Redox Reactions Influencing Lead Concentrations in Drinking Water: Formation and Dissolution of Lead(IV) Oxide and Impact of Galvanic Corrosion

by

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Two approaches have been used to mitigate lead release to drinking water are optimizing water chemistry to form stable lead corrosion products and replacing lead service lines with lead-free materials. The present study investigated the effects of water chemistry on the formation and dissolution of the lead corrosion product lead(IV) oxide (PbO$_2$). The impact of galvanic corrosion on lead release following simulated partial lead service line replacements (PLSLRs) was also determined.

The extent and identity of PbO$_2$ formation was determined as a function of pH, the presence of dissolved inorganic carbon (DIC), and free chlorine concentrations with different lead(II) starting phases. PbO$_2$ formed both with and without DIC. The intermediate solids formed affected the identity of the PbO$_2$ (scrutinyite versus plattnerite) product. When no intermediate solids formed, scrutinyite formed from hydrocerussite, and mixtures of scrutinyite and plattnerite formed from lead(II) chloride and massicot.

The dissolution rates of PbO$_2$ were quantified at various pH values and concentrations of DIC, free chlorine, and iodide using continuously stirred tank reactors (CSTRs). Increasing the
pH decreased the dissolution rate. The presence of free chlorine inhibited PbO$_2$ dissolution, while the presence of iodide greatly accelerated PbO$_2$ dissolution. The reductive dissolution of PbO$_2$ was proposed to be a coupled process involving chemical reduction of Pb(IV) to Pb(II) at the PbO$_2$ surface followed by detachment of Pb(II) to solution. The dissolution rate was directly correlated with the surface species of PbO$_2$ that participated in the reaction.

The impact of galvanic corrosion on lead release was investigated with aged lead pipes harvested from two different distribution systems connected to copper tubing by four types of couplings: brass, brass dielectric, plastic, and plastic with external electric wires. Experiments were performed in a recirculating flow mode with intermittent stagnation periods. Relative to the plastic-coupled pipe assemblies, which always had the lowest lead release, the lead release increased in the order of the systems coupled with plastic with external wires, brass dielectric, and brass. The enhancement of lead release was attributed to galvanic corrosion. Galvanic corrosion primarily caused release of particulate lead. It is a localized effect with much higher lead release in the region closest to the coupling.
Chapter 1. Introduction

1.1 Background

1.1.1 Lead Concentrations and Regulation in Drinking Water

Lead pipes were widely used in drinking water distribution systems in North America at
the beginning of the 20th century due to the durability and malleability of lead. However, lead
and its compounds are toxic and even low levels of lead can cause adverse health effects,
especially in children (Yule, 1992). The U.S. Environmental Protection Agency (EPA)
prohibited the installation of lead pipe, plumbing fittings or fixture, and solder after 1986.
Although new construction does not use lead pipe, many old buildings still retain their original
lead service lines (i.e. lead pipes).

From reactions with water in the pipe, lead corrosion products develop on the inner surface
of lead pipes, and these corrosion products then control lead release to drinking water (Figure
1.1) (Schock, 1989; Schock, 1999). Drinking water is one of the main sources of lead exposure,
estimated by the U.S. EPA to contribute 14 – 20 % of total childhood lead exposure in the United
States (Miranda et al., 2006). An increase of blood lead levels for children younger than 1.3
years in Washington DC during 2001 – 2003 was highly correlated with the elevated lead
concentrations in DC drinking water during that time (Edwards et al., 2009).

To reduce lead concentrations in drinking water, the U.S.EPA developed the Lead and
Copper Rule (LCR) that set an action level of 0.015 mg/L for lead for a 1-L first draw sample of
tap water (USEPA, 1991). For homes having lead service lines or other lead-containing materials
in the premise plumbing, if the lead concentrations in more than 10% of the samples are above
this value, then actions must be taken for corrosion control and the public should be informed.

There are two overall approaches to mitigating lead release to drinking water. The first one is to optimize the water chemistry to form stable lead corrosion products that have low solubility. The second solution is to replace the lead-containing materials like lead pipes with lead-free materials. Lead service line replacement is required by the LCR if the lead concentrations cannot be lowered below the action level by using optimization of water chemistry for corrosion control.

![Figure 1.1. Schematic view of lead corrosion products formed in drinking water distribution systems (Adapted from Noel and Giammar (2007))](image)

### 1.1.2 Lead Corrosion Products

Corrosion products observed in drinking water distribution systems include lead(II) oxides, lead(II) carbonates, lead(II) phosphates, and lead(IV) oxides (Edwards and McNeill, 2002; Schock, 1999; Schock et al., 2008; Schock et al., 2005a). The formation of the corrosion products is affected by water chemistry parameters that include pH, dissolved inorganic carbon (DIC) concentration, the presence of orthophosphate, and the type and concentration of chlorine disinfectant.

Compared to lead(II) solids, lead(IV) oxide (PbO₂) is much less soluble and can maintain lead concentrations well below the action level (Figure 1.2). PbO₂ has been found in distribution systems that use free chlorine as a disinfectant. Both of its polymorphs, scrutinyite (α-PbO₂) and
plattnerite (β-PbO₂), have been observed (Kim and Herrera, 2010; Lytle and Schock, 2005; Schock and Giani, 2004; Schock et al., 2005b). PbO₂ formation requires strongly oxidizing conditions that can only be achieved when free chlorine (i.e. HOCl and OCl⁻) is present as the residual disinfectant in a distribution system (Lytle and Schock, 2005; Switzer et al., 2006).

**Figure 1.2.** Dissolved lead concentrations in equilibrium with (a) two polymorphs of lead(IV) oxide at oxidizing conditions and (b) the lead(II) carbonates cerussite and hydrocerussite with 50 mg C/L DIC and the lead(II) phosphate hydroxylpyromorphite with 50 mg C/L DIC and 1 mg P/L orthophosphate.

The formation of PbO₂ as a corrosion product in scales on lead pipes is a two-step process. First, lead(0) metal is oxidized to lead(II) corrosion products, like lead(II) oxides and carbonates. Then these lead(II) compounds are further oxidized to lead(IV) oxide by free chlorine; common oxidants including oxygen and monochloramine are not strong enough to oxidize Pb(II) to PbO₂. Both water chemistry parameters and the lead(II) precursor phases affect the extent and identity of PbO₂ formed. In studying PbO₂ formation from PbCl₂ solutions in the presence of DIC, Lytle and Schock (2005) found that higher pH favored the formation of scrutinyite while lower pH favored the formation of plattnerite. Liu and co-workers determined the formation of PbO₂ from
the lead(II) carbonates cerussite (PbCO$_3$) and hydrocerussite (Pb$_3$(OH)$_2$(CO$_3$)$_2$), and they observed a phase transition from hydrocerussite to cerussite. They suggested that cerussite might be a required intermediate phase in the formation of PbO$_2$ (Liu et al., 2008). Orthophosphate is often added at water treatment plants as a corrosion inhibitor (McNeill and Edwards, 2002). The presence of orthophosphate inhibited the formation of PbO$_2$ from a PbCl$_2$ solution (Lytle et al., 2009). Despite the previous work, the pathways of PbO$_2$ formation remain insufficiently understood for predicting the prevalence of PbO$_2$ in distribution systems.

PbO$_2$ is often found coexisting with lead(II) corrosion products in the scales from actual pipes, indicating that the systems are not at equilibrium (Kim and Herrera, 2010; Schock and

Figure 1.3. Predominance area diagrams of the Pb(0) - Pb(II) - Pb(IV) system with a total lead concentration 0.015 mg/L and 20 mg C/L. The dashed lines represent the stability limits of water (P$_{O_2}$ = 0.21 atm and P$_{H_2}$ = 1 atm)
Giani, 2004). For systems containing PbO₂, the dissolution rate rather than the equilibrium solubility of PbO₂ probably controls lead concentrations in tap water. PbO₂ is only stable in systems with high oxidation reduction potential (ORP), which is provided by the consistent use of free chlorine (Figure 1.3). Although the lead concentrations in the systems where free chlorine is present to maintain the Pb(IV) oxidation state are higher than the predicted equilibrium solubility of PbO₂, they are still below the lead action level (Xie et al., 2010a). PbO₂ is such a strong oxidant that its reduction by water is even thermodynamically favorable (Lin and Valentine, 2008a; Xie et al., 2010b). The presence of other reductants, including chloramines, natural organic matter (NOM), Fe^{2+}, Mn^{2+}, Br⁻, and I⁻, have been found to greatly accelerate the dissolution of PbO₂ (Dryer and Korshin, 2007; Lin and Valentine, 2008a; Lin et al., 2008; Lin and Valentine, 2010; Shi and Stone, 2009a; b). Table 1.1 summarizes recent studies of PbO₂ reductive dissolution. Most of these studies were conducted in batch reactors and were not designed to give quantitatively estimates of the dissolution rates of PbO₂.

The mechanism of PbO₂ reductive dissolution has been determined at acidic conditions using Br⁻ as a model reductant (Lin and Valentine, 2010). At pH 3.5 – 4.5 the reductive dissolution of PbO₂ can be described by a coupled process of chemical reduction and detachment. In the chemical reduction step the reductant attaches to the surface of PbO₂ and the surface Pb(IV) species are reduced to surface Pb(II) species; in the second step the surface Pb(II) species detach from the surface and are released to the solution. The mechanisms of PbO₂ dissolution at the circumneutral and slightly basic pH values that are typical for drinking water distribution are still not well understood. Elucidating the mechanisms of PbO₂ dissolution at conditions relevant to drinking water distribution can provide a quantitative view to estimate lead
concentrations and enact strategies to limit lead release in distribution systems with PbO₂ present.

**Table 1.1. Summary of previous studies on the dissolution of PbO₂**

<table>
<thead>
<tr>
<th>Reductants</th>
<th>Experimental conditions</th>
<th>Experimental mode</th>
<th>Dissolution rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOM</td>
<td>pH 7</td>
<td>Batch</td>
<td>Increased with increasing NOM concentration</td>
<td>(Dryer and Korshin, 2007)</td>
</tr>
<tr>
<td>NOM, water</td>
<td>pH 6 – 9</td>
<td>Batch</td>
<td>Increased with increasing NOM concentration and decreasing pH</td>
<td>(Lin and Valentine, 2008a)</td>
</tr>
<tr>
<td>Iodide</td>
<td>pH 6 – 8</td>
<td>Batch</td>
<td>Increased with increasing iodide concentration and decreasing pH</td>
<td>(Lin et al., 2008)</td>
</tr>
<tr>
<td>NH₂Cl, NOM</td>
<td>pH 7</td>
<td>Batch</td>
<td>NOM &gt; NOM + NH₂Cl &gt; NOM + Cl₂</td>
<td>(Lin and Valentine, 2009)</td>
</tr>
<tr>
<td>Mn²⁺, Fe²⁺</td>
<td>pH 3 – 8.5</td>
<td>Batch</td>
<td>Increased with increasing Fe²⁺ concentration and increasing Mn²⁺ concentration</td>
<td>(Shi and Stone, 2009a)</td>
</tr>
<tr>
<td>NOM</td>
<td>pH 6.5, no NaHCO₃ 45 mg C/L, NOM</td>
<td>Batch</td>
<td>coagulation treated NOM &gt; granular activated carbon treated NOM</td>
<td>(Shi and Stone, 2009b)</td>
</tr>
<tr>
<td>Bromide</td>
<td>pH 3.5 – 4.5</td>
<td>Batch</td>
<td>Increased with increasing bromide concentration and decreasing pH</td>
<td>(Lin and Valentine, 2010)</td>
</tr>
<tr>
<td>Water</td>
<td>pH 7.5 – 10</td>
<td>Flow-through</td>
<td>Increased with increasing DIC concentration</td>
<td>(Xie et al., 2010b)</td>
</tr>
<tr>
<td>Water, NH₂Cl</td>
<td>pH 7.5 – 8.5 4.2 mM NaHCO₃ 2 mg/L as Cl₂, NH₂Cl</td>
<td>Flow-through</td>
<td>Increased with decreasing ORP</td>
<td>(Xie et al., 2010a)</td>
</tr>
</tbody>
</table>

**1.1.3 Lead Service Line Replacement**

Replacing lead pipes with lead-free materials including copper tubing is a strategy to control lead concentrations in tap water. Lead service line replacement (LSLR) has been adopted by several water utilities for control of lead concentrations. However, utilities usually have ownership of the lead service line up to the property line, and the remainder of the service line is
privately owned. Due to the cost of the replacement, most owners choose not to replace their portion of the service line when the utility is replacing the utility-owned portion (Swertfeger et al., 2006). Thus, the lead service line is only partially replaced and the new connection of a building to the water main has copper tubing connected to the remaining lead pipe. Following such a partial lead service line replacement (PLSLR), if the lead pipe and copper tubing are electrically connected, such as by direct end-to-end contact or connection with a metal coupling, then galvanic corrosion of the lead pipe may occur.

Galvanic corrosion is a particular type of corrosion that involves accelerated oxidation of one metal that is electrically connected with a different metal (Davis, 2000). The driving force for galvanic corrosion is the differences in the electrochemical potentials of the two different metals. The metal with the lower electrochemical potential is oxidized, serving as the anode. Chemical reduction of a species in solution occurs on the metal with the higher electrochemical potential, which serves as the cathode. After PLSLRs, a lead pipe connected to copper tubing can be a galvanic couple with the lead serving as the anode (Figure 1.4). Electrons released by lead oxidation can travel through the electrically-connected system to the copper tubing where a reduction reaction occurs; the reduction reaction may involve reduction of dissolved oxygen \( \text{O}_2(\text{aq}) \) to water on the copper surface or other reactions. The water in the pipe serves as the electrolyte for ionic transport from the anode to the cathode to maintain the charge balance. The net reaction of the galvanic reaction is shown in equation 1.1.

\[
2\text{Pb}(s) + \text{O}_2 + 4\text{H}^+ = 2\text{Pb}^{2+} + 2\text{H}_2\text{O} \tag{1.1}
\]

This net reaction accelerates oxidation of the elemental lead in the lead pipe, and the resulting \( \text{Pb}^{2+} \) can be released to the water to increase the lead concentration.
Figure 1.4. Process of galvanic corrosion between the electrically connected lead pipe and copper tubing in water.

The lead concentrations in tap water following PLSLRs were monitored by several water utilities. Generally partial replacement had no significant benefit for mitigating lead release for the 2-month period after replacement (Sandvig et al., 2009). Muylwyk et al. (2011) measured lead concentrations in tap water in Guelph, Ontario following PLSLRs (94 replacements tracked) and found that for some locations high lead concentrations persisted for at least 18 months. In determining lead concentrations following PLSLRs in Cincinnati, Swertfeger et al (2006) found that the lead concentrations were only slightly lower for partial replacements than for those retained the lead service lines even after 1 year of replacement. They suggested that the persistence of lead concentrations following PLSLRs might be attributed to galvanic corrosion.

The impact of galvanic corrosion on lead release following PLSLRs has been evaluated by several lab-scale studies (Arnold, 2011a; Arnold, 2011b; Boyd et al., 2012; Cartier, 2012; Cartier et al., 2012; Clark et al., 2011; Triantafyllidou and Edwards, 2011a). The extent and duration of galvanic corrosion was strongly affected by the water chemistry, flow regime, presence of the pipe scales, and methods to connect lead pipe and copper tubing, as summarized in Table 1.2. Most of the previous studies used new or cleaned lead pipes but not aged lead pipes. Due to the presence of pre-existing scales on their internal surfaces, aged lead pipes may behave differently.
than new or cleaned lead pipes when they are connected to copper tubing. In addition, it is important to use the same connection methods in laboratory studies as those are used in practice.

Table 1.2. Summary of previous studies on galvanic corrosion between lead pipe and copper tubing

<table>
<thead>
<tr>
<th>Study</th>
<th>Method to connect lead and copper</th>
<th>Lead pipe</th>
<th>Flow regime</th>
<th>Water chemistry</th>
<th>Main Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Arnold, 2011a)</td>
<td>External galvanic wire</td>
<td>new</td>
<td>continuously recirculating flow</td>
<td>pH: 8.8 – 9.2 Free chlorine or chloramines: 4 mg Cl₂/L CSMR: 2.5</td>
<td>Galvanic corrosion disappeared for the system with free chlorine after 45 days; while it persisted for the system with chloramines.</td>
</tr>
<tr>
<td>(Arnold, 2011b)</td>
<td>External galvanic wire</td>
<td>new</td>
<td>stagnant</td>
<td>pH: 7.3 CSMR: 2.5 NOM: 0 – 4 mg/L as TOC PO₄: 0 – 2 mg P/L</td>
<td>Galvanic corrosion enhanced lead release at all the conditions.</td>
</tr>
<tr>
<td>(Clark et al., 2011)</td>
<td>Direct connection; Brass fitting; Brass valve</td>
<td>new</td>
<td>stagnant</td>
<td>pH: 8.5 CSMR: 0.9</td>
<td>Lead concentrations increased in the order of: direct connection &lt; brass fitting &lt; brass valve.</td>
</tr>
<tr>
<td>(Triantafyllidou and Edwards, 2011a)</td>
<td>External galvanic wire</td>
<td>new</td>
<td>stagnant</td>
<td>pH 8.0 CSMR: 0.2 and 16</td>
<td>Galvanic corrosion enhanced lead release for months. Increasing the CSMR increased lead release.</td>
</tr>
<tr>
<td>(Boyd et al., 2012)</td>
<td>Direct connection</td>
<td>clean</td>
<td>continuously recirculating flow</td>
<td>pH: 7.0 – 8.4 PO₄: 0 – 1 mg/L as PO₄ CSMR: ~0.66</td>
<td>Galvanic corrosion was a transient effect.</td>
</tr>
<tr>
<td>(Cartier, 2012)</td>
<td>Brass fitting</td>
<td>old</td>
<td>once-through flow with stagnation</td>
<td>pH: 7.7 and 8.3 CSMR: 0.9 and 0.3 PO₄: 0 and 1 mg P/L</td>
<td>Orthophosphate did not mitigate lead release from galvanic corrosion. Decreasing the CSMR decreased lead concentrations.</td>
</tr>
<tr>
<td>(Cartier et al., 2012)</td>
<td>External galvanic wire</td>
<td>new</td>
<td>once-through flow with stagnation; Three flow rates: 1.3, 8, 32 L/min</td>
<td>pH: 7.4 CSMR: 2.5 PO₄: 0.5 mg P/L</td>
<td>Lead release was not enhanced at a flow rate of 1.3 L/min. Lead release was greatly enhanced at flow rates of 8 and 32 L/min.</td>
</tr>
</tbody>
</table>

1.2 Research Objectives
The overall objective of this project was to advance our understanding of oxidation-reduction processes on lead pipes that affect lead concentrations in drinking water. Three specific research objectives were pursued.

**Objective 1:** Determine the extent, products, and pathways of PbO$_2$ formation as a function of water chemistry and lead-containing precursor.

**Objective 2:** Quantify the rates and elucidate the mechanisms of the reductive dissolution of PbO$_2$.

**Objective 3:** Evaluate the extent and duration of galvanic corrosion on lead release following PLSLRs.

In pursuit of these objectives, the project yielded results that provided insights into predicting the lead release and evaluating the efficacy of different strategies for mitigating lead release to drinking water.

### 1.3 Overview of Dissertation

This project was divided into three tasks (Figure 1.5), and each task corresponded to one of the specific objectives. Tasks 1 and 2 determined the effect of water chemistry on the formation and dissolution of PbO$_2$. The results of these tasks can be used to predict lead release following a switch of water chemistry and to design a strategy to minimize lead concentrations by optimizing the water chemistry. Task 3 evaluated the impact of galvanic corrosion on lead release following PLSLRs.

