

# **Water Chemistry Effects on Dissolution Rates of Lead Corrosion Products [Project #4064]**

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## **PRINCIPAL INVESTIGATORS:**

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## **OBJECTIVES:**

The primary objective of the project was to provide new information to the water supply community that advances understanding of lead corrosion product dissolution and transformation rates. Specific objectives were to (1) summarize the state-of-knowledge regarding dissolution rates of lead corrosion products; (2) determine dissolution and transformation rates of lead corrosion products as a function of pH and concentrations of orthophosphate, dissolved inorganic carbon, and chloramines; and (3) evaluate lead release rates from corrosion products on lead pipes by applying fundamental dissolution rate information developed for Objective 2.

## **BACKGROUND:**

The internal corrosion of lead-containing pipe, fittings, and solder in premise plumbing is the most significant source of lead to drinking water. Although new construction does not use lead pipe, many older buildings retain original lead service lines and internal plumbing. Concern over lead concentrations in drinking water motivated the passage of the Lead and Copper Rule (LCR) in 1991. The LCR requires utilities to implement methods to control lead corrosion if the 90<sup>th</sup> percentile of samples exceeds the action level of 0.015 mg/L. Lead concentrations in tap water are strongly influenced by distribution system water chemistry. In response to changes in water chemistry, high lead concentrations can also be observed in systems with no previous history of a lead problem.

Lead concentrations in drinking water are affected by chemical reactions that occur within lead service lines and premise plumbing. Lead may be released directly from pipe, lead-containing corrosion products on the pipe surface, and from brass and solder that contain lead. Lead corrosion products observed on lead pipes include lead(II) carbonates and phosphates and, more recently, lead(IV) oxide ( $\text{PbO}_{2(s)}$ ). Solubility and dissolution rates of corrosion products are affected by water chemistry parameters including pH, dissolved inorganic carbon, orthophosphate, and the concentration and type of disinfectant residual.

Information on dissolution rates of lead corrosion products can be particularly valuable as water suppliers consider process changes that affect water chemistry such as switching disinfectant type or dose, adjusting pH, or adding a corrosion inhibitor. While the formation of lead corrosion products can passivate the pipe surface and limit further lead release, changes in water chemistry can cause dissolution of the corrosion products and

lead release to solution. An improved understanding of the effects of water chemistry on lead release rates can be used to identify strategies that inhibit dissolution and minimize lead release. Information on corrosion product dissolution rates can also help quantify the influence of stagnation time on lead concentrations to which consumers are exposed and upon which monitoring protocols are based.

#### **APPROACH:**

The three objectives were addressed in a research approach that was divided into three corresponding research tasks. Task 1 was a literature review regarding the dissolution rates of lead(II) carbonate, lead(II) phosphate, and lead(IV) oxide precipitates. Task 2 was a systematic experimental investigation of the dissolution rates of three important lead corrosion products. Task 3 extended the study of dissolution rates of pure solids to release rates from pipe scales. Tasks 2 and 3 involved bench-scale laboratory experiments with integrated analysis of the aqueous solutions and the solid phases.

#### **RESULTS/CONCLUSIONS:**

##### **Task 1: Review of Lead Carbonate, Phosphate, and Oxide Dissolution Rates**

The review introduces the impact of the dissolution of lead corrosion products on drinking water quality. It then presents an overview of the equilibrium solubility of lead (II) carbonates and phosphates and lead(IV) oxides. The dissolution rates of these solids are then summarized and compared with the rates of other divalent metal carbonate and phosphate precipitates. The presentation of rates describes an approach that accounts for the effects of pH and the distance of the solution from equilibrium solubility. The dissolution rates of both carbonate and phosphate solids increase with decreasing pH; however, the majority of these studies observed such effects at pH values below 7, and measurements over a neutral pH range are less pH-dependent. Dissolution rates of lead carbonates and phosphates are comparable to those of the much more frequently studied calcium carbonates and phosphates. Dissolution rates are lower at lower temperatures.

##### **Task 2: Quantification of Dissolution and Transformation Rates of Lead Corrosion Products**

Combinations of pH and concentrations of dissolved inorganic carbon (DIC), orthophosphate, and chloramines were evaluated for all three of the lead corrosion products. In total, 23 conditions were evaluated for hydrocerussite, 21 for hydroxylpyromorphite, and 21 for plattnerite. For the simplest aqueous compositions (i.e., no DIC, orthophosphate, or chloramines), hydrocerussite had dissolution rates that were about two orders of magnitude greater than those of plattnerite and hydroxylpyromorphite. The effects of specific water chemistry parameters and combinations of water chemistry parameters were examined for each solid.

