

Corrosion Control, Flint, and What Utilities Should be Doing Now

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Corrosion Chemistry

- Alkalinity, pH, and DIC
- Corrosion inhibitors
- Hardness (calcium and magnesium)
- Buffer Intensity
- Dissolved oxygen (DO)
- Oxidation reduction potential (ORP)
- Ammonia, chloride, and sulfate
- Natural organic matter (NOM)
- Iron, aluminum, and manganese

pH & Alkalinity

- pH = measure of acidity/ hydrogen ion concentration (H^+ or H_3O^+)
 - Best Practice: measure pH in the field at the time of sample collection using a calibrated instrument
 - pH can fluctuate due to interactions between water and pipe material, microbiological activity, and changes in disinfectant residual
- Alkalinity = capacity of water to neutralize acid
 - Primarily the sum of carbonate, bicarbonate, and hydroxide anions
$$\text{Alkalinity} = 2CO_3^{2-} + HCO_3^- + OH^- - H^+$$
(Stumm and Morgan, 1981)
 - Best Practice : measure alkalinity using a certified method, which will likely report as mg/L as calcium carbonate ($CaCO_3$).

DIC (Dissolved Inorganic Carbon)

- DIC is an estimate of the total amount of inorganic carbon usually reported in mg/L as carbon (mg/L as C)



- DIC cannot be measured but can be predicted based on the pH, alkalinity, ionic strength, and temperature of the water
- Why DIC?
 - Directly measures the availability of carbonate species that can react with lead and copper to form passivating scales

Hardness

- Hardness is primarily the sum of calcium and magnesium in water
 - Best Practice : measured in the laboratory and is typically reported as mg/L as CaCO_3 (calcium carbonate)
- If finished water has high hardness, increasing the pH to control lead release can cause calcium carbonate precipitation, or scaling, in the distribution system.
 - Langelier Saturation Index (LSI): provides maximum pH adjustment that can be employed without causing precipitation, not to evaluate Pb/Cu control
 - Ryznar Index: indicator of scaling conditions
 - Calcium carbonate precipitation potential (CCPP): indicator of scaling conditions

Buffer Intensity

- Buffering Intensity = water's ability to resist changes in pH
 - Also called buffer capacity
- Buffer intensity depends on the alkalinity, DIC, and pH of the water.
- The highest buffer intensity at a pH of approximately 6.3
- Minimum intensity at pH values between 8.0 and 8.5.
 - Waters with pH between 8 and 8.5 and low DIC (less than about 10 mg/L as C) may have more variable pH within the distribution system
 - Increasing DIC in waters with pH values in the 8 – 8.5 range will not result in appreciable increases in buffer intensity.
- Additional buffer intensity may result when phosphate or silicate chemicals are dosed at a high concentration relative to DIC.

Dissolved Oxygen

- Oxygen is slightly soluble in water
 - generally concentration ≤ 15 mg/L
- Well-aerated Water = 8 or 9 mg/L, depending on water temperature
- Can be measured in the field using a calibrated DO meter
- DO concentration affects the solubility of iron, manganese, lead, and copper:
 - Increasing DO in the water can increase copper corrosion, converting Cu(I) to Cu(II).
 - High DO levels may provide corrosion benefits under some circumstances, by facilitating the production of different and more protective lead oxide scales

Oxidation Reduction Potential

- Oxidation-reduction potential (redox potential or ORP) = the electric potential (Eh) required to transfer electrons from one compound (the oxidant) to another compound (the reductant)
- ORP varies with pH, temperature, and DIC
 - Moderated by the type and concentration of disinfectant in the water (e.g., chlorine or chloramines) and the DO concentration
- Changes in water quality parameters that cause a reduction in pH or ORP cause PbO₂ (insoluble) to convert to Pb(II) (soluble) compounds and release lead into the water.
 - Triggers may include a change in disinfection practices can (e.g., switching from chlorine to chloramines in the distribution system),
- The high Eh values needed for PbO₂ formation may be found in systems that have a high chlorine residual (i.e., > 2 mg/L as free chlorine) for extended periods of time.
- PbO₂ has been observed to form between pH 7 and 9.5, with formation occurring more quickly at higher pH values.