**Task 1: Investigate the effect of water chemistry and precursors on the formation of PbO$_2$**

Task 1 is addressed in Chapter 2. The extent and identity of PbO$_2$ formation from various Pb(II) precursors was determined as a function of pH, the presence of DIC, and free chlorine.
concentrations. Solid transformation was probed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A conceptual model was proposed to describe the pathways of PbO$_2$ formation from Pb(II) phases.

**Task 2: Establish the rate-controlling processes and quantify associated kinetic parameters of PbO$_2$ reductive dissolution**

Task 2 is the subject of Chapters 3 and 4. The dissolution rate of PbO$_2$ was quantified as a function of pH, concentrations of DIC, iodide, and free chlorine using continuously stirred tank reactors (CSTRs) (Chapter 3). The reductive dissolution of PbO$_2$ was described by a coupled process of chemical reduction and Pb(II) detachment. The dissolution rate was directly correlated with the surface speciation of PbO$_2$ (Chapter 4).

**Task 3: Determine the impact of connection methods and water chemistry on lead release following simulated PLSLRs.**

Task 3 is addressed in Chapters 5 and 6. Aged lead pipes harvested from two different distribution systems were connected with copper tubing by different types of couplings used in the field. Experiments were conducted in a recirculation flow mode with intermittent stagnation periods. The enhancement of lead release due to galvanic corrosion was quantified in terms of both dissolved and particulate lead. The primary focus of Chapter 5 was to determine whether galvanic corrosion would occur following connecting lead pipes to copper tubing and Chapter 6 expanded the study to more coupling types and changes in water chemistry.

Chapter 7 summarizes the results of the present work and makes recommendations for future research.
Two ways to control lead concentrations in drinking water

Optimize water chemistry to control corrosion products

Task 1: PbO$_2$ Formation

Task 2: PbO$_2$ Dissolution

Task 3: Impact of Galvanic Corrosion

Lead service line replacement

Figure 1.5. Overview of research tasks and their connections.
Chapter 2. Formation of Lead(IV) Oxides from Lead(II) Compounds

Results of this chapter have been published in Environmental Science & Technology, 2010, 44(23), 8950 – 8956.

Abstract

Lead(IV) oxide (PbO₂) is a corrosion product that can develop on lead pipes used for drinking water supply, and its stability can control lead concentrations in tap water. A set of batch experiments were performed to determine the extent of PbO₂ formation as a function of time, pH, the presence of dissolved inorganic carbon (DIC), and free chlorine concentration. Experiments were conducted with four lead(II) compounds that are precursors of PbO₂ formation: dissolved lead(II) chloride, massicot (β-PbO), cerussite (PbCO₃), and hydrocerussite (Pb₃(OH)₂(CO₃)₂). While PbO₂ formed in the presence and absence of DIC, the presence of DIC accelerated PbO₂ formation and affected the identity of the PbO₂ (scrutinyite vs. plattnerite) product. For some conditions intermediate solids formed that affected the identity of the PbO₂ produced. When no intermediate solids formed, hydrocerussite led to the formation of pure scrutinyite and lead(II) chloride and massicot led to mixtures of scrutinyite and plattnerite. Based on the experimental results, a conceptual model of lead(IV) oxide formation pathways was proposed.

2.1 Introduction
The dissolved lead concentration in drinking water can be controlled by the interactions of the water with corrosion products that form on lead-containing pipes and fittings. The corrosion products include lead(II) carbonates, lead(II) oxides, and lead(IV) oxides (Frenkel and Korshin, 1999; Hozalski et al., 2005; Schock, 1999; Schock et al., 2008). The pH, dissolved inorganic carbon (DIC), and oxidation reduction potential (ORP) can affect the dissolved lead concentration. The Lead and Copper Rule set the lead action level to 0.015 mg/L for a 1 L first draw sample of tap water (USEPA, 1991).

Lead release to drinking water remains a concern, especially after the observation of high lead concentrations in Washington D.C. from 2001 – 2004, which occurred following a change of disinfectant from free chlorine to chloramines (Renner, 2004; 2007). Before the switch, a relatively high free chlorine concentration facilitated the formation of PbO$_2$ on lead pipes. The switch to chloramines lowered the ORP, thus causing the reductive dissolution of low solubility PbO$_2$ to more soluble lead(II) species (Boyd et al., 2008; Lytle and Schock, 2005; Switzer et al., 2006).

PbO$_2$ has been found as a corrosion product on lead pipes used for water distribution, and both of its polymorphs - scrutinyite ($\alpha$-PbO$_2$) and plattnerite ($\beta$-PbO$_2$) - have been observed (Schock and Giani, 2004; Schock et al., 2005b; Vasquez et al., 2006). A recent study of lead pipes from 34 domestic water systems found that 9 had PbO$_2$ present (Schock et al., 2005b). PbO$_2$ is only stable in water with high ORP, which can be provided by the consistent use of free chlorine or chlorine dioxide as disinfectants. Chemical reduction of PbO$_2$ to Pb(II) species can result in lead release to solution. Reductants like natural organic matter (NOM), Fe(II) and Mn(II) species, bromide, and iodide can reductively dissolve PbO$_2$ (Dryer and Korshin, 2007; Lin and Valentine, 2008b; 2010; Lin et al., 2008; Shi and Stone, 2009a; b).
The formation of PbO\textsubscript{2} is affected by the water chemistry. Lytle and Schock (Lytle and Schock, 2005) studied PbO\textsubscript{2} formation from lead(II) chloride solutions and found that higher pH favored the formation of scrutinyite and lower pH favored plattnerite. DIC is thought to play an important role in PbO\textsubscript{2} formation. Liu et al. (Liu et al., 2008) observed a phase transformation from hydrocerussite to cerussite during the PbO\textsubscript{2} formation process. Previous research showed that lead(II) carbonates formed as intermediates in the formation of PbO\textsubscript{2} (Liu et al., 2008; Lytle and Schock, 2005). However, it is not known whether carbonates are required for PbO\textsubscript{2} formation. Phosphate inhibited the formation of PbO\textsubscript{2} from lead chloride solution; after 600 days of contact with free chlorine, hydroxylpyromorphite (Pb\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}OH) was the only mineral phase formed (Lytle et al., 2009).

Despite the previous work, the pathways of PbO\textsubscript{2} formation remain insufficiently understood for predicting the prevalence of PbO\textsubscript{2} in distribution systems. Schock and Giani (Schock and Giani, 2004) found that PbO\textsubscript{2} and Pb(II) phases coexisted in used lead pipes, which indicated that the pipe-water systems often do not reach equilibrium. PbO\textsubscript{2} formed in some systems using free chlorine but not in others. Scrutinyite and plattnerite may have different properties (e.g. solubility), and the conditions controlling which phase forms are unknown. The primary aim of the present study was to (1) determine the effect of pH, DIC, and free chlorine concentration on the extent and identity of PbO\textsubscript{2} formation and (2) identify the pathways of PbO\textsubscript{2} formation from various lead(II) species.

2.2 Materials and Methods

2.2.1 Materials
Dissolved lead(II) chloride (PbCl$_2$) and the lead(II) solids cerussite (PbCO$_3$), hydrocerussite (Pb$_3$(OH)$_2$(CO$_3$)$_2$), and massicot (β-PbO) were studied as precursor phases to the formation of PbO$_2$. A PbCl$_2$ solution was prepared from a PbCl$_2$ salt (Fisher Scientific). Reagent grade massicot was purchased (Aldrich). Hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$) and cerussite (PbCO$_3$) were synthesized using methods described previously (Noel and Giammar, 2007). Briefly, hydrocerussite was synthesized by simultaneous addition of 0.1 M NaHCO$_3$ and 0.15 M Pb(NO$_3$)$_2$ solutions to ultrapure water while maintaining pH 9.0 ± 0.5 by periodic addition of 1.0 M NaOH. To make cerussite, 0.1 M NaHCO$_3$ and 0.1 M Pb(NO$_3$)$_2$ were simultaneously added to ultrapure water while maintaining pH 7.0 ± 0.5. The identities of the precursor solids were confirmed with X-ray diffraction (XRD) (Figure 2-S1 of the Supporting Information). As determined with BET-N$_2$ adsorption (Quantachrome Instruments), the specific surface areas of massicot, cerussite, and hydrocerussite were 0.21, 1.09, and 4.77 m$^2$/g respectively. Reagent grade Pb(NO$_3$)$_2$, NaHCO$_3$, NaOH, NaOCl solution, and HNO$_3$ were purchased (Fisher Scientific). Ultrapure water (resistivity >18.2 MΩ-cm) was used to prepare solutions.

2.2.2 PbO$_2$ Formation Experiments

PbO$_2$ formation was examined as a function of the form in which lead was added (i.e., the precursor), pH, and the concentrations of free chlorine and DIC. Experiments were performed at room temperature (21 ± 1 ºC) in 500 mL polypropylene batch reactors. Lead precursors were added to achieve a total lead concentration of 0.5 mM. The desired concentration of DIC (0 or 20 mg C/L) was provided by addition of a 1 M NaHCO$_3$ stock solution, and aliquots of a stock NaOCl solution were added to provide the target free chlorine concentrations (4, 20, or 42 mg/L as Cl$_2$). In most experiments free chlorine concentrations were monitored and maintained at the
initial value by periodic addition of NaOCl, but in some experiments the free chlorine
cconcentrations were allowed to decrease from their initial values. The pH was adjusted to 7.5,
8.5, or 10 and subsequently maintained by addition of NaOH or HNO₃. To prevent the
photodegradation of free chlorine, the reactors were covered with aluminum foil. To minimize
the uptake of CO₂ from the atmosphere, the solutions were stirred in sealed bottles. Experiments
with no DIC were conducted in an argon-filled glovebox with the atmosphere circulated through
a 0.5 M NaOH solution to absorb any remaining CO₂. To minimize the initial presence of CO₂ in
the solutions, the water used for preparing the solutions was boiled. Solid samples were
collected and centrifuged for XRD and scanning electron microscopy (SEM) analysis after 1, 7,
and 28 days of reaction. Aqueous samples were taken periodically, filtered with 0.22 μm
nitrocellulose membranes, and analyzed for free chlorine.

2.2.3 Analytical Methods

XRD was performed on a Rigaku Geigerflex D-MAX/A diffractometer using Cu-Ka
radiation. Electron microscopy was performed on a JEOL 7001LVF field emission scanning
electron microscope. Free chlorine concentrations were determined by the standard DPD
colorimetric method (4500-Cl Chlorine G) with a spectrophotometer (Perkin Elmer Lambda 2S)
(Clesceri et al., 1999). Solution pH was measured with a glass pH electrode and pH meter
(Accumet).

2.3 Results and Discussion

2.3.1 Effect of Dissolved Inorganic Carbon
Figure 2.1. X-ray diffraction patterns of solids following reaction of PbCl₂ solution and massicot (PbO) in the presence and absence of dissolved inorganic carbon (in mg C/L) with 20 mg/L as Cl₂ free chlorine after 28 days. Dominant peaks associated with plattnerite (P), scrutinyite (S), and massicot (M) are indicated, and reference powder diffraction file patterns are included for these phases (01-071-4820, 04-008-7674, and 00-005-0570, respectively).

The effect of DIC on PbO₂ formation was studied using both massicot and PbCl₂ solution as precursors. A typical range of DIC in drinking water is 0 – 50 mg/L (Schock, 1989), and 0 and 20 mg/L was used in experiments. Lead(II) carbonates are widely observed as corrosion products in drinking water distribution systems (Noel and Giammar, 2007), and they have been observed as intermediate solids in the formation of PbO₂ (Liu et al., 2008; Lytle and Schock, 2005). A mixture of scrutinyite and plattnerite formed from massicot in the absence of DIC with 20 mg/L free chlorine (Figure 2.1). After 28 days of reaction, an XRD peak at 2θ of 28° that is
characteristic of scrutinyite appeared at both pH 7.5 and pH 10, and characteristic peaks of plattnerite at 25° and 32° also appeared. The higher intensity of the PbO₂ peaks relative to the massicot peaks at pH 10 than pH 7.5 qualitatively indicated that PbO₂ formation was faster at pH 10, although XRD does not detect amorphous phases and particle size may affect peak intensity. PbO₂ also formed from PbCl₂ in the absence of DIC at pH 7.5 and 10 with 20 mg/L free chlorine (Figure 2.1). After 28 days of reaction, at pH 7.5 a mixture of scrutinyite and plattnerite formed, while pure plattnerite formed at pH 10. As expected, no lead(II) carbonate phases formed as intermediate solids from massicot or PbCl₂ in the absence of DIC (Figures 2-S3 - 4 of the Supporting Information). These results demonstrate that PbO₂ formation does not require lead(II) carbonates as precursors or intermediate phases.

![Figure 2.2. Potential mechanisms of PbO₂ formation from initial Pb(II) phases.](image)

While PbO₂ could form without DIC, the presence of DIC accelerated PbO₂ formation from massicot. The peaks of massicot disappeared after 28 days of reaction in the presence of DIC, but they still coexisted with PbO₂ after 28 days in the absence of DIC (Figure 2.1). The rapid
disappearance of massicot is very likely the result of the formation of soluble Pb(II)-carbonate complexes, which have been shown to accelerate the dissolution of other lead(II) solids (Hulsmann, 1990). PbO₂ could then form through multiple possible pathways (Figure 2.2), including an aqueous pathway (1A-2B-3A/3B in Figure 2.2).

2.3.2 Effect of pH on PbO₂ Formation

The pH affected the formation of PbO₂ both in the presence and absence of DIC when using massicot as a starting phase. After 28 days of reaction with 20 mg/L free chlorine and 20 mg/L DIC, mixtures of plattnerite and scrutinyite formed; plattnerite was dominant at pH 7.5 and scrutinyite at pH 10 (Figure 2.1). A similar trend was observed using 4 mg/L free chlorine (Figure 2-S5 of the Supporting Information). In the presence of DIC, lead(II) carbonates (cerussite and hydrocerussite at pH 7.5 and pure hydrocerussite at pH 10) formed as intermediate solids (Figures 2-S6 - 7 of the Supporting Information). A previous study of lead chloride reaction with free chlorine in the presence of DIC also found that cerussite and plattnerite developed around pH 7 and that hydrocerussite and scrutinyite formed near pH 10 (Lytle and Schock, 2005).

No trend in the identity of the PbO₂ phase with pH was seen in the absence of DIC. A mixture of plattnerite and scrutinyite formed at both pH 7.5 and 10 after 28 days of reaction. In the absence of DIC, PbO₂ formed faster at pH 10 than at pH 7.5. This may be due to the higher dissolved lead concentrations at pH 10 from the formation of lead hydroxyl complexes (i.e. Pb(OH)⁺, Pb(OH)₂) that promote PbO₂ formation through an aqueous pathway (1A-2B-3A/3B in Figure 2.2). Based on equilibrium calculations using published equilibrium constants (Table 2-S2 of the Supporting Information) (Benjamin, 2002), with no DIC at pH 7.5, 38% of dissolved
lead is comprised of lead hydroxyl complexes, and at pH 10 these complexes comprise almost 100% of dissolved lead.

2.3.3 Effect of Free Chlorine Concentration on PbO₂ Formation

Massicot was used as the starting phase to determine the effect of free chlorine concentration on PbO₂ formation. The effects of free chlorine concentration strongly depended

![Figure 2.3. X-ray diffraction patterns of solids following reaction of massicot at pH 7.5 with and without 20 mg C/L dissolved inorganic carbon with different free chlorine concentrations (in mg/L as Cl₂) after 7 and 28 days. Dominant peaks associated with plattnerite (P), scrutinyite (S), massicot (M), and cerussite (C) are indicated, and reference powder diffraction file patterns are included for these phases (01-071-4820, 04-008-7674, 00-005-0570, and 01-085-1088, respectively).]
on the DIC (Figure 2.3). In the presence of DIC, higher free chlorine concentrations accelerated the formation of PbO$_2$. After 7 days of reaction with 4 mg/L free chlorine at pH 7.5 and 20 mg/L DIC, a small XRD peak indicative of plattnerite appeared at 2θ of 32°. However, the dominant solid phases were massicot and cerussite. When the free chlorine concentration was increased to 20 mg/L, all solids were transformed to plattnerite and scrutinyite within 7 days. SEM provided additional evidence that the dominant solids at 4 mg/L free chlorine were bar-shaped cerussite particles, and that at 20 mg/L free chlorine they were agglomerates of small PbO$_2$ particles (Figure 2-S8a - b of the Supporting Information).

In the absence of DIC, more PbO$_2$ actually formed at the lower free chlorine concentration. By comparing the solids formed after 28 days of reaction at pH 7.5, the dominant phases with 4 mg/L free chlorine were scrutinyite and plattnerite, while the dominant crystalline phase with 20 mg/L free chlorine was still massicot (Figure 2.3). In the absence of DIC, the inhibited formation of PbO$_2$ at a high free chlorine concentration may be attributed to the PbO$_2$ formation pathway. In the absence of DIC, PbO$_2$ could form through two parallel pathways: 1) direct oxidation of PbO$_{(s)}$ to PbO$_2(s)$ (reaction 2.1, 2A in Figure 2.2) and 2) oxidation of dissolved lead that was released to solution from PbO$_{(s)}$ (reactions 2.2-2.3, 1A-2B-3A/B in Figure 2.2):

\[
PbO_{(s)} + HOCl = PbO_{2(s)} + H^+ + Cl^- \quad (2.1)
\]

\[
PbO_{(s)} + 2H^+ = Pb^{2+} + H_2O \quad (2.2)
\]

\[
Pb^{2+} + HOCl + H_2O = PbO_{2(s)} + Cl^- + 3H^+ \quad (2.3)
\]

High free chlorine concentration may facilitate the formation of PbO$_2$ from direct oxidation of PbO, which is indicated by the formation of a possible PbO$_2$ layer on the surface of PbO at 20 but not 4 mg/L free chlorine (Figure 2-S8d - e). This PbO$_2$ layer may have prevented further chlorine attack of PbO and decreased the dissolution of PbO, thus inhibiting the further
formation of PbO₂. Equilibrium speciation calculations (Table 2-S2 of the Supporting Information) determined that lead(II) chloride complexes were insignificant at the compositions of the aqueous solutions and would not affect Pb(II) oxidation.

The presence of DIC could help form intermediate lead(II) carbonate solids, which may participate in the formation of PbO₂ and change the formation pathways and mechanisms. As previously noted, DIC could accelerate Pb(II) release from massicot by forming lead(II)-carbonate complexes, thus increasing the rate of reaction 2, which would allow reaction 3 to proceed faster than reaction 1. The increased dissolution of PbO at high DIC probably prevented the accumulation of PbO₂ on the PbO surface, thus allowing continued PbO dissolution at greater production of PbO₂.

2.3.4 Effect of Precursor Identity on PbO₂ Formation

Because cerussite and hydrocerussite were found as intermediate solids in the formation of PbO₂ from massicot in the presence of DIC, experiments were conducted to evaluate the effect of precursors on PbO₂ formation. Four different Pb(II) compounds (lead chloride, massicot, cerussite, hydrocerussite) were chosen as starting phases at pH 10 with 4 or 20 mg/L free chlorine and no DIC. While PbO₂ formed from all four compounds at these conditions (Figure 2.4), the starting phase affected the extent of PbO₂ formation and the identity of the solid phases formed.

When starting with PbCl₂ solution with 20 mg/L free chlorine, pure plattnerite formed after 7 days, and no further solid transformation was observed over the remaining 21 days of the experiment (Figure 2.4a). With 4 mg/L free chlorine, an intermediate lead(II) oxide chloride solid (Pb₄O₃Cl₂·H₂O) was observed after 1 day but disappeared after 7 days, and 28 days of
reaction resulted in pure plattnerite (Figure 2-S9 of the Supporting Information). No lead(II) oxide chloride was observed in the reaction with 20 mg/L free chlorine, but it is possible that the faster reaction with 20 mg/L free chlorine may have produced and consumed the intermediate solid before the 1 day sampling time. The formation of pure plattnerite at pH 10 may be due to the formation of the intermediate solid lead(II) oxide chloride.