Hydrocerussite dissolution rates were affected by pH and the concentrations of DIC and orthophosphate. Dissolution rates of plattnerite, which is only stable in the presence of a free chlorine residual, provide information about the rates of lead release when the water

contacting pipe scales no longer contains free chlorine. The dissolution rates of hydroxylpyromorphite were affected by all four water chemistry parameters.

### **Task 3: Evaluation of Lead Release from Pipe Scales**

The lead pipe scales used for release experiments were characterized before their use in release rate experiments.

- The pipe sections provided by the Massachusetts Water Resources Authority (MWRA) from one of its customer communities contained primarily hydrocerussite and some cerussite. The formation of these phases is consistent with the water chemistry in the distribution system.
- For the new lead pipes conditioned in the laboratory, the dominant corrosion products were hydrocerussite and litharge (PbO). Pipes conditioned for 8 months had minor amounts of the lead(IV) oxides scrutinyite and plattnerite, but pipes conditioned for 3 months did not have any of these phases. The thickness of the corrosion product layer was about 30  $\mu\text{m}$  for the pipes conditioned for 8 months and about 15  $\mu\text{m}$  for 3 months of conditioning. During pipe conditioning, the dissolved lead concentrations stabilized around 50  $\mu\text{g/L}$  within 50 days, but the concentrations were much higher in the initial phases of conditioning. This relatively high free chlorine concentration of 3.5 mg/L as  $\text{Cl}_2$  was chosen to promote the development of lead(IV) oxides in pipe scales. Even after lead concentrations stabilized, oxidation of the pipe was still significant as indicated by the continued consumption of free chlorine.

Lead release from the laboratory-conditioned pipes was affected by the composition of the solution in the pipes. Releases were measured at conditions that represent a change in water chemistry from that with which the pipe scales had acclimated.

The influence of water chemistry on lead release from the actual lead service line pipe sections was similar to its influence on the release from the laboratory-conditioned pipes. The pipes were reacted with solutions of different compositions than experienced when they were most recently in use, and the pipe sections were used directly without any reacclimation period.

#### **APPLICATIONS/RECOMMENDATIONS:**

Information on the specific water chemistry and corrosion products is valuable in predicting and controlling lead release from scales on lead service lines. When collecting samples for compliance with the LCR, utilities could gain insights into processes controlling lead concentrations by measuring pH, dissolved inorganic carbon concentrations or alkalinity, free and/or combined chlorine concentrations, and orthophosphate concentrations. Information on the identity of the corrosion products can be gained by sampling and analyzing portions of pipe scales when lead service lines are removed from a system. Archiving of sections of these lead service lines may also be useful for experimentally testing the response of lead concentrations to proposed changes in distribution system water chemistry.

The effectiveness of corrosion control strategies will vary depending on the source water chemistry and the composition of the pipe scales. For pipe scales with significant amounts of the lead(IV) oxides plattnerite or scrutinyite, low lead concentrations are achieved when a free chlorine residual is maintained. In the absence of free chlorine, the lead(IV) oxides will breakdown, but the release of lead to solution can be mitigated by control of the water chemistry. Less lead is released at higher pH values. The dissolution of hydrocerussite, which is a frequently observed corrosion product, was also slower at high pH. While increasing alkalinity can help in achieving and stabilizing higher pH values, associated increases in dissolved inorganic carbon can actually increase rates of lead release from plattnerite and had complex effects of hydrocerussite dissolution. The addition of orthophosphate dramatically decreased rates of lead release from both plattnerite and hydrocerussite. One mechanism through which orthophosphate mitigates lead release is the formation of hydroxylpyromorphite. Hydroxylpyromorphite has a low solubility and dissolves slowly. Low lead concentrations can be maintained with 1 mg P/L orthophosphate and possibly less. A minimal dose may be established that mitigates lead release effectively and minimizes cost and the potential for negative side effects of biological growth and the need for orthophosphate removal in wastewater treatment.

**PARTICIPANT:**

Massachusetts Water Resources Authority