Ammonia, Chloride, and Sulfate

- Nitrification occurs when nitrifying bacteria convert ammonia into nitrite and nitrate, which may lower the pH and alkalinity of the water.
 - This can accelerate brass corrosion and cause problems with lead release
 - Ammonia may also form compounds with lead and copper, which can interfere with the effectiveness of CCT.
 - Excess ammonia from source water and/or the use of chloramines
- The ratio of chloride (Cl^-) to sulfate (SO_4^{2-}) in the water can be an indicator of potential lead release:
 - Lower chloride-to-sulfate ratios may be indicative of lower lead release due to the formation of an insoluble sulfate precipitate with lead.
 - Higher ratios may result in the formation of a soluble chloride complex, where lead is galvanically connected to another metal such as copper

Natural Organic Matter (NOM)

- NOM is a complex mixture of organic compounds that occur in both ground and surface water sources (more prevalent in surface water)
 - Difficult to measure directly, so many utilities use UV254 as a surrogate
- The impact of NOM on metals release is unclear
 - NOM in finished water can help form the protective films that reduce corrosion
 - Or may react with corrosion products to form soluble complexes with lead, which may increase lead levels in the water
- Organic matter can also provide nutrients for microorganisms
 - Exacerbate problems with biofilm growth
 - Depleting chlorine residuals
 - May cause microbially-induced copper corrosion (pinhole leaks) through localized decreases in pH or through the formation of sulfide

Iron, Manganese, and Aluminum

- Iron & Manganese
 - Groundwater sources & lower depths of thermally stratified lakes and reservoirs
 - secondary maximum contaminant levels (SMCLs) for iron and manganese of 0.3 mg/L and 0.05 mg/L, respectively (aesthetic issues – no health based MCL)
- Increases in pH for lead and copper control may oxidize Iron & Manganese
 - Iron and manganese removal at the treatment plant
 - Sequestering agents or silicates, can be used in these cases
- Iron and Manganese reacts with dissolved lead and
 - form deposits on lead service lines and in premise plumbing (Madison, WI)
 - Manganese can also interfere with the formation of PbO_2 and other passivating films

Iron, Manganese, and Aluminum

- Aluminum can interfere with orthophosphate effectiveness
 - Forms aluminum phosphate precipitates and scales
 - Aluminum scales are less stable than orthophosphate scales & are prone to sloughing with changes in flow or water quality, or when physically disturbed
 - Dislodged scales may become entrapped in the interior (premise) plumbing and/or the faucet screen
 - May reduce the effective diameter of the pipes, resulting in loss of hydraulic capacity and increases in system headloss and operational costs

Physical and Hydraulic Factors

- Any physical disturbance may result in lead particulate release
 - Meter installation/replacement
 - External shut-off valve repair/replacement
 - Auto-meter-reader installation
 - Significant street excavation
 - Service line repair/partial replacement
 - Repair or replacement of home plumbing fixtures or piping
- Air in the line may scour deposits
 - Occurs during interior plumbing repairs or infrastructure upgrades
 - Tap flushing to remove air bubbles can disrupt pipe scales and release lead, copper, and scales

Physical and Hydraulic Factors

- High velocity water
 - Transports the corrosion inhibitor to pipe surfaces at a higher rate (reduce lead and copper release)
 - Increase the rate at which the oxidants in water come into contact with the metal surface (mobilize lead and copper)
 - can also mobilize loosely adherent scale and cause sporadic lead release
- Reduced flow rate
 - Prevents corrosion control inhibitor delivery to the pipe walls, preventing the formation of passivating scales
 - Increased water age from less frequent use can cause water quality changes
 - reductions in pH and loss of free chlorine residual exacerbating corrosion & microbial problems