When starting with cerussite and no DIC, a phase transformation to hydrocerussite was observed after 1 day, and a mixture of scrutinyite and plattnerite formed after 28 days (Figure 2.4b). Scrutinyite was more abundant than plattnerite. Lytle and Schock (Lytle and Schock, 2005) observed formation of pure plattnerite from cerussite at pH 6.7-7.8. The formation of a PbO$_2$ mixture in our study and not pure plattnerite may be due to the partial transformation of cerussite to hydrocerussite at the higher pH of our experiments. When starting with hydrocerussite and no DIC, no intermediate solids were observed with XRD, and pure scrutinyite formed after 28 days of reaction (Figure 2.4c), which is in agreement with a previous study that observed scrutinyite as the final oxidation product of hydrocerussite in the presence of DIC (Liu et al., 2008). Because DIC can be released during the transformation from cerussite/hydrocerussite to PbO$_2$, the lack of DIC probably had little effect on the transformation of Pb(II) carbonate solids. Field observations showed that plattnerite was more abundant than scrutinyite (Schock et al., 2005b). The different observations may be due to the broader range of precursors and longer contact times in distribution systems than in the present laboratory experiments.
When starting with massicot, no intermediate solids were observed, and a mixture of scrutinyite and plattnerite formed after 28 days of reaction (Figure 2.4d). However, massicot was still the dominant solid phase after 28 days of reaction, indicating that the formation of \( \text{PbO}_2 \) from massicot was slower than from the other precursors.

2.3.5 Formation Pathways of \( \text{PbO}_2 \) from Lead(II) Species
The observed formation of PbO$_2$ from different precursors at different conditions is summarized in Figure 2.5. PbO$_2$ could form from Pb(II) species through several possible pathways (Figure 2.2), depending on the starting phases and the aqueous composition. When dissolved Pb(II) species are used as starting phases and no intermediate solids are formed, then PbO$_2$ forms through an aqueous phase oxidation pathway (2B-3A). When Pb(II) solids are used as starting phases or are generated as intermediate solids, then the formation mechanisms can be more complicated. In addition to dissolving to release Pb(II) that is oxidized to Pb(IV) (1A-2B-3A), Pb(II) solids could be directly oxidized to PbO$_2$ through solid state oxidation (2A) or a Pb(II) solid could serve as substrates in the heterogeneous nucleation of PbO$_2$ (1A-2B-3B).

The aqueous phase oxidation pathway is best illustrated by the reaction of PbCl$_2$ solution at pH 7.5 with free chlorine in the absence of DIC. While an intermediate lead(II) oxide chloride solid formed at pH 10, XRD patterns had no evidence of intermediate solids at pH 7.5 (Figure 2-S10 of the Supporting Information). The formation mechanism involves oxidation of dissolved Pb(II) to dissolved Pb(IV) followed by homogenous nucleation and precipitation of PbO$_2$ (2B-3A). The solids agglomerated after 1 day of reaction and individual particles were too small to be resolved well by SEM (Figure 2.6a). Energy dispersive X-ray (EDX) analysis showed that the solids were composed exclusively of Pb and O, which excluded the possibility of the solids being lead oxide chloride. These small particles might be amorphous PbO$_2$ nanoparticles. From the aqueous oxidation pathway, the final products were a mixture of scrutinyite and plattnerite.

When lead(II) solids participate in the formation of PbO$_2$, solid-mediated and aqueous pathways may occur together, making the dominant pathways difficult to distinguish. For oxidative iron oxide formation, a solid state oxidation pathway (2A) occurred when the precursor had a similar structure to the final product and oxidation was much faster than dissolution.
Figure 2.5. Formation products from Pb(II) starting phases (dashed lines indicate pathways that were not observed to occur in this study). When mixtures of scrutinyite and plattnerite were produced, the vertical positions of the lines qualitatively indicate their relative abundances. When intermediate solid phases were produced prior to PbO₂ formation, they are indicated.
Figure 2.6. Electron micrographs of PbO₂ products from reaction of (a) lead chloride after 1 day at pH 7.5 with no DIC and 20 mg/L free chlorine; (b) cerussite after 1 day at pH 7.5 with no DIC and 42 mg/L free chlorine; (c) cerussite after 7 days at pH 7.5 with no DIC and 20 mg/L free chlorine; (d) massicot after 1 day at pH 7.5 with no DIC and 4 mg/L free chlorine; (e) massicot after 1 day at pH 10 with no DIC and 4 mg/L free chlorine; and (f) massicot after 1 day at pH 10 with 20 mg/L DIC and 20 mg/L free chlorine.
(Cornell and Schwertmann, 2003); similar solid state oxidation to produce PbO₂ may also occur. This pathway would be suggested by the preservation of the shape of the precursor during oxidation. At high free chlorine concentrations, clusters of PbO₂ that preserved the shapes of hydrocerussite (Figure 2.6b) and cerussite (Figure 2.6c) were observed, suggesting that a solid state oxidation pathway can occur in the formation of PbO₂ from hydrocerussite and cerussite.

A pathway involving dissolution followed by heterogeneous nucleation (1A-2B-3B) could have occurred in the formation of PbO₂. The dissolved lead(II) species would first be released from the surface of the precursor solid, resulting in the formation of the steps and kink sites on the precursor surface (Figure 2.6d). Then lead(II) could be oxidized in solution to lead(IV). When solids are present, heterogeneous nucleation of PbO₂ could be favorable to homogenous nucleation due to the lower interfacial energy of the solid-solid interface relative to that of the solid-water interface (AWWA, 2005). Growth of PbO₂ on the surface of massicot (Figure 2.6e) and edges of hydrocerussite (Figure 2.6f) suggest formation of PbO₂ that began with heterogeneous nucleation. The formation of hydrocerussite formed scrutinyite and lead oxide chloride formed plattnerite may result from specific trends in solid-solid interfacial free energies. The dependence of the products on the identity of the solid precursor is unique to the solid state pathways and would not have been observed in the aqueous pathway.

2.4 Environmental Implications

PbO₂ solids have frequently been found on lead pipes exposed to free chlorine as a residual disinfectant. The presence of PbO₂ can maintain low dissolved lead concentrations. Increasing free chlorine concentration could accelerate PbO₂ formation in the presence of DIC, and a threshold value of free chlorine for PbO₂ formation is less than 4 mg/L. In actual distribution
systems the free chlorine concentration is typically 0.5 to 1.5 mg/L, and the formation of PbO₂ is still thermodynamically favorable and has been observed on pipes at these concentrations. The use of free chlorine to control lead concentrations must be balanced against the formation of chlorinated disinfection byproducts (DBPs) from reactions of free chlorine with dissolved organic carbon.

While the present study evaluated the effects of pH, DIC, and free chlorine on PbO₂ formation, additional water chemistry parameters may also influence PbO₂ formation. In particular, the presence of natural organic matter (NOM) can affect the stability of PbO₂ (Dryer and Korshin, 2007; Lin and Valentine, 2008b) and the morphology of lead corrosion products (Korshin et al., 2005), and NOM may affect PbO₂ formation through consumption of free chlorine and other processes.

Both scrutinyite and plattnerite formed, and the relative abundance of these two polymorphs depended on the precursors and water chemistry. The difference of their Gibbs free energies of formation indicates that these two polymorphs have different solubilities, with plattnerite being more insoluble (Tables 2-S2 – 2-S3 of the Supporting Information) (Pourbaix, 1974; Wang et al., 2010). Equilibrium calculations predict the formation of pure plattnerite, and the observed formation of scrutinyite alone or mixed with plattnerite indicates that the systems do not reach equilibrium and that kinetics play an important role in PbO₂ formation.

Adjusting pH and alkalinity has been used to control lead concentrations in drinking water. The increased DIC that accompanies chemical additions to raise the pH and alkalinity can affect the dissolved lead concentration in two different ways. Although DIC is not required for PbO₂ formation, the presence of DIC can accelerate the formation of PbO₂ under high free chlorine concentrations, thus mitigating lead release from pipe scales. However, if PbO₂ is present in the
system and a free chlorine residual is not maintained, then DIC may also accelerate the
dissolution of PbO$_2$, thus increasing the dissolved lead concentration (Xie et al., 2010b).
Therefore, the optimal DIC for lead concentration control will depend on the water chemistry of
a specific system.

**Acknowledgements**

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was done in the Center for Materials Innovation.
Chapter 2. Supporting Information

Contents: Three tables (2-S1–2-S3)

Seven figures (2-S1–2-S10)

Table 2-S1. Experimental conditions and summary of the resulting solid phases

<table>
<thead>
<tr>
<th>Precursor</th>
<th>DIC (mg C/L)</th>
<th>Free Chlorine (mg/L as Cl₂)</th>
<th>pH 7.5</th>
<th>pH 8.5</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1d</td>
<td>7d</td>
<td>28d</td>
<td>1d</td>
<td>7d</td>
</tr>
<tr>
<td>PbO (massicot)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0.5 mM)</td>
<td>0</td>
<td>M</td>
<td>S/P</td>
<td>S/P</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>M</td>
<td>M/S/P</td>
<td>M/S/P</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>M/H</td>
<td>M/C</td>
<td>C/M</td>
<td>M/H</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>M/H</td>
<td>M/C</td>
<td>P</td>
<td>M/H</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>M/C/H</td>
<td>P/S</td>
<td>P/S</td>
<td>M/H</td>
</tr>
<tr>
<td>PbCl₂ (0.5 mM)</td>
<td>0</td>
<td>N</td>
<td>N</td>
<td>S/P</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>N</td>
<td>S/P</td>
<td>S/P</td>
<td>N</td>
</tr>
<tr>
<td>Cerussite (0.5 mM)</td>
<td>0</td>
<td>C/S</td>
<td>S/P</td>
<td>S/P</td>
<td>H/C</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>C/S</td>
<td>P/S</td>
<td>P/S</td>
<td>C/S</td>
</tr>
<tr>
<td></td>
<td>42*</td>
<td>C/H/S</td>
<td>S/P</td>
<td>S/P</td>
<td>H/S</td>
</tr>
<tr>
<td>Hydrocerussite</td>
<td>0</td>
<td>C/H/S</td>
<td>S/P</td>
<td>S/P</td>
<td>H/S</td>
</tr>
<tr>
<td>(0.5 mM)</td>
<td>20</td>
<td>C/H/S</td>
<td>S/P</td>
<td>S/P</td>
<td>H/S</td>
</tr>
</tbody>
</table>

S: Scrutinyite; P: Plattnerite; H: Hydrocerussite; C: Cerussite; M: Massicot; L: litharge; Cl:

Pb₄O₃Cl₂·H₂O; O: PbO₂, which was only identified by SEM.

Bold: predominant solid phase in mixture

*: free chlorine concentration not maintained at constant value; concentration is the initial concentration.
Table 2-S2. Equilibrium constants for aqueous species

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Log K</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pb$^{2+}$ + H$_2$O = PbOH$^+$ + H$^+$</td>
<td>-7.71</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>Pb$^{2+}$ + 2H$_2$O = Pb(OH)$_2$$^{0+}$ + 2H$^+$</td>
<td>-17.12</td>
<td>[1]</td>
</tr>
<tr>
<td>3</td>
<td>Pb$^{2+}$ + 3H$_2$O = Pb(OH)$_3^-$ + 3H$^+$</td>
<td>-28.06</td>
<td>[1]</td>
</tr>
<tr>
<td>4</td>
<td>Pb$^{2+}$ + 4H$_2$O = Pb(OH)$_4^{2-}$ + 4H$^+$</td>
<td>-39.70</td>
<td>[1]</td>
</tr>
<tr>
<td>5</td>
<td>Pb$^{2+}$ + Cl$^-$ = PbCl$^+$</td>
<td>1.6</td>
<td>[1]</td>
</tr>
<tr>
<td>6</td>
<td>Pb$^{2+}$ + 2Cl$^-$ = PbCl$_2$</td>
<td>1.8</td>
<td>[1]</td>
</tr>
<tr>
<td>7</td>
<td>Pb$^{2+}$ + 3Cl$^-$ = PbCl$_3^-$</td>
<td>1.7</td>
<td>[1]</td>
</tr>
<tr>
<td>8</td>
<td>Pb$^{2+}$ + 4Cl$^-$ = PbCl$_4^{2-}$</td>
<td>1.38</td>
<td>[1]</td>
</tr>
<tr>
<td>9</td>
<td>Pb(IV)$_2$(plattnerite) + 4H$^+$ = Pb$^{4+}$ + 2H$_2$O</td>
<td>-8.91</td>
<td>Calculated</td>
</tr>
<tr>
<td>10</td>
<td>Pb(IV)$_2$(scrutinyite) + 4H$^+$ Pb$^{4+}$ + 2H$_2$O</td>
<td>-8.26</td>
<td>Calculated</td>
</tr>
</tbody>
</table>

The equilibrium constants for Reactions 9 and 10 were calculated from molar Gibbs free energies of formation ($G_{i,j}^0$) for each component ($i$). The Gibbs free energies of formation used in these calculations are listed in Table S3.
Table 2-S3: Chemical potentials for various aqueous species.

<table>
<thead>
<tr>
<th>Species</th>
<th>$G^0_{f,i}$ (J/mol)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-PbO$_2$(s)</td>
<td>-218,987</td>
<td>[2]</td>
</tr>
<tr>
<td>$\beta$-PbO$_2$(s)</td>
<td>-222,674</td>
<td>[3]</td>
</tr>
<tr>
<td>Pb$^{4+}$</td>
<td>302,498</td>
<td>[2]</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.00</td>
<td>[1]</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>-157,300</td>
<td>[1]</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-237,180</td>
<td>[1]</td>
</tr>
</tbody>
</table>

For example the Gibbs free energy for Reaction 9 can be calculated as,

$$
\Delta G_r = \sum_{i=1}^{k} G^0_{f,i} N_i
$$

(1)

Where $\Delta G_r$ = Gibbs free energy of reaction (r), joules (J/mol)

$G^0_{f,i}$ = Gibbs free energy of formation of species (i), joules per mole (J/mol)

$N_i$ = stoichiometric coefficient

$$
\Delta G_{f,g} = \mu_{p^{4+}} + 2\mu_{H_2O} - \mu_{PbO_2(plattnerite)} - 4\mu_{H_2O} = 50,812J
$$

(2)

The equilibrium constant can then be calculated by Equation 3:

$$
Log K_{eq} = -\frac{\Delta G_r}{2.303RT}
$$

(3)

Where $R$ = equilibrium gas constant, joules per mole per Kelvin (J/mol•K)

$T$ = temperature, Kelvin (K)

$$
Log(K_{eq}) = -\frac{50,812}{2.303RT} = -8.91
$$

(4)
Figure 2-S1. X-ray diffraction patterns of the materials used in the study.
Figure 2-S2. Electron micrographs showing the morphology of the pure (a) cerussite, (b) hydrocerussite, and (c) massicot that were used as precursors to PbO$_2$ formation.
Figure 2-S3. X-ray diffraction patterns of solids following reaction of massicot at pH 10 in the absence of DIC with 20 mg/L as Cl₂ free chlorine. Dominant peaks associated with plattnerite (P), scrutinyite (S), and massicot (M), are indicated (Reference patterns are listed at the bottom; patterns for cerussite and hydrocerussite are included to show that they did not form as intermediate solids).
Figure 2-S4. X-ray diffraction patterns of solids following reaction of lead chloride solution at pH 10 in the absence of DIC with 20 mg/L as Cl₂ free chlorine. Dominant peaks associated with plattnerite (P) are indicated (Reference patterns are listed at the bottom; patterns for cerussite and hydrocerussite are included to show that they did not form as intermediate solids).
**Figure 2-S5.** X-ray diffraction patterns of solids following 28 days of reaction of massicot with 20 mg C/L DIC and 4 mg/L as Cl₂ free chlorine. Dominant peaks associated with plattnerite (P), and scrutinyite (S) are indicated.
Figure 2-S6. X-ray diffraction patterns of solids following reaction of massicot at pH 7.5 with 20 mg/L DIC and 20 mg/L as Cl₂ free chlorine. Dominant peaks associated with plattnerite (P), scrutinyite (S), massicot (M), cerussite (C), and hydrocerussite (H) are indicated.
Figure 2-S7. X-ray diffraction patterns of solids following reaction of massicot at pH 10 with 20 mg/L DIC and 20 mg/L as Cl₂ free chlorine. Dominant peaks associated with plattnerite (P), scrutinyite (S), massicot (M), and hydrocerussite (H) are indicated.
Figure 2-S8. Electron micrographs of solids from massicot reaction at pH 7.5 with (a) 4 mg/L free chlorine, DIC 20 mg C/L, after 7 days; (b) 20 mg/L free chlorine, DIC 20 mg C/L, after 7 days; (c) 4 mg/L free chlorine, no DIC, after 28 days; (d and e) 20 mg/L free chlorine, no DIC, after 28 days. Panel e is a higher magnification image of a section from panel d.
Figure 2-S9. X-ray diffraction patterns of solids following reaction of lead chloride solution at pH 10, in the absence of DIC, with 4 mg/L as Cl₂ free chlorine. Dominant peaks associated with plattnerite (P), scrutinyite (S), and lead(II) oxide chloride (Cl) are indicated.
Figure 2-S10. X-ray diffraction patterns of solids following reaction of lead chloride solution at pH 7.5, in the absence of DIC, with 20 mg/L as Cl$_2$ free chlorine. Dominant peaks associated with plattnerite (P), and scrutinyite (S) are indicated.
Chapter 3 Kinetics of the Reductive Dissolution of Lead(IV) Oxide by Iodide

Results of this chapter have been published in Environmental Science & Technology, 2012, 46(11), 5859 - 5866.

Abstract

Lead(IV) oxide (PbO$_2$) is a corrosion product found in lead service lines used to convey drinking water. The presence of reductants can accelerate PbO$_2$ dissolution and enhance lead release to drinking water. The dissolution rate rather than the equilibrium solubility of PbO$_2$ can control the dissolved lead concentrations in water distributed through pipes containing PbO$_2$. Iodide, a known reductant for PbO$_2$, was selected as a model reductant for investigating the kinetics and mechanisms of the reductive dissolution of PbO$_2$. The dissolution rate of plattnerite ($\beta$-PbO$_2$) was determined as a function of pH, iodide concentration, and dissolved inorganic carbon (DIC) concentration using continuously stirred tank reactors. The dissolution rate of plattnerite increased with decreasing pH and increasing iodide concentrations. The presence of 10 mg C/L DIC accelerated plattnerite dissolution, but further increases in DIC concentration did not affect the dissolution rate. The reductive dissolution of PbO$_2$ can be interpreted as a coupled process involving chemical reduction of Pb(IV) to Pb(II) at the PbO$_2$ surface followed by detachment of Pb(II) to solution. The data suggest that chemical reduction is the rate-limiting step for PbO$_2$ dissolution in the presence of iodide.


3.1 Introduction

Lead service lines are widely for drinking water distribution in the United States (Renner, 2006). Through interaction with water in the pipes, lead corrosion products that include lead(II) oxides, lead(II) carbonates, and lead(IV) oxides develop on the pipe surfaces (Hozalski et al., 2005; Schock, 1999; Schock et al., 2008). The formation of corrosion products is influenced by pH, dissolved inorganic carbon (DIC) concentration, and the type and concentration of chlorine disinfectant (Liu et al., 2008; Lytle and Schock, 2005; Wang et al., 2010). Lead release to drinking water from these corrosion products poses a threat to public health. The Lead and Copper Rule (LCR) set the lead action level to 15 μg/L for a 1 L first draw sample of tap water (USEPA, 1991).

