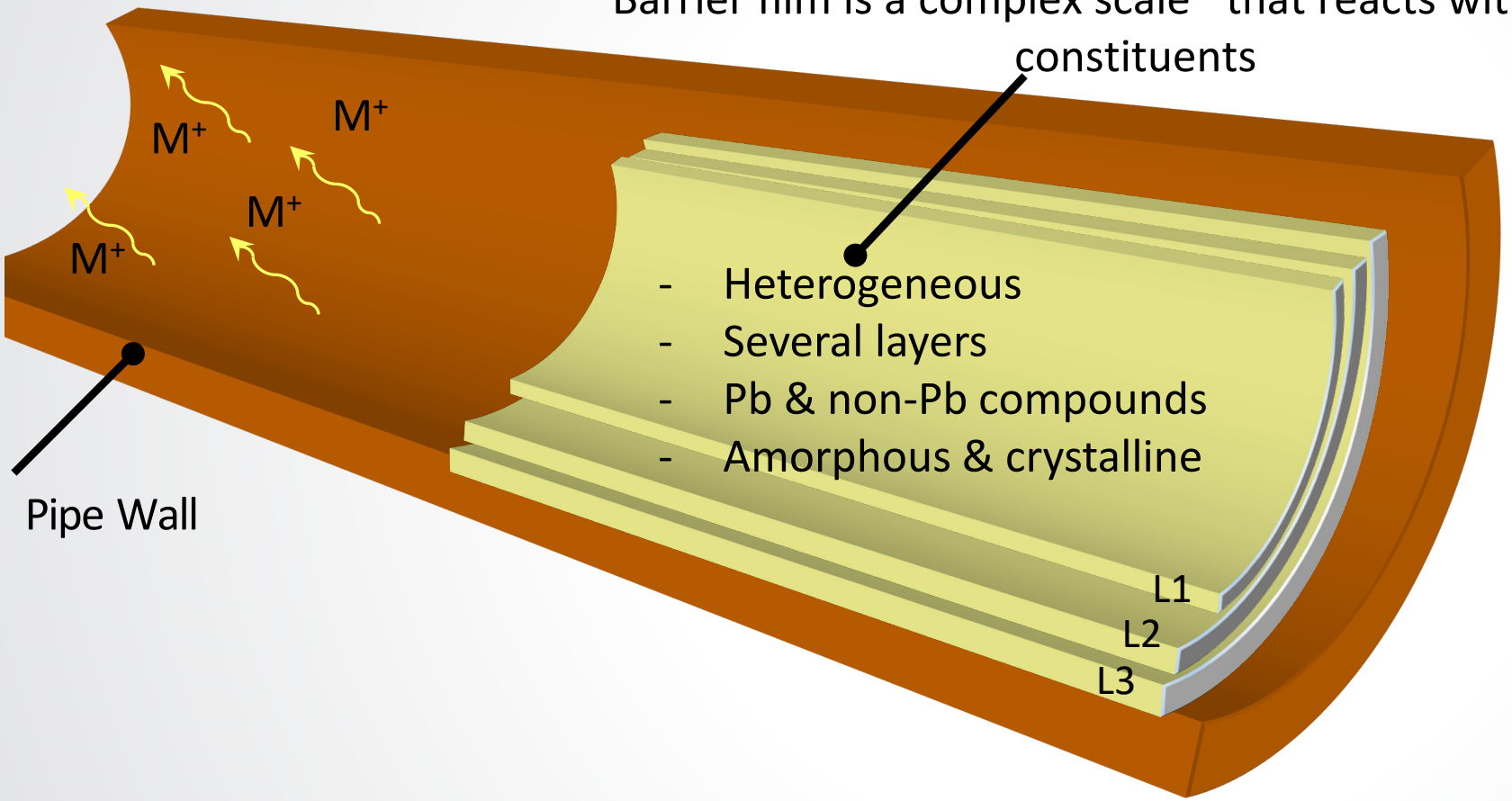
Barrier film would allow to:

- Protect ALL pipe materials
- Monitor corrosion based on one chemical reaction

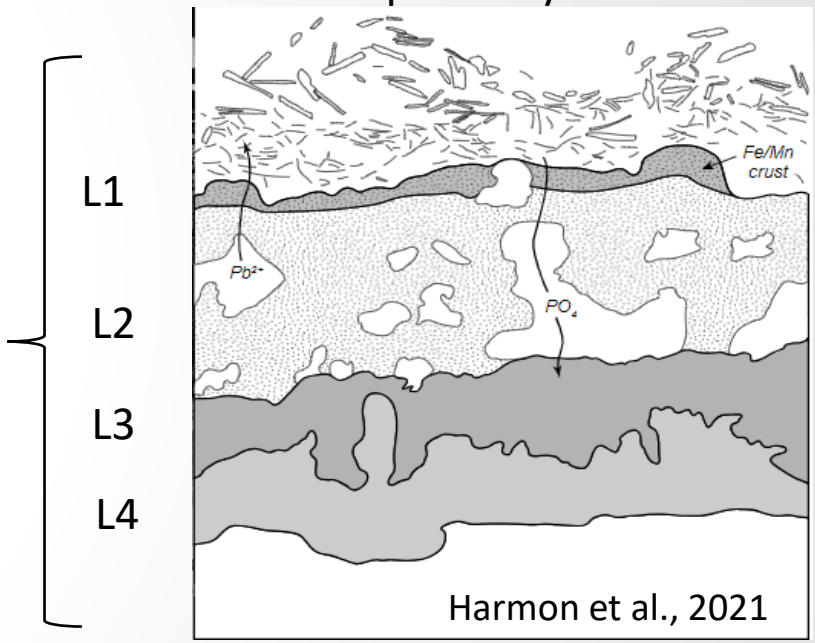
Although barrier film would be convenient for important reasons, the $CaCO_3$ hypothesis has not been proven

In excavated pipe samples that the EPA analyzed

Barrier film is a complex scale* that reacts with water constituents



*Scale layer illustration, for an LSL sample analyzed at ORD



Although barrier film would be convenient for important reasons, the $CaCO_3$ hypothesis has not been proven and scale is overall more complex

Are these "corrosion" indices?

Index	Equation	Range	Water Condition
Langelier Saturation Index	$LSI = pH_{actual} - pH_s$	LSI>0 LSI<0	• Supersaturated, tends to precipitate $CaCO_3$ • Undersaturated, tends to dissolve $CaCO_3$
Ryznar Stability Index	$RSI = 2pH_s - pH_{actual}$	RSI>6 RSI<6	• Undersaturated, tends to dissolve $CaCO_3$ • Supersaturated, tends to precipitate $CaCO_3$
Aggressive Index	AI=pH+ log(AH)	AI<10 10<AI<12 AI>12	• Highly Aggressive • Moderately Aggressive • Non-aggressive
Larson Scold Index	$Ls=[Cl^- + SO_4^{-2}]$/ Alkalinity	Ls<0.8 0.8<Ls<1.2 Ls>1.2	• Chloride & Sulfate will not likely interfere with natural film formation • chloride & sulfate may interfere with natural film formation • Tendency for higher localized corrosion rates

- The LSI and subsequent variations predict $CaCO_3$ **scaling**, not corrosion or metal release
- Calcium carbonate was not the active inhibition mechanism in the hundreds lead and copper pipes analyzed by EPA
- When used outside their definition/limitations, these indices become unreliable

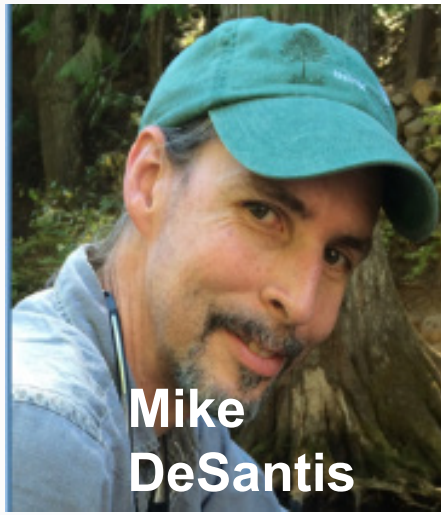
Summary

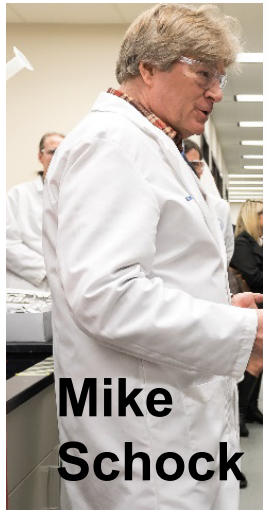
- Materials inventory is critical to know where and what lead sources still exist
- To conceptually understand corrosion and lead release, it is important to keep up with pH, the carbonate system (i.e., dissolved inorganic carbon and alkalinity), and disinfectants (i.e., oxidation-reduction potential)
- There are many types of scale on lead pipe with different solubilities:

Solubility of Pb(+4) solids << Solubility of Pb(+2) solids

- Corrosion inhibitor efficiency depends on type and sufficient dose/concentration for the background pH and other reactive water quality constituents
- Lead service lines analyzed at EPA often have complex heterogeneous scales of several layers, with many constituent elements aside from lead and with formed solids that rarely contain $CaCO_3$.
- Overall, CCT is intertwined with all treatments affecting water chemistry, and $CaCO_3$ saturation indices are not good lead corrosion predictors.

Thanks to EPA ORD's CESER Lead Team





How we communicate our research & technical support

Recent examples

Peer-review journal articles:

Our journal articles now become freely accessible after about a year of publication in a journal!

- Triantafyllidou, S., Burkhardt, J., Tully, J., Cahalan, K., DeSantis, M., Lytle, D., Schock, M. Variability and Sampling of Lead (Pb) in Drinking Water: Assessing Potential Human Exposure Depends on the Sampling Protocol. Environment International, 2020. https://doi.org/10.1016/j.envint.2020.106259 **[JOURNAL OPEN ACCESS]**
- Doré, E., Lytle, D.A., Wasserstrom, L., Swertfeger, J., Triantafyllidou, S. Field Analyzers for Lead Quantification in Drinking Water Samples. Critical Reviews in Environmental Science and Technology, 2020. https://doi.org/10.1080/10643389.2020.1782654
- Burkhardt, J. B., Woo, H., Mason, J., Triantafyllidou, S., Schock, M., Lytle, D., Murray, R. A Framework for Modeling Lead in Premise Plumbing Systems using EPANET. Journal of Water Resources Planning and Management, 2020. https://doi.org/10.1061/(ASCE)WR.1943-5452.0001304
- DeSantis, M.K., Schock, M. R. Tully, J., Bennett-Stamper, C. Orthophosphate Interactions with Destabilized PbO2 Scales. Environmental Science and Technology, 2020. https://pubs.acs.org/doi/abs/10.1021/acs.est.0c03027
- Lytle, D.A., Schock, M. R., Formal, C., Bennett-Stamper, C., Harmon, S., Nadagouda, M.N., Williams, D., DeSantis, M. K., Tully, J., Pham, M. Lead Particle Size Fractionation and Identification in Newark, New Jersey's Drinking Water. Environmental Science and Technology, 2020 https://pubs.acs.org/doi/10.1021/acs.est.0c03797
- Tully, J.; DeSantis, M. K.; Schock, M. R. Water Quality–Pipe Deposit Relationships in Midwestern Lead Pipes. AWWA Water Science 2019, 1 (2), e1127. https://doi.org/10.1002/aws2.1127**[JOURNAL OPEN ACCESS in March 2019],** https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7336533/ **[EPA PUBLIC ACCESS in July 2020]**

How we communicate our research & technical support

Recent examples

EPA Science Matters Newsletters (Freely accessible at https://www.epa.gov/sciencematters)

- Scaling Back: EPA Researchers Help Communities Protect Drinking Water Systems from Lead, *April 8, 2019*
- Revealing the Complicated Nature of Tap Water Lead Contamination: A Madison, Wisconsin, Case Study, *July 30, 2018*
- Identifying the Best Lead Sampling Techniques to Protect Public Health, *October 22, 2018*

Fact Sheets (Freely accessible)

- How to Identify Lead Free Certification Marks for Drinking Water System and Plumbing Products
- Consumer Tool for Identifying POU Drinking Water Filters Certified to Reduce Lead

Workshops

- EPA 17th Small Drinking Water Systems Annual Workshop in Cincinnati, September 1-3, 2020.

- Presentations: Lead Particulate Release (Lytle), Practical Insights from Theoretical Lead Solubility Modeling (Wahman)

- Break-out sessions and training sessions on corrosion

Technical Support Summaries, including lead (Freely accessible)

Technical Support Summary, Water Infrastructure Division, Fiscal Year 2019

Webinars

- ORD/OW Small Systems Monthly Webinar Series

Lead Management in Homes and Buildings, DeSantis, Tully, and Latham, March 26, 2019

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