Physical and Hydraulic Factors

- Flow reversals and hydraulic pressure transients
 - Pressure transients may occur when valves are closed to perform maintenance or due to backflow from a cross connection
 - Residential backflow is common
 - Hydraulic pressure transients due to sudden changes in water velocity due to valves slamming shut, power outages, or pump start/stop cycles
- Water temperature can't be generalized
 - Impacts depend on the water chemistry and type of plumbing material
 - More lead is mobilized during warmer weather seasons
 - Orthophosphate reacts more quickly at higher temperatures
 - Reduction in lead levels may take longer in colder months than in warmer months.
 - Higher temperature can exacerbate copper corrosion or facilitate a better passivating copper pipe scale
 - PWS should collect WQP and lead & copper data all year to determine trends

Corrosion Chemistry

- Corrosion: the electrochemical interaction between a metal surface such as pipe wall or solder and water
- (1) **uniform corrosion**, where the electrochemical interaction occurs along the pipe wall, resulting in a relatively uniform loss of metal across the entire surface;
- (2) **non-uniform corrosion**, where metal is lost from a localized point, causing pitting and mounding in some cases; and
- (3) **galvanic corrosion** which comes from a coupling of dissimilar metals or internally in metallic alloys

Types of Lead and Copper Releases

- Three Types of Pb/Cu releases:
 - dissolved
 - colloidal
 - particulate (i.e., bound up with other compounds such as iron and aluminum)
- Pipe scales can be complex and can include:
 - (1) passivating films that form when pipe material and water react directly with each other
 - (2) deposited scale material that forms when substances in the water (e.g., iron, manganese, aluminum, calcium) precipitate out or sorb to, and then build up on the pipe surface
- Scales can have layers and are influenced by treatment history

Types of Lead and Copper Releases

- Without corrosion inhibitors lead scales result from the reaction of carbonate leading to the formation of divalent lead compounds (Pb⁺⁺ or Pb(II))
 - Hydrocerussite $[(Pb_3(CO_3)_2(OH)_2)]$
 - Cerussite (PbCO₃)
 - Plumbonacrite $[Pb_{10}(CO_3)_6(OH)_6O]$
 - co-occurs with Pb(II) carbonate compounds in scales and can be a predominant form in systems with high pH (>10)
 - Massicot and Litharge (which are both forms of PbO) form under higher alkalinity conditions
 - Carbonate containing scales are often off-white and slightly chalky when dry

Types of Lead and Copper Releases

- Pb(IV) compounds/lead oxide (PbO_2)
 - can be the predominant compounds in lead pipe scales under highly oxidative conditions
 - under low organic matter conditions
- Crystalline Pb(II) orthophosphate compounds such as hydroxypyromorphite [$\text{Pb}_9(\text{PO}_4)_6$, or $\text{Pb}_3(\text{PO}_4)_2$]
 - Association with orthophosphate use
 - Scales in systems with blended phosphates do not follow the same trends as orthophosphate and seem to be influenced by calcium concentrations and phosphorus speciation

Types of Lead and Copper Releases

- Copper-based scales
 - cuprite (Cu_2O)
 - cupric hydroxide ($\text{Cu}(\text{OH})_2$)
 - tenorite (CuO)
 - malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$)
- Orthophosphate leads to the formation of various copper phosphate scales

Corrosion Inhibitors

- The most common corrosion inhibitors are phosphate-based, which include orthophosphate (PO_4^{3-}) in their formulation
- Polyphosphates
 - polymers containing linked orthophosphate ions in various structures are used mainly for sequestering iron and manganese
 - They work by binding or coordinating the metals into their structures so they cannot precipitate on sinks or clothes
 - May also sequester lead and copper, keeping them in the water and actually increasing the risk of exposure
 - Can revert to orthophosphate in the distribution system, but it is difficult to predict if and when this occurs
 - **Research has confirmed that polyphosphates are generally not effective on their own for controlling the release of lead and copper**