Lead(IV) oxide (PbO₂) has been widely found as a corrosion product in drinking water distribution systems using free chlorine as a disinfectant. Both scrutinyite (α-PbO₂) and plattnerite (β-PbO₂) have been observed (Kim and Herrera, 2010; Lytle and Schock, 2005; Schock and Giani, 2004; Schock et al., 2005b; Switzer et al., 2006), and plattnerite is more abundant than scrutinyite in both field observations (Kim and Herrera, 2010; Schock et al., 2005b) and experimental studies (Wang et al., 2010). Based on published thermodynamic constants, plattnerite is more stable than scrutinyite (Pourbaix, 1974; Risold et al., 1998). PbO₂ is only stable in systems with high oxidation reduction potentials (ORP), which could be provided by the consistent use of free chlorine. Experiments confirmed that the presence of free chlorine led to the formation of PbO₂ from Pb(II) precursors (Lytle and Schock, 2005; Wang et al., 2010), while PbO₂ did not form in the presence of chloramines (Switzer et al., 2006). PbO₂ has a very low solubility that can control lead concentrations at levels far below 15 μg/L (Pourbaix, 1974).
The stability of PbO$_2$ is strongly affected by soluble oxidants and reductants. While the dissolution rate of PbO$_2$ was slow in the presence of free chlorine (Xie et al., 2010a), a change from free chlorine to chloramines lowers the ORP of the system and significantly enhances PbO$_2$ dissolution (Lin and Valentine, 2008c). In Washington D.C., high lead concentrations were observed from 2001 to 2004 after such a switch of disinfectant from free chlorine to chloramines (Renner, 2004;2007). These high concentrations have been attributed to the reductive dissolution of PbO$_2$ to more soluble Pb(II) species (Boyd et al., 2008;Vasquez et al., 2006). In addition to chloramines, common reductants in drinking water that include natural organic matter (NOM), Fe$^{2+}$, Mn$^{2+}$, and I$^-$. have been shown to accelerate PbO$_2$ dissolution (Dryer and Korshin, 2007;Lin et al., 2008;Lin and Valentine, 2008b;Shi and Stone, 2009a;b).

While PbO$_2$ will be a stable low solubility solid for systems that maintain a free chlorine residual, there are scenarios in which PbO$_2$ can be exposed to reductants that would accelerate its dissolution. First, for systems that have recently switched to chloramines as the residual disinfectant after a history of free chlorine use, the PbO$_2$ in the pipe scales that had developed during exposure to free chlorine is exposed to water without free chlorine. Because PbO$_2$ dissolution is quite slow in the absence of reductants, it may persist long after the cessation of free chlorine addition. A recent investigation in our laboratory observed PbO$_2$ in the scales of pipes harvested from Washington, DC in 2011 even though regular use of free chlorine had cased more than ten years earlier (Welter et al., 2012). Second, even for systems that have a free chlorine residual, when this residual becomes depleted as it may during stagnation of water in lead service lines, lead release may be significantly increased due to the dissolution of PbO$_2$ by reductants including NOM to more soluble Pb(II) species (Lin and Valentine, 2009;Xie and Giammar, 2011).
In studying the mechanisms of PbO₂ dissolution at acidic conditions using Br⁻ as a model reductant, Lin and Valentine observed that the dissolution rate increased with increasing Br⁻ and H⁺ concentrations at pH 3.5-4.5 (Lin and Valentine, 2010). They described the dissolution of PbO₂ using a mechanism involving coupled chemical reduction and detachment steps. In the first step the reducants attach to the PbO₂ surface and reduce the surface Pb(IV) species to Pb(II) species; in the second step the Pb(II) species detach from the surface and are released to the solution. The chemical reduction step was suggested to be more important in controlling PbO₂ dissolution at acidic conditions.

The mechanisms of PbO₂ dissolution at the circummneutral and slightly basic pH of drinking water distribution systems remain poorly understood. Iodide is present in natural waters (Fuge and Johnson, 1986) and is capable of reducing PbO₂ at drinking water conditions with the formation of aqueous iodine species (Lin et al., 2008). The reaction of iodide with PbO₂ in the presence of NOM may form the carcinogen iodoform (Lin et al., 2008). While iodide may not be the most significant reductant in most waters, it was used in the present study as a model reductant for understanding the rates and mechanisms of PbO₂ dissolution. Dissolved inorganic carbon (DIC) is abundant in drinking water with typical concentrations of 0 – 50 mg/L (Schock, 1989). Carbonate is a good complexing ligand for Pb²⁺, and previous research showed that carbonate increased the dissolution rate of PbO₂, probably by forming lead(II)-carbonate complexes that facilitate the detachment of lead(II) from the PbO₂ surface (Xie et al., 2010b). The primary aims of the present study were to (1) determine the dissolution rate of PbO₂ as a function of iodide and DIC concentrations and (2) elucidate the mechanisms of the reductive dissolution of PbO₂ at pH and DIC conditions relevant to drinking water distribution. Information provided in the present study can help the water supply community make
scientifically-based decisions regarding the management of lead concentrations when making changes to the distribution system water chemistry.

3.2 Materials and methods

3.2.1 Materials

\[ \text{PbO}_2 \] was purchased (Acros), and X-ray diffraction (XRD) patterns confirmed that it was pure plattnerite (Figure 3-S1 of the Supporting Information). The specific surface area of the plattnerite was 3.6 m\(^2\)/g as measured by BET-N\(_2\) adsorption. Reagent grade KI, MOPS, NaNO\(_3\), NaHCO\(_3\), NaOH, NaOCl solution, and concentrated HNO\(_3\) were used (Fisher Scientific). Solutions were prepared with ultrapure water (resistivity >18.2 MΩ-cm).

3.2.2 \text{PbO}_2 Dissolution Experiments

\text{PbO}_2 dissolution was examined as a function of pH (6.7 - 8.5) and the concentrations of iodide (0 – 100 μM) and DIC (0 – 200 mg C/L) (Table 3.1). Experiments to quantify the dissolution rate were performed at room temperature (21 ± 1 °C) in 84-mL continuously stirred tank reactors (CSTRs) with 1 g/L PbO\(_2\). A 0.22-μm mixed cellulose filter membrane was used to filter the effluent and prevent the loss of solid from the reactor. A peristaltic pump (Cole-Parmer) provided an influent flow rate of 2.8 ml/min, so the hydraulic residence time of the reactor was 30 minutes. The effluent pH of the reactors was monitored and aqueous samples were periodically collected over 24 hours and preserved for dissolved lead analysis. Previous studies found that the 0.22-μm membrane can effectively remove PbO\(_2\) particles, and the lead concentrations in the filtered sample represent dissolved lead.\(^{23}\) In the present study selected
samples were further filtered using 0.02-μm polyethersulfone (PES) syringe filters and their close agreement with the 0.22-μm filtered samples confirmed that the filtrate from the 0.22-μm filters represents dissolved lead.

Influent compositions were varied to evaluate the effect of different factors on \( \text{PbO}_2 \) dissolution. The influents were prepared in 10-L plastic (Tedlar) bags to minimize the transfer of \( \text{CO}_2 \) between the atmosphere and solution. Ultrapure water was purged of \( \text{CO}_2 \) by sparging with \( \text{N}_2 \) and then pumped into the bags. The desired concentrations of DIC (0, 10, 50, or 200 mg C/L) were provided by addition of a 1 M \( \text{NaHCO}_3 \) stock solution. For the experiments without DIC at pH 7.6, an aliquot of 0.5 M 3-(N-morpholino)propanesulfonic acid (MOPS) solution was injected to achieve a concentration of 1 mM. MOPS was selected as a pH buffer due to its low affinity for metal complexation and relatively little effect on \( \text{PbO}_2 \) dissolution. An aliquot of 1.0 M \( \text{NaNO}_3 \) solution was added to the bags to control the ionic strength at 0.01 M. The pH was adjusted to 6.7, 7.6, or 8.5 by addition of concentrated \( \text{HNO}_3 \) or freshly prepared 0.5 M \( \text{NaOH} \) solutions. Finally an aliquot of 10 mM KI stock solution was injected to the bags to provide the target iodide concentration (0, 1, 2, 5, 10, 20, and 100 μM). Each experimental condition was run in duplicate.

Dissolution rates were determined by operating the reactors for 24 hours (48 hydraulic residence times) to allow the systems to reach steady state. This flow-through approach avoids the accumulation of reaction products and minimizes the effect of any initial labile phases on dissolution rates (Samson and Eggleston, 2000). When the system reaches steady state, the dissolution rate can be quantified by Equation 3.1 (Xie et al., 2010b),

\[
\frac{r_{\text{exp}}}{V_{\text{r}} \cdot \text{A}[\text{solids}]} = \frac{C_{\text{ss}}}{\tau \cdot \text{A}[\text{solids}]}
\]

\[3.1\]
where \( R_{\text{exp}} \) is the dissolution rate (mol·m\(^{-2}\)·min\(^{-1}\)); \( C_{\text{ss}} \) is the steady-state effluent lead concentration (mol·L\(^{-1}\)); \( Q \) is flow rate (L·min\(^{-1}\)); \( V_R \) is the volume of the reactor (L); \( \tau \) is the hydraulic residence time (i.e., \( V_R/Q \) (min)); [solid] is the solid concentration in the reactor (g·L\(^{-1}\)); and \( A \) is the specific surface area of the solid (m\(^2\)·g\(^{-1}\)). No lead was in the influent. The steady-state concentration was calculated as the average concentration from at least 8 consecutive samples that did not vary by more than 20% and spanned at least 8 residence times. Solids remaining at the end of selected experiments were collected and centrifuged prior to XRD and scanning electron microscopy (SEM) analysis.

### 3.2.3 Analytical Methods

Dissolved lead (Pb) concentrations were measured by inductively coupled plasma mass spectroscopy (ICP-MS) on an Agilent 7500ce instrument. A Rigaku Geigerflex D-MAX/A diffractometer with Cu-Ka radiation was used for XRD measurements. The instrument is equipped with a vertical goniometer and a scintillation counter. Electron microscopy was performed on a JEOL 7001LVF field emission scanning electron microscope. BET-N\(_2\) adsorption was performed on a BET-Autosorb (Quantachrome Instruments). The pH was measured with a glass pH electrode and pH meter (Accumet).

### 3.3 Results and Discussion

#### 3.3.1 Overview of the Dissolution of Plattnerite by Iodide

The reductive dissolution of PbO\(_2\) by iodide can be described by half reactions involving PbO\(_2\) reduction (Reaction 3.2) and iodide oxidation (Reaction 3.3) (Lin et al., 2008):
4H⁺ + PbO₂ + 2e⁻ = Pb²⁺ + 2H₂O  \hspace{1cm} (3.2)

2I⁻ = I₂ + 2e⁻ \hspace{1cm} (3.3)

The I₂ can then hydrolyze to form HOI (Reaction 3.4) (Cotton and Wilkinson, 1988). In the presence of excess iodide, I₂ can also transform to I₃⁻ (Reaction 3.5).

**Table 3.1.** Summary of PbO₂ dissolution experiments in this study.

<table>
<thead>
<tr>
<th>Experiment ID a</th>
<th>pH</th>
<th>DIC (mg C/L)</th>
<th>Iodide (μM)</th>
<th>Measured pH b</th>
<th>Steady state effluent lead (nM)</th>
<th>Dissolution rate X 10¹⁰ (mol/m²·min)</th>
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</thead>
<tbody>
<tr>
<td>1A</td>
<td>6.7</td>
<td>50</td>
<td>10</td>
<td>6.84</td>
<td>1205</td>
<td>111.6</td>
</tr>
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<td>10</td>
<td>6.84</td>
<td>1159</td>
<td>107.3</td>
</tr>
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<td>2A</td>
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<td>1</td>
<td>7.63</td>
<td>29</td>
<td>2.7</td>
</tr>
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<td>1</td>
<td>7.65</td>
<td>36</td>
<td>3.3</td>
</tr>
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<td>2</td>
<td>7.65</td>
<td>106</td>
<td>9.8</td>
</tr>
<tr>
<td>3B</td>
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<td>2</td>
<td>7.64</td>
<td>65</td>
<td>6.1</td>
</tr>
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<td>5</td>
<td>7.69</td>
<td>336</td>
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</tr>
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<td>5</td>
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<td>7.60</td>
<td>800</td>
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<td>100</td>
<td>7.65</td>
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</tr>
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<td>7.64</td>
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<td>10</td>
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<td>10B</td>
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<td>10</td>
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<td>487</td>
<td>45.1</td>
</tr>
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<td>200</td>
<td>10</td>
<td>7.65</td>
<td>402</td>
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<td>200</td>
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<td>8.47</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
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<td>50</td>
<td>5</td>
<td>8.46</td>
<td>22</td>
<td>2.0</td>
</tr>
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<td>13B</td>
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<td>50</td>
<td>10</td>
<td>8.48</td>
<td>59</td>
<td>5.5</td>
</tr>
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<td>50</td>
<td>20</td>
<td>8.48</td>
<td>198</td>
<td>18.3</td>
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<td>14B</td>
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<td>20</td>
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<td>10</td>
<td>10</td>
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<td>74</td>
<td>6.9</td>
</tr>
<tr>
<td>15B</td>
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<td>10</td>
<td>10</td>
<td>8.39</td>
<td>100</td>
<td>9.2</td>
</tr>
<tr>
<td>16A</td>
<td>8.5</td>
<td>200</td>
<td>10</td>
<td>8.55</td>
<td>55</td>
<td>5.1</td>
</tr>
<tr>
<td>16B</td>
<td>8.5</td>
<td>200</td>
<td>10</td>
<td>8.54</td>
<td>67</td>
<td>6.2</td>
</tr>
</tbody>
</table>

a The letters A-B indicate duplicate experiments.

b The reported pH is the average effluent pH for the steady-state period. Over this period the pH varied by less than 0.05 pH units from the average.

c Cerussite formed in this condition from some of the lead released by PbO₂ dissolution, so the effluent lead concentration cannot be used to calculate the dissolution rate.
\[ \text{I}_2 + \text{H}_2\text{O} = \Gamma + \text{HOI} + \text{H}^+ \quad (3.4) \]
\[ \Gamma + \text{I}_2 = \text{I}_3^- \quad (3.5) \]

At the present experimental conditions, I\(_2\) and HOI were the dominant products of iodide oxidation and I\(_3^-\) is insignificant based on calculations using published equilibrium constants (Burger and Liebhafsky, 1973). Since I\(_2\) and HOI rapidly equilibrate with one another, together they represent “active iodine” and for the sake of simplicity will be referred to hereafter just as I\(_2\). The overall redox reaction between PbO\(_2\) and iodide can therefore be expressed as:

\[ \text{PbO}_2 + 2\Gamma + 4\text{H}^+ = \text{Pb}^{2+} + \text{I}_2 + 2\text{H}_2\text{O} \quad (3.6) \]

At all pH values studied, the presence of 10 \(\mu\)M iodide accelerated the dissolution of PbO\(_2\), illustrating the importance of reductive dissolution for the stability of PbO\(_2\) (Figure 3.1). The measured dissolution rates of PbO\(_2\) at all of the pH values and concentrations of iodide and DIC are compiled in Table 3.1. The dissolution rates were calculated using Equation 3.1, and time series of the effluent lead concentrations that were used to quantify the dissolution rates are included in the Supporting Information.

The dissolution rates determined in the present continuous-flow experiments were compared to those acquired in batch studies of PbO\(_2\) with reductants commonly found in drinking water (Table 3.2). In all of these previous studies, the reductants accelerated PbO\(_2\) dissolution relative to reductant-free conditions. In the present study, the PbO\(_2\) dissolution rate was \(4.7 \times 10^{-9}\) mol·m\(^{-2}\)·min\(^{-1}\) at pH 7.6 with 10 mg C/L DIC and 10 \(\mu\)M iodide. Lin and Valentine investigated the initial dissolution of PbO\(_2\) by iodide in a phosphate buffered system (Lin et al., 2008). A comparable rate of \(2.1 \times 10^{-9}\) mol·m\(^{-2}\)·min\(^{-1}\) at pH 7.0 and 10 \(\mu\)M iodide was calculated using the general rate expression that they provided. NOM is abundant in drinking water and a previous study investigated its effect on the dissolution of PbO\(_2\) at pH 7.0 with 20 mg/L NOM in
batch reactors (Lin and Valentine, 2008b). Approximately 20 μg/L dissolved lead was released after 1 day of reaction and the dissolution rate was calculated as $4.0 \times 10^{-9} \text{ mol} \cdot \text{m}^2 \cdot \text{min}^{-1}$. At pH 7.8, the dissolution rates of plattnerite in the presence of 40 μM Fe$^{2+}$ and 20 μM Mn$^{2+}$ were about $1.3 \cdot 10^{-6}$ and $3.2 \cdot 10^{-6} \text{ mol} \cdot \text{m}^2 \cdot \text{min}^{-1}$ (Shi and Stone, 2009a), respectively, which were about two orders of magnitude higher than those measured with 10 μM iodide. For comparable concentrations of the reducants just discussed, the order of PbO$_2$ dissolution rates can be summarized as NOM $< \Gamma < \text{Mn}^{2+}, \text{Fe}^{2+}$.

Figure 3.1. Effect of pH on the dissolution rate of plattnerite with 50 mg C/L DIC in the absence and presence of 10 μM iodide using flow-through reactors with 1 g/L plattnerite and a residence time of 30 min. Error bars represent one standard deviation from duplicate experiments.
Table 3.2. Summary of the dissolution rate of PbO\(_2\) by different reductants.

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Experimental Condition</th>
<th>Dissolution Rate (mol·m(^{-2}·)min(^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>DIC (M)</td>
<td>Reductant conc.</td>
</tr>
<tr>
<td>NOM</td>
<td>7.0</td>
<td>10(^{-4})</td>
<td>10 mg/L</td>
</tr>
<tr>
<td>NOM</td>
<td>7.0</td>
<td>10(^{-3})</td>
<td>20 mg/L(^{b})</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>7.8</td>
<td>0</td>
<td>40 µM</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>7.8</td>
<td>0</td>
<td>20 µM</td>
</tr>
<tr>
<td>I(^{-})</td>
<td>7.0</td>
<td>0</td>
<td>500 µM</td>
</tr>
<tr>
<td>I(^{-})</td>
<td>7.0</td>
<td>0</td>
<td>10 µM</td>
</tr>
<tr>
<td>I(^{-})</td>
<td>7.6</td>
<td>8.3·10(^{-4})</td>
<td>10 µM</td>
</tr>
</tbody>
</table>

\(^{a}\) The dissolution rate was calculated from the data included in the figures of the cited reference.

\(^{b}\) The carbon content of the NOM was 40%.

\(^{c}\) The dissolution rate was calculated using the rate expression provided in reference 21 with an extrapolated experimental conditions similar to present study.

3.3.2 Effect of pH

When iodide (10 µM) and DIC (50 mg C/L) were both present, the PbO\(_2\) dissolution rate increased with decreasing pH (Figure 3.1). The effect of pH may be caused by its effects on the electrochemical driving force for PbO\(_2\) reduction and by its impact on the kinetics of a rate-limiting step in the overall dissolution process. Decreasing the pH would increase the electrochemical potential (\(\Delta E_H\)) of Reaction 6, and based on the Nernst equation and published \(E_{H^0}\) values for the relevant half reactions (Reactions 3.2 and 3.3), \(\Delta E_H\) will increase by 0.118V for a 1 pH unit decrease. A previous study that investigated the impacts of disinfectants on PbO\(_2\) stability found that the dissolution rate increased with increasing \(\Delta E_H\) (Xie et al., 2010a). From a
kinetic point of view, increasing the H\(^+\) concentration in Reaction 3.6 would increase the overall dissolution. Further the extent of iodide adsorption onto the PbO\(_2\) surface will be greater at lower pH, which may also lead to faster dissolution at lower pH. The apparent reaction order with respect to proton concentration was 0.75 at pH 6.7 - 8.5 in the present study. Lin and Valentine observed a comparable order of 0.66 for the proton concentration for plattnerite dissolution by iodide at pH 6.0 – 8.0 (Lin et al., 2008). Decreasing the pH was also found to increase the rate of reductive dissolution of MnO\(_2\) by iodide. During the reductive dissolution of birnessite (\(\delta\)-MnO\(_2\))
with 1 mM iodide at pH 4.5 – 6.25, iodide was lost more quickly at lower pH values, suggesting that increasing H\(^+\) concentrations increased the rate of birnessite reductive dissolution by iodide with an apparent reaction order for H\(^+\) of 1.02 (Fox et al., 2009).

### 3.3.3 Effect of iodide concentration

Increasing the iodide concentration accelerated the dissolution of plattnerite at both pH 7.6 and 8.5 when 50 mg C/L DIC was present (Figure 3.2). At pH 7.6 the dissolution rate with 1 \(\mu\)M iodide was not significantly different from the rate in the experiment without iodide, but increasing the iodide concentration to 2 \(\mu\)M doubled the dissolution rate. The observations at low iodide concentrations suggest that a threshold iodide concentration for enhancing PbO\(_2\) dissolution was between 1 and 2 \(\mu\)M at pH 7.6. The threshold value at pH 8.5 was higher (between 5 and 10 \(\mu\)M), which is qualitatively in agreement with equilibrium calculations based on Reaction 6 that indicate that higher iodide concentrations are required at higher pH to result in comparable PbO\(_2\) dissolution extents as at lower pH. However, the exact mechanisms responsible for a threshold iodide concentration for PbO\(_2\) dissolution remain unclear. Possible causes for the effect include impacts of pH on iodide adsorption to the PbO\(_2\) surface and the possible requirement for a critical surface loading of iodide before reduction becomes favorable.

Trends in the PbO\(_2\) dissolution rate acquired from flow-through experiments were different from those for initial dissolution rates measured in batch experiments at pH 7.0 by Lin and Valentine (Lin et al., 2008). They determined the dissolution rate based on the first 3 minutes of reaction and observed that the dissolution rate increased with increasing iodide concentrations with a reaction order of 1.68 with respect to iodide. Due to the potential presence of labile surface phases and highly reactive sites, the initial dissolution rates of metal oxides can be more
variable and much faster than the rates determined over longer time periods (Samson and Eggleston, 2000). The continuous-flow experiments in the present study examine the long-term steady-state dissolution rates of PbO$_2$. By continuously flushing the dissolution products out of the reactor, the measured dissolution rates are not affected by the dissolution of any labile surface phases. Indeed, the effluent lead concentrations over the first few residence times were more variable than the steady-state lead concentrations, and for iodide concentrations above 5 µM initial lead release rates were higher than the rates observed at steady state (Figure 3-S3 of the Supporting Information).

Fast initial dissolution of PbO$_2$ with high iodide concentration may release sufficient Pb(II) to induce the formation of Pb(II)-precipitates. The Pb(II) carbonate cerussite (PbCO$_3$) was observed by XRD following PbO$_2$ reaction with 100 µM iodide and 50 mg C/L DIC at pH 7.6 (Figure 3-S5 of the Supporting Information), and cerussite formation at this condition was confirmed by SEM (Figure 3-S6 of the Supporting Information). The large release of aqueous Pb(II) species from fast initial dissolution of PbO$_2$ caused the system to become oversaturated with respect to cerussite. The formation of the secondary Pb(II) precipitates provides a sink for Pb(II) species and could change the available surface area of PbO$_2$. Therefore the steady-state lead effluent concentration at this condition represents the balance between PbO$_2$ dissolution and cerussite precipitation, so a dissolution rate for 100 µM iodide could not be acquired from Equation 3.1.

3.3.4 Effect of Dissolved Inorganic Carbon

The presence of DIC accelerated the dissolution of PbO$_2$ relative to systems without DIC. At pH 7.6 with either 5 or 10 µM iodide, the dissolution rates of PbO$_2$ with 50 mg C/L DIC were
nearly double the rates in the absence of DIC (Figure 3.3). In the carbonate-free experiments, the pH was buffered using 1 mM MOPS. Organic buffers, like MES and HEPES, were found to enhance the dissolution of PbO$_2$, which was probably caused by their chemical reduction of PbO$_2$ (Xie et al., 2010b). Although MOPS did slightly enhance the dissolution of PbO$_2$ in batch and flow-through experiments (Figure 3-S7 and 3-S8 of the Supporting Information), the enhancement with 1 mM MOPS was mild and did not obscure the effect of adding DIC. Even after accounting for the effect of MOPS on PbO$_2$ dissolution, the dissolution rates of PbO$_2$ in the absence of DIC were still significantly lower than those with 50 mg C/L DIC. Carbonate from
DIC can serve as a complexing ligand that enhances the dissolution of metal oxides by forming soluble metal-CO$_3^{2-}$ complexes (Bruno et al., 1992; Ulrich et al., 2008; Xie et al., 2010b).

Although the presence of DIC accelerated the dissolution of PbO$_2$, once DIC was present its exact concentration had little effect on the dissolution rate. Varying the DIC concentration from 10 to 200 mg C/L did not affect the dissolution rate at pH 7.6 or 8.5 with 10 μM iodide (Figure 3.4). The reductive dissolution of PbO$_2$ can be described as a coupled process of chemical reduction and detachment, and carbonate may affect the detachment of Pb(II) from PbO$_2$ surface (Xie et al., 2010b). The present results suggest that once a small amount of DIC is present, then
detachment is no longer a rate-controlling step in the dissolution of PbO$_2$ by iodide. This result is consistent with a previous study’s conclusion that chemical reduction was more important than Pb$^{2+}$ detachment in regulating the reductive dissolution of PbO$_2$ by bromide in acidic solutions (Lin and Valentine, 2010).

3.3.5 Mechanism of PbO$_2$ Reductive Dissolution

For reductive dissolution of a metal oxide, several steps are involved: adsorption of the reductant to the surface of the metal oxide, electron transfer from the metal to the reductant, and detachment of the reduced metal ions from the surface of the metal oxide (Hering and Stumm, 1990; Stone and Morgan, 1984). The reductive dissolution of metal oxides has been studied using Fe(III) or Mn(III, IV) oxides, and the reaction rates were controlled by surface reactions in well-mixed laboratory conditions (Hering and Stumm, 1990). The reductive dissolution of PbO$_2$ will follow these general reaction steps, and it was proposed to have two separate one-electron transfer reactions when bromide was used as a reductant (Lin and Valentine, 2010).

Considering Pb$^{2+}$ and I$_2$ as reaction products, the dissolution of PbO$_2$ by iodide can be described by the following steps.

(a) adsorption of iodide to the PbO$_2$ surface to form a precursor surface complex:

$$
>Pb(IV)OH + I^- + H^+ \xrightarrow{k_1} > Pb(IV)I + H_2O
$$

(b) two one-electron transfers between the surface Pb(IV) species and iodide:

$$
>Pb(IV)I \xrightarrow{k_2} > Pb(III)I \xrightarrow{fast} > Pb(II)OH
$$
The Pb(III) species after the first one-electron transfer should be unstable, so the second electron transfer step is much faster than the first electron transfer step. The surface Pb(II) species (i.e. >Pb(II)OH) after electron transfer can also be written as >Pb(IV)OPb(II)OH.

(c) detachment of the Pb(II) species from the PbO₂ surface to solution:

\[ >PB(IV)OPb(II)OH + 2H^+ \rightleftharpoons Pb^{2+} + >PB(IV)OH + H_2O \]  \quad (3.9)

After a Pb(II) species detaches from the PbO₂ surface, a new Pb(IV) surface site is then exposed. The detachment process is reversible and, depending on the solution composition, some Pb(II) may remain adsorbed to the PbO₂ surface. Further details and the full derivation of the resulting rate equations are provided in the Supporting Information. Iodide is involved in steps (a) and (b), and together these steps will be referred to as the chemical reduction process. From Reaction 3.9, the dissolved lead release rate (i.e. dissolution rate of PbO₂) is expressed as

\[ r = k_d[>PB(II)OH][H^+]^2 - k_a[>PB(IV)OH][Pb^{2+}] \]  \quad (3.10)

where [] denotes the concentration of the surface species, \( k_d \) is the rate constant of the detachment step, and \( k_a \) is the rate constant for adsorption. The adsorption of Pb(II) species to the PbO₂ surface may reach equilibrium rapidly and the rate of approach will be affected by \( k_d \) and \( k_a \). The presence of Pb(II)-complexing ligands may increase \( k_d \), thus increasing the rate of detachment and decreasing the extent of Pb(II) adsorption. When the system approaches steady state, the net rates of formation or consumption of all intermediate species are zero. Combining Reactions 3.8 and 3.9, the following relationship can be acquired:

\[ k_d[>PB(II)OH][H^+]^2 - k_a[>PB(IV)OH][Pb^{2+}] = k_2[>PB(IV)I] \]  \quad (3.11)

where \( k_2 \) is the rate constant of the first electron transfer step. Therefore Equation 3.10 can be written as:

\[ r = k_2[>PB(IV)I] \]  \quad (3.12)
In Equation 3.12 [\textgt{Pb(IV)I}] is a function of [\textgt{Pb(IV)OH}]:

\[
[\textgt{Pb(IV)I}] = \frac{k_1}{k_{-1} + k_2} [\textgt{Pb(IV)OH}][H^+][I^-]
\]  \hspace{1cm} (3.13)

where \(k_1\), and \(k_{-1}\) are the rate constants for iodide adsorption and desorption and [\textgt{Pb(IV)OH}] represents the concentration of Pb(IV) surface sites that are not associated with iodide. Assuming that the total surface area does not change during the reactions, the concentration of surface sites is constant and is denoted as \(S_t\) (mol·L\(^{-1}\)). The concentrations of the surface Pb(III) intermediates would be small and can be neglected, and \(S_t\) can then be expressed by:

\[
S_t = [\textgt{Pb(IV)OH}] + [\textgt{Pb(IV)I}] + [\textgt{Pb(II)OH}]
\]  \hspace{1cm} (3.14)

Carbonate from DIC could serve as a complexing ligand that accelerates the Pb(II) detachment step (Reaction 3.9). The dissolution rate in the presence of DIC was much higher than in the absence of DIC at pH 7.6. Once some DIC was present, varying its concentration did not affect the dissolution rate of PbO\(_2\) by iodide, indicating that the detachment step was fast in comparison with the reduction steps in the system containing DIC and that only a limited fraction of PbO\(_2\) surface sites were covered by adsorbed Pb(II) species. Therefore the concentrations of \(\textgt{Pb(II)OH}\) are small at steady state and can be neglected in Equation 3.14, which can then be simplified to:

\[
S_t = [\textgt{Pb(IV)OH}] + [\textgt{Pb(IV)I}]
\]  \hspace{1cm} (3.15)

Changing the iodide concentrations will affect the chemical reduction steps (Reactions 3.7 and 3.8). The observed increases in PbO\(_2\) dissolution rates with increasing iodide concentrations suggest that the chemical reduction steps were rate-limiting. Combining Equations 3.12, 3.13 and 3.15, the steady-state dissolution rate of PbO\(_2\) at a specific pH in a system with DIC can then be expressed as:
\[ r = k' \frac{k[I^-]}{1 + k[I^-]} \]  

(3.16)

where

\[ k = \frac{k_1[H^+]}{k_{-1} + k_2} \]  

(3.17)

\[ k' = k_2S_t \]  

(3.18)

When DIC was present, the chemical reduction steps were rate-limiting and the dissolution of PbO\(_2\) by iodide followed Langmuir-Hinshelwood kinetics, which are consistent with the form of Equation 3.16 just derived. At low iodide concentrations the dissolution rate is first order with respect to iodide concentration, and the dissolution rates plateau as the iodide concentrations increase further. Langmuir-Hinshelwood kinetics has been used to explain the kinetics of the reductive dissolution of Fe(III) oxides by cysteine (Amirbahman et al., 1997) and Mn(IV) oxides by hydroquinone (Stone and Morgan, 1984).

The pH might affect the adsorption of iodide to PbO\(_2\) as well as the surface speciation of PbO\(_2\), thus affecting the dissolution rate. The constants k and k’ in Equation 3.16 are specific to a given pH. Considering the following two surface reactions:

\[ \text{>Pb(IV)OH}_2^+ \Rightarrow \text{Pb(IV)OH} + H^+ \quad K_{\text{int1}}^s \]  

(3.19)

\[ \text{>Pb(IV)OH} \Rightarrow \text{Pb(IV)O}^- + H^+ \quad K_{\text{int2}}^s \]  

(3.20)

A change in pH might alter the distribution of the surface species among >Pb(IV)OH\(_2^+\), >Pb(IV)OH, and >Pb(IV)O\(^-\), and a general rate equation as a function of pH would be more complicated than Equation 3.16.

Employing the nonlinear regression of the experimental data at pH 7.6 to Equation 3.16, an optimal value of \(k'\) was \(99 \cdot 10^{-10} \text{ (mol} \cdot \text{m}^2 \cdot \text{min}^{-1})\) and of \(k\) was \(8.1 \cdot 10^{-2} \text{ (μM}^{-1})\). The value of \(k'\)
determines the maximum dissolution rate at a given pH, and k accounts for the steady-state surface coverage of the >Pb(IV)I precursor complex. A comparison of the model using Equation 16 and the measured rate at pH 7.6 shows that the model overestimates the dissolution rate of PbO₂ at the lowest iodide concentrations (Figure 3.2). This is consistent with a threshold value for the iodide concentration that must be exceeded to accelerate PbO₂ dissolution. The model assumed that the adsorption of iodide to the surface of PbO₂ followed Langmuir adsorption. In reality, the adsorption behavior might be more complicated to account for the threshold value. Due to the limited amount of data at pH 8.5, the model was not optimized to fit the experimental dissolution rates at this pH. However, the lower dissolution rates at pH 8.5 than at pH 7.6 are in agreement with the expected trend of a lower electrochemical potential for the driving force of Reaction 3.6, a rate law for Reaction 3.6 with a fractional order dependence on the H⁺ concentration, and less iodide sorption with increasing pH.

### 3.4 Environmental Implications

Dissolved lead concentrations in tap water may be strongly influenced by the dissolution rate of PbO₂ in lead service lines and not by equilibrium solubility. Because PbO₂ is inherently unstable in water without free chlorine, the rate of reductive dissolution is critical for controlling the amounts of lead released to the water. Calculation of lead release from a 1-foot section of aged lead pipe with a 0.75-inch inner diameter and PbO₂ on its inner surface illustrates the potential significance of dissolution rates. For such a pipe section a conservative estimate of the surface area of the PbO₂ of 0.02 m² is made assuming that PbO₂ smoothly covers the entire surface of the pipe. In reality, porous pipe scales can have surface areas of corrosion products significantly higher. Using the rates determined in this study, the lead concentrations after a 6
hour stagnation period with and without a reductant can be calculated. For water containing 50 mg C/L DIC at pH 7.6 that is in contact with this pipe scale, the lead concentrations will only reach 5 µg/L because of the slow dissolution of PbO₂ in the absence of a reductant. However, if 10 µM iodide is present in this same water, then a lead concentration of 99 µg/L, which is well above the lead action level of 15 µg/L, can be achieved during 6 hours of stagnation.

The role of iodide as a reductant for PbO₂ can be compared with the potential roles of other reductants by considering the dissolution rates and relevant concentrations of reductants. The rate in the presence of 10 µM iodide was comparable to that with 20 mg/L NOM (Lin and Valentine, 2008b) but significantly lower than that with 20 µM Mn²⁺ (1.1 mg/L) or 40 µM Fe²⁺ (2.2 mg/L) (Shi and Stone, 2009a). In actual distribution systems, the Mn²⁺ concentrations could be as high as 0.2 mg/L (4 µM) (Cerrato et al., 2006), and the NOM concentration could be several mg C/L (Volk et al., 2002); the typical iodide concentration is below 20 µg/L (0.16 µM) (National Academy of Sciences, 1980). This iodide concentration is below the threshold value observed in the present study for acceleration of PbO₂ dissolution. Therefore iodide might play a less important role than NOM or Mn²⁺ and Fe²⁺ in enhancing PbO₂ dissolution in typical distribution systems. Nevertheless, the mechanism of the reductive dissolution of PbO₂ proposed in the present work may be applicable to interpreting the reactions of PbO₂ with other reductants in distribution systems.

Controlling water chemistry is crucial to mitigating lead release to drinking water. An understanding of the factors controlling PbO₂ dissolution can be valuable for systems that have switched from free chlorine to chloramines as the residual disinfectant since PbO₂ is not stable without the high ORP provided by free chlorine. The pH and DIC are often adjusted to control lead corrosion. The pH is important in regulating the dissolution rate of PbO₂. Both in the present
study and previous work, (Lin et al., 2008; Lin and Valentine, 2008b) increasing the pH was found to significantly inhibit the dissolution of PbO$_2$ by reductants. The present study found that detachment of the Pb(II) from the PbO$_2$ surface was fast with DIC present in the system, but altering the DIC concentration had little effect on the dissolution rate of PbO$_2$ in the presence of iodide. Consequently, adjusting the carbonate alkalinity of a drinking water would be expected to have little effect on lead release for systems with PbO$_2$ present other than the associated effects on pH. Lead release induced by reductive dissolution of PbO$_2$ could also be mitigated by maintaining the free chlorine concentration in the distribution system to prevent PbO$_2$ reduction, consume the reductants, and re-oxidize soluble Pb(II) species.

**Acknowledgements**

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Chapter 3 Supporting Information

Contents: Two sections (3-S1 – 3-S2)
   Two tables (3-S1 – 3-S2)
   Ten figures (3-S1 – 3-S10)

Section 3-S1. Effect of Organic Buffer on Plattnerite Dissolution

3-(N-morpholino)propanesulfonic Acid (MOPS) was selected as the pH buffer in the experiments without dissolved inorganic carbon (DIC) at pH 7.6. Previous study suggested that organic buffers, like 4-(2-hydroxyethyl)-1-piperazinethanesulfonic acid (HEPES), and 2-(N-morpholino)ethanesulfonic acid (MES), could significantly enhance the dissolution of PbO₂, probably by acting as reductants for PbO₂, which is a strong oxidant. Therefore the effect of MOPS on the dissolution of plattnerite was evaluated using both batch reactors and flow-through reactors.

Batch experiments were conducted at room temperature (21 ± 1 °C) in 500 mL polypropylene batch reactors. In each experiment aliquots of a 0.5 M NaHCO₃ stock solution were used to adjust the DIC concentration to 50 mg C/L. Then the desired MOPS concentration (0, 1, or 10 mM) was provided by addition of an aliquot of 0.5 M MOPS stock solution. The pH was then adjusted to 7.6 by addition of concentrated HNO₃ or freshly prepared 0.5 M NaOH solution. Finally PbO₂ solids were added to provide a solid loading of 50 mg/L. Experiments were conducted up to 24 hours and samples were collected at different time intervals, filtered through 0.22 μm polyether sulfone (PES) syringe filters, acidified to 2% HNO₃, and preserved for dissolved lead analysis. Each experimental condition was run in duplicate.
Flow-through experiments were performed using the continuously stirred tank reactor (CSTR) described in the manuscript, and the influent was prepared in the same way as described in the manuscript. Experiments were conducted at pH 7.6 with 50 mg C/L DIC and 10 mM NaNO$_3$ in the absence and presence of 1 mM MOPS for 24 hours. Each experimental condition was run in duplicate.