Corrosion Inhibitors

- Blended phosphates (mixture of orthophosphate and polyphosphate)
 - Corrosion control
 - Sequester iron and manganese
- Silicate-based inhibitors
 - Reduce lead and copper levels in first draw-samples at the tap
 - Full-scale use has been limited

A Closer Look at Flint, Michigan

- Changed from Detroit to Flint River in April 2014
- Lead concentrations between 9/15/2015 & 6/30/2016
 - Range: non-detect to 22,905 ppb
 - 48.4% of samples were non-detect for lead
 - 91.9% of samples were at or below the Action Level (15 ppb)
 - 90th percentile between 9/15/2015 & 12/31/2015: 11 ppb
 - Range non-detect to 2,516 ppb
 - 90th percentile between 01/01/2016 & 6/30/2016: 12 ppb
 - Range non-detect to 22,905 ppb
 - Highest sample collected on 4/18/2016 at 3328 Walton Avenue (48504)
- Flint switched back to Detroit water in October 2015

A Closer Look at Flint, Michigan

- Large disparities in lead impacts by zip code
 - 48503 90th percentile for 2016 is 14 ppb
 - Range non-detect to 13,295 ppb
 - 48504 90th percentile for 2016 is 14 ppb
 - Range non-detect to 22,905 ppb
 - 48505 90th percentile for 2016 is 10 ppb
 - Range non-detect to 5,245 ppb
 - 48506 90th percentile for 2016 is 9 ppb
 - Range is non-detect to 9,416 ppb

A Closer Look at Flint, Michigan

Sample Number	Date Submitted	Analysis (Lead)	Lead (ppb)	Analysis (Copper)	Copper (ppb)	Street #	Street Name	City	Zip Code
LG09935	2/5/2016	Lead	0	Copper	0	1418	WALTON AVE	FLINT	48532
LG27928	3/24/2016	Lead	1	Copper	120	3007	WALTON AVE	FLINT	48504
LG49269	6/2/2016	Lead	0	Copper	60	3100	WALTON AVE	FLINT	48504
LG27914	3/24/2016	Lead	0	Copper	90	3128	WALTON AVE	FLINT	48504
LG06521	1/31/2016	Lead	0	Copper	0	3250	WALTON AVE	FLINT	48504
LG12540	2/12/2016	Lead	0	Copper	0	3323	WALTON AVE	FLINT	48504
LG31194	4/2/2016	Lead	11,070	Copper	5,120	3328	WALTON AVE	FLINT	48504
LG37030	4/18/2016	Lead	22,905	Copper	4,492	3328	WALTON AVE	FLINT	48504
LG37987	4/21/2016	Lead	0	Copper	0	3328	WALTON AVE	FLINT	48504
LG37988	4/21/2016	Lead	0	Copper	0	3328	WALTON AVE	FLINT	48504
LG37989	4/21/2016	Lead	43	Copper	60	3328	WALTON AVE	FLINT	48504
LG37990	4/21/2016	Lead	3	Copper	0	3328	WALTON AVE	FLINT	48504
LG37991	4/21/2016	Lead	10,450	Copper	1,720	3328	WALTON AVE	FLINT	48504
LG38086	4/22/2016	Lead	1	Copper	110	3328	WALTON AVE	FLINT	48504
LG38087	4/22/2016	Lead	1	Copper	0	3328	WALTON AVE	FLINT	48504

So what can utilities do?

1. Communicate with the DWP when planning to change sources or corrosion control treatments
 - Treatment changes must be approved by the DWP
2. Contact the DWP when changes in WQP are observed
3. Update infrastructure inventory when new information becomes available
4. Notify homeowners immediately & collect a confirmatory sample when elevated lead results occur
5. Try to determine the cause of elevated lead results
 - Improper sample collection
 - Extended stagnation
 - Cross connection
 - Corrosion control not reaching a portion of the distribution

Questions?

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