In the batch experiments the presence of MOPS enhanced the dissolution of plattnerite, and the dissolved lead concentrations after 24 hours of reaction increased with increasing MOPS concentrations (Figure S7 of the Supporting Information). While around 7 ug/L dissolved lead was released in the absence of MOPS, the dissolved lead concentration increased to about 20 ug/L with 1 mM MOPS and 200 ug/L with 10 mM MOPS. In the flow-through experiments, the steady-state effluent lead concentration without MOPS was about 30 nM, and it increased to 50 nM with 1 mM MOPS present (Figure S8 of the Supporting Information). Therefore the dissolution rate of plattnerite in the presence of 1 mM MOPS was only 1.7 times higher than without MOPS. Although the presence of 1 mM MOPS slightly promoted the dissolution of plattnerite, this slight enhancement was acceptable for the experiments on the effects of DIC the effect of DIC was much greater than that of MOPS. The MOPS was critical to maintaining a stable pH while probing the effects of DIC.

**Section 3-S2. Proposed Reactions of the Reductive Dissolution of Plattnerite by Iodide**

Considering Pb$^{2+}$ and I$_2$ as reaction products, the overall reaction can be written as:

$$\text{PbO}_2 + 2\Gamma + 4\text{H}^+ = \text{Pb}^{2+} + \text{I}_2 + 2\text{H}_2\text{O}$$

(1)

The following reaction mechanism was proposed to describe the dissolution of PbO$_2$ by iodide.
(a) adsorption of iodide to the PbO$_2$ surface to form a precursor surface complex:

\[ > \text{Pb}^{(IV)}\text{OH} + I^- + H^+ \xrightleftharpoons[k_d]{k_i} > \text{Pb}^{(IV)}I + H_2O \]  

(2)

(b) two one-electron transfers between the surface Pb(IV) species and iodide:

\[ > \text{Pb}^{(IV)}I \xrightarrow{k_2} > \text{Pb}^{(III)}I^* \]  

(3)

\[ > \text{Pb}^{(III)}I^* + \text{H}_2\text{O} \xrightarrow{k_3} > \text{Pb}^{(III)}\text{OH} + H^+ + I^- \]  

(4)

\[ > \text{Pb}^{(III)}\text{OH} + I^- + H^+ \xrightarrow{k_4} > \text{Pb}^{(III)}I + \text{H}_2\text{O} \]  

(5)

\[ > \text{Pb}^{(III)}I \xrightarrow{k_5} > \text{Pb}^{(II)}I^* \]  

(6)

\[ > \text{Pb}^{(II)}I^* + \text{H}_2\text{O} \xrightarrow{k_6} > \text{Pb}^{(II)}\text{OH} + H^+ + I^- \]  

(7)

(c) detachment of the Pb(II) species from the PbO$_2$ surface to solution

\[ > \text{Pb}^{(IV)}\text{OPb}^{(II)}\text{OH} + 2H^+ \xrightleftharpoons[k_d]{k_i} \text{Pb}^{2+} + > \text{Pb}^{(IV)}\text{OH} + \text{H}_2\text{O} \]  

(8)

(d) formation of I$_2$ from I· radicals

\[ 2I^- \xrightarrow{k_9} I_2 \]  

(9)

>Pb(IV)OPb(II)OH and >Pb(II)OH are describing the same surface Pb(II) species. Reactions 4 to 7 are considered to be very fast, and their forms would not affect the final rate equation acquired. From Reaction 8, the dissolved lead release rate (i.e. dissolution rate of PbO$_2$) can be expressed as

\[ r = k_d[ > \text{Pb}^{(II)}\text{OH}][H^+]^2 - k_a[ > \text{Pb}^{(IV)}\text{OH}][\text{Pb}^{2+}] \]  

(10)

where [] denotes the concentration of the surface species, $k_d$ is the rate constant of the detachment step, and $k_a$ is the rate constant of adsorption. Adsorption equilibrium may be reached rapidly with the rate of approach being affected by $k_a$ and $k_d$. The presence of Pb(II)-complexing ligands may increase $k_d$, and $k_d$ would then be a function of the ligand identity.
Therefore the extent of adsorption of Pb(II) adsorption to the PbO₂ surface may be decreased in the presence of Pb(II)-complexing ligands.

When the system approaches steady state, the net formation and consumption rates of all intermediate species are zero, which can be expressed as:

\[
\frac{d[>Pb(IV)I]}{dt} = k_1[>Pb(IV)OH][I^-][H^+] - k_{-1}[>Pb(IV)I] - k_3[>Pb(IV)I] = 0
\]  

(11)

\[
\frac{d[>Pb(III)I^*]}{dt} = k_2[>Pb(IV)I] - k_3[>Pb(III)I^*] = 0
\]  

(12)

\[
\frac{d[>Pb(III)OH]}{dt} = k_3[>Pb(III)I^*] - k_4[>Pb(III)OH][I^-][H^+] = 0
\]  

(13)

\[
\frac{d[>Pb(III)I]}{dt} = k_4[>Pb(III)OH][I^-][H^+] - k_5[>Pb(III)I] = 0
\]  

(14)

\[
\frac{d[>Pb(II)I^*]}{dt} = k_5[>Pb(III)I] - k_6[>Pb(II)I^*] = 0
\]  

(15)

\[
\frac{d[>Pb(II)OH]}{dt} = k_6[>Pb(II)I^*] - k_d[>Pb(II)OH][H^+]^2 + k_d[>Pb(IV)OH][Pb^{2+}] = 0
\]  

(16)

where \(k_1, k_{-1}, k_2, k_3, k_4, k_5, k_6, k_d, \) and \(k_8\) are rate constants.

Solving Equations 11 – 16, the following relationship can be acquired:

\[
k_d[>Pb(II)OH][H^+]^2 - k_d[>Pb(IV)OH][Pb^{2+}] = k_2[>Pb(IV)I]
\]  

(17)

Therefore Equation 10 can be rewritten as:

\[
r = k_2[>Pb(IV)I]
\]  

(18)

And \([>Pb(IV)I]\) can be expressed as a function of \([>Pb(IV)OH]\):

\[
[>Pb(IV)I] = \frac{k_1}{k_{-1} + k_2}[>Pb(IV)OH][H^+][I^-]
\]  

(19)

where \([>Pb(IV)OH]\) represents the concentration of total surface Pb(IV) species that are not bound to iodide at a given pH. Since less than 1% of the total PbO₂ solids were consumed over
the experiment period, the total surface area could be assumed as constant. The total surface site concentration, denoted as \( S_t \) (mol·L\(^{-1}\)), is then also constant. The concentrations of the active surface Pb(III) intermediates are anticipated to be small since their formation and consumption are probably very fast (Reactions 4 - 7). So \( S_t \) can be approximately expressed by:

\[
S_t = [\text{>Pb(IV)OH}] + [\text{>Pb(IV)I}] + [\text{>Pb(II)}] \tag{20}
\]

Carbonate could serve as a complexing ligand that accelerates the Pb(II) detachment step (Reaction 8). The dissolution rate in the presence of DIC was much higher relative to that in the absence of DIC at pH 7.6. For systems in which DIC was present, varying the DIC concentration did not affect the dissolution rate of PbO\(_2\) by iodide, which indicates that the detachment step was fast as compared to the reduction steps, and the adsorption of soluble Pb(II) species onto PbO\(_2\) would have a very limited effect on the overall dissolution of PbO\(_2\). Therefore only a small portion of the PbO\(_2\) surface would be covered by adsorbed Pb(II) species (\( \text{>Pb(II)OH} \)) at steady state and the \( \text{>Pb(II)OH} \) concentration can be neglected in Equation 20, which can then be simplified to Equation 21 for systems with DIC present:

\[
S_t = [\text{>Pb(IV)OH}] + [\text{>Pb(IV)I}] \tag{21}
\]

Changing the iodide concentrations could affect the reaction steps involving the adsorption of I\(^-\) to the PbO\(_2\) surface and the reduction of surface Pb(IV) (Reactions 2 and 3). Increasing the iodide concentration accelerated the dissolution of PbO\(_2\) in the present study, suggesting that the chemical reduction steps were slow enough to be the rate-limiting steps. Combining Equations 18, 19 and 21, the steady state dissolution rate of PbO\(_2\) at a specific pH in a system with DIC can be expressed by:

\[
r = k' \frac{k[I^-]}{1 + k[I^-]} \tag{22}
\]

where
\[ k = \frac{k[H^+]}{k_1 + k_2} \]  \hspace{1cm} (23)

\[ k' = k_2 S \]  \hspace{1cm} (24)
Table 3-S1. Summary of the experimental conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.7, 7.6, 8.5</td>
</tr>
<tr>
<td>DIC (mg C/L)</td>
<td>0, 10, 50, 200</td>
</tr>
<tr>
<td>Iodide concentration (uM)</td>
<td>0, 1, 2, 5, 10, 20</td>
</tr>
</tbody>
</table>

Table 3-S2. Thermodynamics of PbO\(_2\) reduction and iodide oxidation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E_{H}^0) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO(_2) reduction: (\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Pb}^{2+} + 2\text{H}_2\text{O})</td>
<td>1.45</td>
</tr>
<tr>
<td>Iodide oxidation: (\text{I}_2(\text{aq}) + 2\text{e}^- = 2\text{I}^-)</td>
<td>0.62</td>
</tr>
</tbody>
</table>

\(E_{H}^0\) was calculated using the thermodynamic data from ref.\(^2\).

Figure 3-S1. X-ray diffraction pattern of the commercial PbO\(_2\) used in the present study. Reference powder diffraction file pattern of plattnerite is 01-071-4820.
Figure 3-S2. Effluent lead concentrations (■ and ▲) and pH (□ and △) from CSTRs as a function of the number of hydraulic residence times (τ = 30 min) in the absence of iodide concentrations at pH (a) 6.7, (c) 7.6, and (e) 8.5, and in the presence of 10 μM iodide at pH (b) 6.7, (d) 7.6, and (f) 8.5. Duplicate experiments (represented by rectangles and triangles) were conducted for each condition.
Figure 3-S3. Effluent lead concentrations (■ and ▲) and pH (□ and △) from CSTRs as a function of the number of hydraulic residence times (τ = 30 min) at pH 7.6 with different iodide concentrations. Panels (a) – (f) represents the iodide concentration of 0, 1, 2, 5, 10, 20 μM respectively. Duplicate experiments (represented by rectangles and triangles) were conducted for each condition.
Figure 3-S4. Effluent lead concentrations (■ and ▲) and pH (□ and △) from CSTRs as a function of the number of hydraulic residence times (τ = 30 min) at pH 8.5 with different iodide concentrations. Duplicate experiments (represented by rectangles and triangles) were conducted for each condition.
Figure 3-S5. X-ray diffraction patterns of the plattnerite after 24 hours of reaction at pH 7.6 with 50 mg C/L DIC and different iodide concentrations. Dominant peaks associated with plattnerite (P) and cerussite (C) are indicated, and reference powder diffraction file patterns for plattnerite, cerussite, and hydrocerussite are 01-071-4820, 01-085-1088, and 01-073-4362 respectively. Some cerussite formation is apparent when the iodide concentration was 100 μM.
Figure 3-S6. Electron micrographs of solids: (a) before reaction, and after 24 hours of reaction in the CSTR with 50 mg C/L DIC and (c) 10 μM iodide at pH 7.6, (e) 100 μM iodide at pH 7.6, and (f) 10 μM iodide at pH 8.5. Panels b and d are higher magnification images of sections from panels a and c, respectively.
Figure 3-S7. Dissolved lead concentration from batch reactors over time at pH 7.6 with 50 mg C/L DIC and different concentrations of MOPS.
Figure S8. Effluent lead concentrations from CSTRs as a function of the number of hydraulic residence times ($\tau = 30$ min) at pH 7.6 with 50 mg C/L DIC in the absence (□ and △) and presence of 1 mM MOPS (■ and▲). Duplicate experiments (represented by rectangles and triangles) were conducted for each condition.
Figure 3-S9. Effluent lead concentrations (■ and ▲) and pH (□ and △) from CSTRs as a function of the number of hydraulic residence times (τ = 30 min) at pH 7.6 in the absence of DIC with (a) 5 μM and (c) 10 μM iodide and in the presence of 50 mg C/L DIC with (b) 5 μM and (d) 10 μM iodide. Duplicate experiments (represented by rectangles and triangles) were conducted for each condition.
Figure 3-S10. Effluent lead concentrations (■ and ▲) and pH (□ and △) from CSTRs as a function of the number of hydraulic residence times ($\tau = 30$ min) in the presence of 10 uM iodide at pH 7.6 and 8.5 with different DIC concentrations. Panels (a) – (c) represent iodide concentrations of 10, 50, and 200 mg C/L at pH 7.6. Panels (d) – (f) represent iodide concentrations of 10, 50, and 200 mg C/L at pH 8.5. Duplicate experiments (represented by rectangles and triangles) were conducted for each condition.
Chapter 4. Kinetics of Lead(IV) Oxide (PbO₂)

Reductive Dissolution: Importance of Lead(II) Adsorption and Surface Speciation

Results of this chapter have been published in Journal of Colloid and Interface Science, 2013, 389, 236 – 243.

Abstract

Lead(IV) oxide (PbO₂) is a corrosion product on lead pipes used for drinking water distribution, and its dissolution can control lead release to drinking water. This study evaluated the adsorption of Pb(II) to PbO₂ and its impact on the dissolution rate of PbO₂. The dissolution rate of PbO₂ was determined as a function of pH in the absence and presence of free chlorine using continuously-stirred tank reactors. Pb(II) adsorption was examined as a function of pH and initial Pb(II) concentrations. The dissolution rate of PbO₂ increased with decreasing pH. The presence of free chlorine inhibited PbO₂ dissolution. The dissolution of PbO₂ involves a coupled reduction-detachment process, and a model was developed that accounts for the adsorption of Pb(II) from the reduction. The extent of Pb(II) adsorption to PbO₂ increased with increasing pH and Pb(II) concentrations until reaching a plateau. Adsorption was interpreted with a surface complexation model using the diffuse double-layer model and a single surface complex. The dissolution rate of PbO₂ was directly related to the distribution of the PbO₂ surface species predicted by the surface complexation model. The dissolution rate was predominantly controlled
by \textgreater Pb(IV)OH \textsuperscript{+} for acidic conditions and by \textgreater Pb(IV)OH and \textgreater Pb(IV)O\textsuperscript{-} at neutral to basic conditions.

**Key Words:**

Lead(IV) Oxide, Dissolution, Lead, Adsorption, Surface Complexation Model

### 4.1 Introduction

Lead(IV) oxide (PbO\textsubscript{2}) has been observed as a corrosion product on lead service lines in US drinking water distribution systems, and its dissolution can control lead release to drinking water (Kim and Herrera, 2010; Renner, 2004; Schock and Giani, 2004; Switzer et al., 2006). PbO\textsubscript{2} is a strong oxidant that only forms in systems with a high oxidation reduction potential (ORP). Free chlorine (i.e. HOCl + OCl\textsuperscript{-}), a widely used disinfectant in distribution systems, provides a high ORP that favors PbO\textsubscript{2} formation. (Lytle and Schock, 2005; Switzer et al., 2006; Wang et al., 2010). The presence of reductants that include natural organic matter (NOM), Br\textsuperscript{-}, I\textsuperscript{-}, Mn\textsuperscript{2+}, and Fe\textsuperscript{2+} significantly enhanced the dissolution of PbO\textsubscript{2} (Dryer and Korshin, 2007; Lin et al., 2008; Lin and Valentine, 2008b; 2010; Shi and Stone, 2009a; b; Wang et al., 2012b). The reductive dissolution of PbO\textsubscript{2} by water itself is even thermodynamically favorable (Lin and Valentine, 2008b; Xie et al., 2010b).

The dissolution of metal oxides can be described by several steps: transport of the aqueous reactant from bulk solution to the surface of the metal oxide, adsorption of the reactant to the metal oxide surface, chemical reactions on the metal oxide surface, detachment of the product from the metal oxide surface, and transport of the product to the bulk solution (Stumm and...
Wollast, 1990). In well-mixed laboratory conditions, for most metal oxides the overall dissolution rate is controlled by the surface reactions and not by transport processes (Hering and Stumm, 1990; Stumm and Wollast, 1990). Stumm and co-workers proposed that the dissolution rate of metal oxides strongly depended on the particular surface species that participate in the reaction (Stumm, 1997; Stumm and Wollast, 1990).

The speciation of a metal oxide surface can be described by a surface complexation modeling approach (Dzombak and Morel, 1990). Surface complexation models (SCM) have been applied to interpret acid-base properties of minerals (Hayes et al., 1991; Stumm, 1987), anion and cation adsorption to mineral surfaces (Ghayaza et al., 2011; Gu and Evans, 2007; Hayes and Leckie, 1986; Hayes and Leckie, 1987), and mineral dissolution/precipitation (Pokrovsky et al., 1999a; Pokrovsky et al., 1999b; Van Cappellen et al., 1993). In reviewing the effects of protons and ligands on the kinetics of the non-reductive dissolution of metal oxides, Stumm and Wollast suggested that the dissolution rate was strongly related to the concentrations of the surface species $>$MeL and $>$MeOH$_2^+$ (Stumm and Wollast, 1990). To determine the dissolution kinetics of metal carbonates, Pokrovsky and Schott developed a SCM and proposed that $>$CO$_3$H (protonated carbonate surface groups) and $>$MeOH$_2^+$ controlled the dissolution rate in acidic and neutral to slightly basic conditions, respectively (Pokrovsky and Schott, 2002).

Based on a 2-pK$_a$ model, PbO$_2$ has three surface Pb(IV) species: $>$Pb(IV)OH$_2^+$, $>$Pb(IV)OH, and $>$Pb(IV)O$. The distribution of these surface species depends on the pH and can be described by reactions 4.1 and 4.2:

\[
\begin{align*}
  &\text{4.1} \\
  &\text{4.2}
\end{align*}
\]

\[
\begin{align*}
  >\text{Pb(IV)OH}_2^+ &= >\text{Pb(IV)OH} + \text{H}^+ & K_{\text{int1}}^s \\
  >\text{Pb(IV)OH} &= >\text{Pb(IV)O}^- + \text{H}^+ & K_{\text{int2}}^s
\end{align*}
\]
The pH_{pzc} of PbO\textsubscript{2} has been reported in the range of 4.8 – 7.4 (Shi and Stone, 2009a; Zhang and Lin, 2012) and is the midpoint of the negative logarithms of the two surface deprotonation constants [i.e. pH_{pzc} = 0.5 \cdot (pK_{\text{int1}} + pK_{\text{int2}})], which are affected by the intrinsic chemical potentials of the species and the surface potentials. The surface is positively charged below the pH_{pzc} and negatively charged above it.

The reductive dissolution of PbO\textsubscript{2} can be described by a coupled reduction and detachment process (Wang et al., 2012b). Based on the extremely low solubility of PbO\textsubscript{2} (Pourbaix, 1974) and the instability of PbO\textsubscript{2} in water (Lin and Valentine, 2008b), essentially no dissolved Pb(IV) is expected to be present over the pH range of 2-9. Any dissolved lead will be Pb(II), and the dissolved lead concentration is therefore controlled by rate of reductive dissolution of PbO\textsubscript{2} rather than by a non-reductive dissolution process. Such processes have also been observed for the reductive dissolution of other metal oxides including iron(III) oxides (Amirbahman et al., 1997; Suter et al., 1991) and manganese(IV) oxides (Stone and Morgan, 1984). Although the kinetics of the non-reductive dissolution of metal oxides has been related to the surface chemistry of the metal oxides, the mechanisms of the reductive dissolution of PbO\textsubscript{2} are still not fully understood.

The adsorption of Pb(II) to metal oxides has been studied previously for aluminum oxides (Bargar et al., 1997a), iron oxides (Hayes and Leckie, 1986; Villalobos et al., 2009; Villalobos and Pérez-Gallegos, 2008), manganese oxides (Villalobos et al., 2005), and titanium oxides (Vohra and Davis, 1997; 1998); while little is known about the adsorption of Pb(II) to PbO\textsubscript{2} and its effects on the overall dissolution of PbO\textsubscript{2}. Cations including bismuth (Ito et al., 1984), cobalt (Ahmad et al., 1994), and manganese (Ahmad et al., 1993) can absorb to PbO\textsubscript{2}. It is likely that
some Pb(II) produced by PbO₂ reduction may be retained at the surface as adsorbed species that affect the speciation and reactivity of the PbO₂ surface.

The primary aims of the present study were to (1) determine the effect of pH and free chlorine on the dissolution rate of PbO₂, (2) assess the adsorption of Pb(II) to PbO₂, and (3) evaluate the impacts of this adsorption on the PbO₂ dissolution rate. A model was developed that related the steady-state dissolution of PbO₂ to the predicted PbO₂ surface speciation. This model may also be applicable to the reductive dissolution of other metal oxides.

4.2 Materials and methods

4.2.1 Materials

All solutions were prepared with ultrapure water (resistivity >18.2 MΩ-cm). X-ray diffraction (XRD) patterns of purchased PbO₂ (Acros) confirmed that it was pure plattnerite (β-PbO₂) (Figure 4-S1 of the Supporting Information). The PbO₂ solids were aggregates of roughly spherical particles with primary sizes around 100 nm; some larger particles (100’s of nm) were also present (Figure 4-S2 of the Supporting Information). The specific surface area of the PbO₂ was 3.6 m²/g as measured by BET-N₂ adsorption. The pHₚₑₙ of the PbO₂ was 5.2 as determined by zeta potential measurement (Figure 4-S3 of the Supporting Information), which was similar to the value reported by Shi and Stone (Shi and Stone, 2009a). They found that the pHₚₑₙ of a synthetic PbO₂ was 4.8 as determined by surface titration. Reagent grade NaNO₃, NaHCO₃, NaOH, NaOCl solution, PbCl₂, and concentrated HNO₃ were purchased (Fisher Scientific).

4.2.2 PbO₂ Dissolution Experiments

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The dissolution rate of PbO$_2$ was investigated as a function of pH (2.5 to 8.5) both in the absence and presence of $1.4 \times 10^{-5}$ M (i.e. 1 mg Cl$_2$/L) free chlorine using completely mixed flow reactors (CMFRs) at the ambient laboratory temperature (21 ± 1 °C). The volume of each reactor was 84 mL and PbO$_2$ was loaded to a concentration of 1 g/L. A polypropylene magnetic stir bar was put in the reactor and mixing was achieved by continuous stirring. A 0.22 µm mixed cellulose filter membrane at the reactor outlet prevented the loss of solids from the reactor. Influent was pumped into the reactor at 2.8 mL/min using a peristaltic pump (Cole-Parmer), so the hydraulic residence time was 30 minutes. The effluent pH and free chlorine concentrations were monitored and aqueous samples were periodically collected over 24 hours. To remove any potential colloidal lead phases, the aqueous samples were further filtered using 0.02-µm polyethersulfone (PES) syringe filters. Samples after this additional filtration step were acidified to 2% HNO$_3$ and preserved for dissolved lead analysis.

The influents were prepared in 10-L sealed plastic (Tedlar) bags to minimize the exchange of CO$_2$ between the atmosphere and the solution. Ultrapure water was purged of CO$_2$ by sparging with N$_2$ before being added to the bags. Addition of an aliquot of 1 M NaHCO$_3$ solution provided the DIC concentration of 50 mg C/L. A volume of 1.0 M NaNO$_3$ solution was then injected to the bags to set the ionic strength at 0.01 M. When applicable an aliquot of a NaOCl stock solution was added. The pH was adjusted to the target values by addition of concentrated HNO$_3$ or freshly prepared 0.5 M NaOH solutions. The plastic bags were covered with aluminum foil to prevent the photodegradation of free chlorine. Each experimental condition was run in duplicate.

The dissolution rates were quantified by operating the reactors for 24 hours (48 hydraulic residence times) to allow them to approach steady state. As compared to batch experiments, the
flow-through approach limits the accumulation of reaction products and minimizes the effect of any initial labile phases on the dissolution rates (Samson and Eggleston, 2000). When the system approaches steady state, the dissolution rate can be determined by Equation 4.3,

\[
r_{\text{exp}} = \frac{Q \cdot C_{ss}}{V_R \cdot A \cdot [\text{solids}]} = \frac{C_{ss}}{t_{\text{res}} \cdot A \cdot [\text{solids}]}
\]  

(4.3)

where \( r_{\text{exp}} \) is the dissolution rate (mol·m\(^{-2}\)·min\(^{-1}\)); \( C_{ss} \) is the steady-state effluent lead concentration (mol·L\(^{-1}\)); \( Q \) is the flow rate (L·min\(^{-1}\)); \( V_R \) is the volume of the reactor (L); \( t_{\text{res}} \) is the hydraulic residence time (i.e., \( V_R/Q \)) (min); [solids] is the solid concentration in the reactor (g·L\(^{-1}\)); and \( A \) is the specific surface area of the solid (m\(^2\)·g\(^{-1}\)). The steady-state concentration was calculated as the average concentration from at least 8 consecutive samples that did not vary by more than 20% and spanned at least 8 residence times.

### 4.2.3 Pb(II) Adsorption Experiments

The adsorption of aqueous Pb(II) species to PbO\(_2\) was determined at 21 ± 1 °C using 150-mL well-mixed polypropylene batch reactors. To determine the pH dependence of adsorption, experiments were conducted at 9 points over pH 4.5 to 8.5 with a fixed total lead(II) concentration of 200 µg/L (0.96 µM) and a solid loading of 0.1 g/L PbO\(_2\). Pb(II) adsorption experiments over a wide range of total lead concentrations (20 – 300 µg/L as Pb) were also conducted with a solid loading of 0.05 g/L PbO\(_2\) at fixed pH values of 6.7, 7.6, and 8.5. A lead(II) chloride stock solution was added to each reactor to achieve the desired total lead concentration, and a 0.5 M NaHCO\(_3\) solution was added to provide 50 mg C/L DIC. The pH was adjusted to the target values by the addition of HNO\(_3\) or NaOH. Aliquots of a 1 M NaNO\(_3\) solution were added to set the ionic strength at 0.01 M. Finally, PbO\(_2\) solids were added to the
reactor to provide a solid concentration of either 0.05 or 0.1 g/L. The batch reactors were well-mixed. Experiments were conducted for only 2 hours to avoid any complications in data interpretation from Pb(II) release from PbO₂ dissolution. Preliminary experiments confirmed that very little Pb(II) was released over 2 hours. Previous studies suggested that cations adsorb to PbO₂ so rapidly that adsorption will have reached equilibrium within this time (Ahmad et al., 1993; Ahmad et al., 1994; Ito et al., 1984). The pH stayed within ± 0.1 units of the target value and no pH adjustment was performed during the experiments. After equilibration, aqueous samples were collected, filtered with 0.22 µm PES syringe filters, acidified to 2% HNO₃, and preserved for dissolved lead analysis. The difference between the total lead added to the reactors and the dissolved lead after 2 hours is taken to represent the amount of Pb(II) adsorbed to the PbO₂.

4.2.4 Acid-Base Titration of PbO₂

The acid-base titration of the PbO₂ was performed in 100-mL well-mixed polypropylene batch reactors at the ambient laboratory temperature (21 ± 1 °C). Experiments were conducted in a nitrogen-filled glovebox to minimize the uptake of CO₂ from the air. Ultrapure water used to prepare the solutions was purged of CO₂ by sparging with N₂. A 1.0 M NaNO₃ stock solution was added to each reactor to provide an ionic strength of 0.01 M. Solid PbO₂ was then added to provide a loading of 50 g/L. The pH was adjusted to a starting value of 7.0 by addition of NaOH. Then HNO₃ was added to the solution drop by drop until the pH decreased to 3.0. Titrations were completed within 30 minutes to limit PbO₂ dissolution that would produce Pb(II) and subsequently affect the PbO₂ surface properties and complicate the interpretation of the titration.
curve. The data obtained from the surface acid-base titration was used to determine the equilibrium constants for the surface deprotonation reactions (Reactions 1-2 in Table 4.1).

4.2.5 Analytical Methods

Dissolved lead (Pb) concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500ce instrument with a detection limit of 0.1 µg/L for Pb. The zeta potential was measured over a wide pH range by injecting aliquots of a 1g/L PbO₂ solid suspension into a zeta potential analyzer (Zetasizer 300 Hs Malvern, Southborough, MA). XRD was performed on a Rigaku Geigerflex D-MAX/A diffractometer with Cu-Ka radiation equipped with a vertical goniometer and scintillation counter. A JEOL 7001LVF field emission scanning electron microscope was used for imaging. BET-N₂ adsorption for surface area measurement was performed on a BET-Autosorb instrument (Quantachrome Instruments). The free chlorine concentration was determined by a standard DPD colorimetric method (4500-Cl G) with a spectrophotometer (PerkinElmer Lambda XLS+) (Clesceri et al., 1999). Solution pH was measured with a glass pH electrode and pH meter (Accumet).

4.2.6 Surface Complexation Modeling

The diffuse double-layer surface complexation model was used for the Pb(II) adsorption modeling. The SCM included two surface acid-base reactions, one Pb(II) adsorption reaction, and thirteen aqueous phase Pb(II) and carbonate reactions (Table 4.1). A 2-pKₐ model was used to describe the surface speciation of PbO₂. The surface deprotonation constants were determined by fitting the data of the acid-base titration of PbO₂ and constraining the fit to provide a pH_pzc of 5.2. Adsorbed Pb(II) was assumed to form a monodentate Pb(II) surface complex. The value of
the equilibrium constant of this surface reaction was determined by optimizing the fit of the
SCM simulation to experimental data. The model simulation was performed using MINEQL+ v.
4.6 (Schecher and McAvoy, 2007).

4.3 Results

4.3.1 Dissolution of PbO\textsubscript{2}: Effect of pH and Free Chlorine

The reductive dissolution of PbO\textsubscript{2} by water is thermodynamically favorable and can be
described by half reactions for PbO\textsubscript{2} reduction (Reaction 4.4) and water oxidation (Reaction 4.5)
(Stumm and Morgan, 1996):

\begin{align*}
4H^+ + PbO_2 + 2e^- &= Pb^{2+} + 2H_2O & E_H^o &= 1.45 \text{ V} \\
0.5 O_2(aq) + 2H^+ + 2e^- &= H_2O & E_H^o &= 1.27 \text{ V}
\end{align*}

(4.4) (4.5)

The overall reaction then can be expressed as:

\begin{equation}
PbO_2(s) + 2H^+ = Pb^{2+} + 0.5O_2(aq) + H_2O
\end{equation}

(4.6)

Non-reductive dissolution of PbO\textsubscript{2} may also occur and can be expressed as:

\begin{equation}
PbO_2(s) + 4H^+ = Pb^{4+} + 2H_2O
\end{equation}

\begin{equation}
\log K_{sp} = -8.91
\end{equation}

(4.7)

Based on available equilibrium constants (Pourbaix, 1974; Risold et al., 1998), the predicted
equilibrium solubility for PbO\textsubscript{2} non-reductive dissolution was orders of magnitude lower than the
effluent lead concentrations in the present study. Therefore the contribution of the non-reductive
dissolution of PbO\textsubscript{2} to the overall lead release can be neglected.

The dissolution rate of PbO\textsubscript{2} increased with decreasing pH in the absence and presence of
free chlorine (Figure 4.1 and Table 4.2). The effluent lead concentrations used to determine the
rates using Equation 4.3 are compiled in Figures 4-S5 and 4-S6 of the Supporting Information.
The dissolution rate increased only slightly from pH 8.5 to 6.7, while it increased sharply when the pH was below 5.7. Changing the pH may alter the electrochemical driving force for PbO$_2$ reduction, affect the dissolution kinetics, and influence the adsorption of Pb(II) to PbO$_2$.

Decreasing the pH increases the electrochemical driving force ($\Delta E_H$) for Reaction 6, which could then accelerate the dissolution of PbO$_2$ (Xie et al., 2010a). Based on the Nernst equation, $\Delta E_H$ will increase by 0.059V for a 1 pH unit decrease. From a kinetic point of view, H$^+$ is a reactant in Reaction 6 that may impact the kinetics of a rate-limiting step in the overall dissolution process.

**Figure 4.1.** The dissolution rate of PbO$_2$ in the absence and presence of 1.4·10$^{-5}$ M free chlorine with 50 mg C/L (4.2 mM) dissolved inorganic carbon (DIC) using flow-through reactors with 1 g/L PbO$_2$ and a residence time of 30 min. The upper and lower bounds of range bars represent the higher and lower values of the duplicates. The solid line represents the dissolution rate of PbO$_2$ predicted by Equation 4.13, and the dashed line represents the rate predicted by Equation 4.18.
The adsorption of Pb(II) may affect the distribution of the Pb(IV) surface species on PbO₂. The impact of surface speciation on the dissolution rate of PbO₂ is explored in detail in a later section.

**Table 4.1.** Reactions and equilibrium constants used in the surface complexation model.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Log K</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Reactions</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>&gt;Pb(IV)OH₂⁺ = &gt;Pb(IV)OH + H⁺</td>
<td>-4.00&lt;sup&gt;b&lt;/sup&gt;</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>&gt;Pb(IV)OH = &gt;Pb(IV)O⁻ + H⁺</td>
<td>-6.40&lt;sup&gt;b&lt;/sup&gt;</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>&gt;Pb(IV)OH + Pb⁺²⁺ = &gt;Pb(IV)OPb(II)⁺ + H⁺</td>
<td>0.20</td>
<td>this work</td>
</tr>
<tr>
<td><strong>Aqueous Reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H₂O = H⁺ + OH⁻</td>
<td>-14.00</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>5</td>
<td>H₂CO₃⁻ = 2H⁺ + CO₃²⁻</td>
<td>-16.68</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>6</td>
<td>HCO₃⁻ = H⁺ + CO₃²⁻</td>
<td>-10.33</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>7</td>
<td>Pb⁺²⁺ + H₂O = PbOH⁺⁺ + H⁺</td>
<td>-7.71</td>
<td>(Benjamin, 2002)</td>
</tr>
<tr>
<td>8</td>
<td>Pb⁺²⁺ + 2H₂O = Pb(OH)₂⁰ + 2H⁺</td>
<td>-17.12</td>
<td>(Benjamin, 2002)</td>
</tr>
<tr>
<td>9</td>
<td>Pb⁺²⁺ + 3H₂O = Pb(OH)₃⁻ + 3H⁺</td>
<td>-28.06</td>
<td>(Benjamin, 2002)</td>
</tr>
<tr>
<td>10</td>
<td>Pb⁺²⁺ + 4H₂O = Pb(OH)₄²⁻ + 4H⁺</td>
<td>-39.70</td>
<td>(Benjamin, 2002)</td>
</tr>
<tr>
<td>11</td>
<td>Pb⁺²⁺ + CO₃²⁻ = PbCO₃⁰</td>
<td>6.48</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>12</td>
<td>Pb⁺²⁺ + 2CO₃²⁻ = Pb(CO₃)₂⁻</td>
<td>9.38</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>13</td>
<td>Pb⁺²⁺ + CO₃⁻ + H⁺ = PbHCO₃⁺</td>
<td>13.20</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>14</td>
<td>2Pb⁺²⁺ + 3H₂O = Pb₂(OH)₃⁺ + 3H⁺</td>
<td>-6.40</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>15</td>
<td>3Pb⁺²⁺ + 4H₂O = Pb₄(OH)₄⁺²⁺ + 4H⁺</td>
<td>-23.89</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
<tr>
<td>16</td>
<td>4Pb⁺²⁺ + 4H₂O = Pb₄(OH)₄⁺⁴⁺ + 4H⁺</td>
<td>-19.99</td>
<td>(Schecher and McAvoy, 2007)</td>
</tr>
</tbody>
</table>

<sup>a</sup>The diffuse double-layer model was employed (I = 0.01 M). The PbO₂ site density is 8 sites/nm² and the specific surface area is 3.6 m²/g.

<sup>b</sup>The reported logK values for the surface-associated reactions are for logK<sub>int</sub>.
The presence of $1.4 \times 10^{-5}$ M free chlorine effectively inhibited the dissolution of PbO$_2$ above pH 3.5 (Figure 4.1). The inhibitory effect was more than an order of magnitude at pH 6.7 to 8.5.

The presence of free chlorine may provide a sufficiently high oxidation reduction potential (ORP) that the reductive dissolution of PbO$_2$ is no longer thermodynamically favorable. From a kinetic

![Table 4.2. Summary of PbO$_2$ dissolution experiments in this study.](image-url)
perspective, free chlorine may re-oxidize dissolved Pb(II) species released from PbO₂ and the oxidation of Pb(II) back to PbO₂ would decrease the net dissolution rate of PbO₂. This point will be discussed in detail later. The difference of the electrochemical potentials between the HOCl/Cl⁻ and PbO₂/Pb²⁺ couples becomes smaller with decreasing pH (Figure 4-S7 of the Supporting Information), which suggests the presence of a threshold pH value below which Pb²⁺ will not be re-oxidized by free chlorine. At pH 2.5, the electrochemical potentials between the HOCl/Cl⁻ and PbO₂/Pb²⁺ couples were similar and the presence of free chlorine did not inhibit the dissolution of PbO₂; actually the dissolution rate was higher with free chlorine. The exact mechanism responsible for the enhancement of PbO₂ dissolution by free chlorine remains unclear.

4.3.2 Adsorption of Pb(II) to PbO₂

The adsorption of Pb(II) to PbO₂ was evaluated as a function of pH (Figure 4.2). With a fixed initial Pb(II) loading, the extent of Pb(II) adsorbed to the PbO₂ surface increased with increasing pH. Limited Pb(II) adsorption was observed below pH 5, while the adsorption extent increased sharply above pH 5 until reaching nearly 100% above pH 7. The shape of the pH-dependence of adsorption is similar to that for Pb(II) adsorption to iron(III) oxides, manganese(IV) oxides, and titanium(IV) oxides (McKenzie, 1980; Vohra and Davis, 1997). The maximum sorption density of Pb(II) was determined from experiments with varied Pb(II) loading at fixed pH of 6.7, 7.6, and 8.5. As expected from the experiments with varying pH, the maximum adsorbed Pb(II) increased with increasing pH (Figure 4.3). For most experimental conditions the system is undersaturated with respect to any Pb(II) solids, and therefore it is unlikely to form any surface precipitates; while for the conditions with high lead loading at pH
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8.5, the system is supersaturated with respect to the Pb(II) carbonate solid hydrocerussite (Pb₃(OH)₂(CO₃)₂). However, for the PbO₂-free control experiment conducted at this condition, no precipitation was observed. In addition, the total Pb(II) loading was below the total concentration of surface sites. Since adsorption is a rapid process that would drive dissolved Pb(II) concentrations below saturation, it is likely that no precipitation occurred in the PbO₂ adsorption experiments.

The diffuse double-layer SCM was employed to describe the adsorption of Pb(II) to PbO₂. The reactions used in the model are listed in Table 4.1. The site density of PbO₂ was set at 8

**Figure 4.2.** Adsorption of Pb(II) onto 0.1 g/L PbO₂(s) as a function of pH for an initial Pb(II) concentration of 0.96 µM in the presence of 50 mg C/L (4.2 mM) DIC. Data were from a single set of experiments. The solid line represents the prediction from the surface complexation model. Dashed lines are the predicted dominant aqueous lead(II) species.
sites/nm\(^2\) based on the fit of the model to the data from both varying pH at fixed Pb(II) loading and the maximum adsorption densities at different fixed pH. The site density for metal oxides is commonly in the range of 2 to 10 sites/nm\(^2\) (Davis and Kent, 1990). Three surface Pb(IV) species were considered in the model. The intrinsic surface deprotonation constants were determined as pK\(_{a1}\) = 4.0 and pK\(_{a2}\) = 6.4 by fitting the surface titration data and constraining the values have a midpoint at the measured pH\(_{pzc}\) of 5.2 (Figure 4-S4 of the Supporting Information). The adsorbed Pb(II) is modeled as a monodentate inner sphere complex (Reaction 3 in Table 4.1). Bidentate surface complexes have been observed for Pb(II) adsorption to metal oxide surfaces (Bargar et al., 1997a;b); however, the differences in model fit when using monodentate versus bidentate are often not very large. Additional Pb(II) surface complexes were initially included in the model, but their presence did not significantly improve the fit. Because our primary objective was to develop a model that would provide insights into the effects of PbO\(_2\) surface speciation on dissolution rates, the model was kept simple with only one monodentate inner sphere Pb(II) complex.
The SCM was able to describe both the adsorption edge (Figure 4.2) and adsorption isotherms (Figure 4.3) well. For the adsorption edge the model predicted the transition in Pb(II) adsorption from minimal at pH 5 to essentially 100% at pH 7. Over this pH range the free Pb$^{2+}$ ion was the dominant aqueous Pb(II) species. For the adsorption isotherms the model successfully predicted the trend of increasing adsorption capacity with increasing pH. The model predicted the shapes of the isotherm very well at pH 6.7 and 8.5, while it overestimated the amount of Pb(II) adsorbed for low dissolved lead concentrations at pH 7.6. It should be noted that the model simulations of the adsorption edge and three adsorption isotherms in Figures 4.3 and 4.4, respectively, were achieved using the same SCM and that overall optimization was achieved by fitting just two parameters (site density of PbO$_2$ and logK of Reaction 3 in Table 4.3).
4.1). This approach is different from that of fitting data to Langmuir or Freundlich isotherm equations in which two or more parameters are used to fit a dataset to provide a fit that is only applicable at a given pH.

### 4.4. Discussion

#### 4.4.1. PbO$_2$ Dissolution Mechanism

The reductive dissolution of PbO$_2$ with iodide (Wang et al., 2012b) and bromide (Lin and Valentine, 2010) can be described by the following steps: adsorption of the reductant to the PbO$_2$ surface to form an inner-sphere surface complex, electron transfer between the reductant and the PbO$_2$ surface species, and detachment of the Pb(II) to the solution. If water serves as the reductant, then the reductive dissolution can be simplified as a coupled electron transfer and Pb(II) detachment processes because water will always be at the surface and reductant adsorption can be neglected. The electron transfer process still involves inner-sphere coordination of the water molecule and the reactive Pb(IV) surface site.

The first steps in the reductive dissolution of PbO$_2$ by water involve reduction of surface Pb(IV) species. Electron transfer can occur between all surface Pb(IV) species and water, and the three surface Pb(IV) species (written here as $>\text{Pb(IV)}\text{OPb(IV)}\text{OH}_2^+$, $>\text{Pb(IV)}\text{OPb(IV)}\text{OH}$, and $>\text{Pb(IV)}\text{OPb(IV)}\text{O}^-$ to indicate the underlying Pb(IV) after reduction of the Pb(IV) at the surface) probably have different reduction rates. After the first one-electron transfer, Pb(III) intermediate species form. The Pb(III) intermediate species are unstable and the second one-electron transfer step is much faster than the first one-electron transfer step. The changes in the surface species that result from the reduction reactions are shown as Reactions 4.8-4.10.
Following production of Pb(II) from PbO$_2$ reduction, the Pb(II) species can detach from the PbO$_2$ surface to solution:

$$\text{> Pb(IV)OPb(II)}^+ + \text{H}^+ \leftarrow k_d k_a \rightarrow \text{Pb}^{2+} + \text{> Pb(IV)OH} + \text{H}_2\text{O}$$

(4.11)

After a Pb(II) species detaches from the PbO$_2$ surface, a new Pb(IV) surface site is exposed, and the three surface Pb(IV) species equilibrate with each other instantaneously (Reactions 4.1 and 4.2). The detachment step is reversible so that, as illustrated by the adsorption results, at steady state some Pb(II) can remain adsorbed to the PbO$_2$ surface at equilibrium.

From Reaction 4.11, the net release rate of dissolved lead (i.e. dissolution rate of PbO$_2$) can be expressed as

$$r = k_d[\text{> Pb(IV)OPb(II)}^+][\text{H}^+] - k_a[\text{> Pb(IV)OH}][\text{Pb}^{2+}]$$

(4.12)

Where [] denotes the concentration of surface species, $k_d$ is the rate constant of the detachment step, and $k_a$ is the rate constant for Pb(II) adsorption.

Based on Reactions 4.8-4.11, the net formation rate of >Pb(IV)OPb(II)$^+$ can be expressed as

$$\frac{d[\text{> Pb(IV)OPb(II)}^+]}{dt} = k_1[\text{> Pb(IV)OH}_2^+] + k_2[\text{> Pb(IV)OH}] + k_3[\text{> Pb(IV)O}^-] + k_a[\text{> Pb(IV)OH}][\text{Pb}^{2+}] - k_d[\text{> Pb(IV)OPb(II)}^+][\text{H}^+]$$

(4.13)

When the system reaches steady state, the net formation rate of >Pb(IV)OPb(II)$^+$ (i.e. Equation 13) is zero. By combining Equations 4.12 and 4.13, the dissolution rate of PbO$_2$ at steady state can be simplified as:

$$r = k_1[\text{> Pb(IV)OH}_2^+] + k_2[\text{> Pb(IV)OH}] + k_3[\text{> Pb(IV)O}^-]$$

(4.14)
where $k_1$, $k_2$, and $k_3$ are rate constants of the electron transfer steps in Reactions 4.8-4.10. Equation 4.14 indicates that at steady state, the dissolution rate of PbO$_2$ is determined by the electron transfer rates between all three surface Pb(IV) species and water. The formation of the Pb(II) surface species and the subsequent detachment of Pb(II) to solution is still the final but not rate-limiting step in the overall process.

Since less than 5% of the PbO$_2$ was consumed during the experiments, it is reasonable to assume a constant total surface area of PbO$_2$. The total concentration of surface sites is therefore constant and is denoted as $S_t$ (mol·L$^{-1}$). The concentrations of the intermediate Pb(III) surface species are small because of their transient nature so they can be neglected. Consequently, $S_t$ can be expressed as the sum of the Pb(IV) and Pb(II) surface species:

$$S_t = [>\text{Pb(IV)OH}_2^+] + [>\text{Pb(IV)OH}] + [>\text{Pb(IV)O}^-] + [>\text{Pb(IV)OPb(II)}^+]$$  \hspace{1cm} (4.15)

The steady-state dissolution rate of PbO$_2$ can be acquired by solving Equations 4.14 and 4.15. Electron transfer reactions can only occur for the surface Pb(IV) species and not for the surface Pb(II) species, and therefore at steady state the dissolution rate of PbO$_2$ is only determined by the concentrations of the three surface Pb(IV) species (i.e. $>\text{Pb(IV)OH}_2^+$, $>\text{Pb(IV)OH}$, $>\text{Pb(IV)O}^-$), as shown in Equation 4.14. The Pb(II) surface complex serves as an intermediate species in the reductive dissolution of PbO$_2$ and it can affect the dissolution rate by changing the distribution of the surface Pb(IV) species.

The key factor determining the dissolution rate of PbO$_2$ in water is therefore the concentrations of the surface Pb(IV) species. Assuming that adsorption of Pb(II) to PbO$_2$ reaches equilibrium rapidly, then the surface of PbO$_2$ would be expected to be equilibrated with aqueous Pb(II) at steady state. The concentrations and distribution of the PbO$_2$ surface species may be determined by adsorption models. Given the measured pH and steady-state Pb(II) concentrations
from the PbO₂ dissolution experiments, the concentrations of the Pb(II) and Pb(IV) species on the surface of PbO₂ were determined for each experiment using the SCM developed in this study. The calculated concentrations of different PbO₂ surface species using this approach are listed in Table 4-S1 of the Supporting Information. Employing a nonlinear regression of the dissolution rates and calculated concentrations of surface Pb(IV) species to Equation 14, optimal values of $k_1$, $k_2$, and $k_3$ were $22.16 \cdot 10^{-4}$ min⁻¹, $0.13 \cdot 10^{-4}$ min⁻¹, and $0.17 \cdot 10^{-4}$ min⁻¹, respectively. The 95% confidence intervals were $(11.10 – 33.22) \cdot 10^{-4}$ min⁻¹, $(0 – 1.07) \cdot 10^{-4}$ min⁻¹, and $(0 – 1.60) \cdot 10^{-4}$ min⁻¹ for $k_1$, $k_2$, and $k_3$, respectively. While $k_1$ was significantly higher than $k_2$ and $k_3$, the difference in the values of $k_2$ and $k_3$ were not statistically significant.

4.4.2 Model Parameters

The rate constant for $>\text{Pb(IV)OH}_2^+$ (i.e. $k_1$) reduction was much higher than those for $>\text{Pb(IV)OH}$ (i.e. $k_2$) and $>\text{Pb(IV)O}^-$ (i.e. $k_3$). This suggests that $>\text{Pb(IV)OH}_2^+$ plays a controlling role in the overall dissolution of PbO₂. The dissolution rates are strongly correlated with the calculated $>\text{Pb(IV)OH}_2^+$ concentrations (Figure 4.4); no clear correlations were observed between the dissolution rates and either the $>\text{Pb(IV)OH}$ or $>\text{Pb(IV)O}^-$ concentrations (Figure 4-S8 of the Supporting Information). The protonated sites of minerals have previously been suggested to play a controlling role in affecting the non-reductive dissolution of metal oxides at acidic conditions (Stumm and Wollast, 1990) and metal carbonate minerals at neutral to slight basic conditions (Pokrovsky and Schott, 2002).

While the dissolution rate of PbO₂ was more sensitive to the concentration of $>\text{Pb(IV)OH}_2^+$, it may be controlled by $>\text{Pb(IV)OH}$ and $>\text{Pb(IV)O}^-$ at neutral to basic conditions where $>\text{Pb(IV)OH}_2^+$ is less abundant (Figure 4.5). To further explore the role of $>\text{Pb(IV)OH}_2^+$ in
controlling PbO$_2$ dissolution at neutral to acidic conditions, $k_2$ and $k_3$ in Equation 4.14 were set to zero so that the dissolution rate of PbO$_2$ was solely dependent on the concentration of $>\text{Pb(IV)OH}_2^+$. The optimal $k_1$ was determined to be $23.8 \cdot 10^{-4}$ min$^{-1}$ by nonlinear regression fitting. Using this simplified approach, the dissolution rates at pH 7.6 and 8.5 were underestimated (Figure 4-S9 of the Supporting Information); therefore, predicting the dissolution rate of PbO$_2$ requires the inclusion of $>\text{Pb(IV)OH}$ and $>\text{Pb(IV)O}^-$ at neutral and slightly basic conditions.

The adsorption of Pb(II) affected the dissolution rate of PbO$_2$. Pb(II) adsorption decreased the total concentration of the surface Pb(IV) sites and altered the surface charge and surface...
potential of the PbO₂, which then changed the distribution of the Pb(IV) surface species. As illustrated in Figure 4.6, the concentrations of >Pb(IV)OH and >Pb(IV)OH₂⁺ predicted by the surface complexation model decreased due to Pb(II) adsorption above pH 5.5, while the concentration of >Pb(IV)O⁻ increased in the presence of Pb(II) adsorption. Since the dissolution rate of PbO₂ is directly correlated with the concentrations of surface Pb(IV) species, in describing reductive dissolution, the adsorption of Pb(II) to PbO₂ must be considered. The adsorption of reaction products to the metal oxide surface may also need to be considered in interpreting the reductive dissolution of other metal oxides, including Fe(III) oxides and Mn(IV) oxides.

**Figure 4.5.** The relative contribution of the three PbO₂ surface species to the overall PbO₂ dissolution rate in the absence of free chlorine.
Figure 4.6. Calculated surface site distribution of PbO$_2$ (0.1 g/L) using the surface complexation model (a) without considering the adsorption of Pb(II) and (b) assuming that adsorption reaches equilibrium with a total Pb(II) concentration of 0.96 µM (200 µg/L). The shift in the concentration of >Pb(IV)OH$_2^+$ due to the adsorption of Pb(II) significantly affected the dissolution rate of PbO$_2$ above pH 5.5.
4.4.3 Role of Free Chlorine

The presence of $1.4 \cdot 10^{-5}$ M free chlorine inhibited the dissolution of PbO$_2$ from pH 3.5 to 8.5. Free chlorine may provide a high ORP that makes the reductive dissolution of PbO$_2$ thermodynamically unfavorable. However, the predicted equilibrium solubility for the non-reductive dissolution of PbO$_2$ was orders of magnitude lower than the dissolved lead concentrations in the present study. Therefore it is more likely that free chlorine affected the kinetics of a rate-limiting process in the overall PbO$_2$ dissolution process. Free chlorine may re-oxidize the dissolved Pb(II) species released from PbO$_2$, as shown in Reactions 4.16 and 4.17:

\[
\text{HOCl} + \text{Pb}^{2+} + \text{H}_2\text{O} = \text{PbO}_2 + \text{Cl}^- + 3\text{H}^+ \tag{4.16}
\]
\[
\text{OCl}^- + \text{Pb}^{2+} + \text{H}_2\text{O} = \text{PbO}_2 + \text{Cl}^- + 2\text{H}^+ \tag{4.17}
\]

The oxidation of some dissolved Pb(II) back to PbO$_2$ would decrease the net rate of lead release from PbO$_2$. The new PbO$_2$ was assumed to form on the surface of the original PbO$_2$ and have the same surface properties. Since the amount of lead that would be reoxidized was negligible compared to that of the original PbO$_2$, the reoxidation of Pb(II) would not affect the concentration of the surface sites of PbO$_2$, which was considered as a constant ($S_t$).

The kinetics of Fe(II) oxidation by free chlorine is first order with respect to dissolved Fe(II) species and free chlorine (Crabtree and Schaefer, 1966). Assuming that the oxidation of Pb(II) by free chlorine is also first order and that Reactions 4.16 and 4.17 are irreversible, then the consumption rates of dissolved Pb(II) can be expressed as:

\[
r_{\text{con}} = k_4[\text{Pb(II)}][\text{HOCl}] + k_5[\text{Pb(II)}][\text{OCl}^-] \tag{4.18}
\]

where $k_4$ and $k_5$ are rate constants and [Pb(II)], [HOCl], and [OCl$^-$] denote concentrations. Combining Equations 4.14 and 4.18, the net dissolution rate of PbO$_2$ in the presence of free chlorine can be expressed as:
\[
\begin{align*}
\text{r} &= k_1[\text{Pb(IV)OH}^+] + k_2[\text{Pb(IV)OH}] + k_3[\text{Pb(IV)O}^-] - k_4[\text{Pb(II)}][\text{HOCl}] - k_5[\text{Pb(II)}][\text{OCl}^-] \\
\end{align*}
\]

(4.19)

\(k_1\), \(k_2\), and \(k_3\) were determined from the experiments in the absence of free chlorine as discussed previously. Employing the nonlinear regression of the experimental data in the presence of free chlorine to Equation 19, an optimal value of \(k_4\) was \(1.5 \cdot 10^{-10} \text{ L}^2\cdot \text{m}^{-2}\cdot \text{mol}^{-1}\cdot \text{min}^{-1}\) and \(k_5\) was \(3.3 \cdot 10^{-5} \text{ L}^2\cdot \text{m}^{-2}\cdot \text{mol}^{-1}\cdot \text{min}^{-1}\). The dissolution rates predicted using Equation 4.18 generally matched the experimental results well, especially in acidic conditions. In neutral and basic conditions, the model underestimated the dissolution rate, which may be due to the simplification of the model assumption that adsorption of free chlorine to \(\text{PbO}_2\) surface was neglected. Zhang and Lin reported that free chlorine adsorbed to the \(\text{PbO}_2\) surface rapidly and that equilibrium was reached within 6 hours (Zhang and Lin, 2012). Although they suggested that the adsorption did not affect the reactivity of free chlorine, it may alter the equilibrium distribution of the \(\text{PbO}_2\) surface species, thus affecting the dissolution rate of \(\text{PbO}_2\).

### 4.4.4 Implications for Drinking Water Distribution Systems

In distribution systems containing \(\text{PbO}_2\), the lead concentrations in tap water will probably be controlled by the dissolution rate rather than the equilibrium solubility of \(\text{PbO}_2\). Mechanisms for the reductive dissolution of \(\text{PbO}_2\) were proposed in this study and dissolution rates were found to be strongly related to the concentrations of \(\text{Pb(IV)}\) surface species. Lead release from \(\text{PbO}_2\) on pipes can be mitigated by optimizing the water chemistry to change the distribution of \(\text{Pb(IV)}\) surface species. Increasing the pH would decrease the concentration of \(>\text{Pb(IV)OH}_2^+\), which was the surface species that played a dominant role in \(\text{PbO}_2\) dissolution. The \(\text{Pb(II)}\) generated by reductive dissolution can adsorb to the \(\text{PbO}_2\) surface and decrease the
concentrations of Pb(IV) surface species, thus inhibiting PbO₂ dissolution. Cations in tap water including Cu²⁺, Zn²⁺, and Ca²⁺ may play a similar inhibitory role.

Free chlorine provided a high ORP and its presence effectively inhibited the dissolution of PbO₂. The presence of 1.4·10⁻⁵ M (1 mg Cl₂/L) free chlorine decreased the dissolution rate of PbO₂ by more than an order of magnitude at neutral to slightly basic conditions that were typical of drinking water distribution systems. In order to prevent the formation of disinfectant byproducts (DBPs), water utilities may consider switching the disinfectant from free chlorine to chloramines. However, the potential impact of removing the free chlorine on PbO₂ dissolution should be evaluated in order to make scientifically-based decisions.

4.5 Conclusions

The adsorption of Pb(II) onto PbO₂ was determined at pH 4.5 to 8.5 with various aqueous Pb(II) concentrations. The extent of Pb(II) adsorbed to PbO₂ increased with increasing pH until reaching a plateau above pH 7. The maximum adsorption density of Pb(II) increased with increasing pH from pH 6.7 to 8.5. A surface complexation model was developed to describe the adsorption behavior. A model with three Pb(IV) surface species (i.e. >Pb(IV)OH₂⁺, >Pb(IV)OH, and >Pb(IV)O⁻) and one Pb(II) surface complex (i.e. >Pb(IV)OPb(II)⁺) could successfully simulate the effects of both pH and Pb(II) loading on adsorption.

The dissolution rate of PbO₂ was investigated at pH 2.5 to 8.5 in the absence and presence of 1.4·10⁻⁵ M free chlorine. The steady-state dissolution rate increased with decreasing pH. To account for the pH-dependence of the PbO₂ dissolution rate, the SCM developed from the adsorption experiments was employed. While all three Pb(IV) surface species contribute to the overall PbO₂ reductive dissolution, the dissolution rate was controlled almost entirely
by \( \text{Pb(IV)OH}_2^+ \) below pH 6.7. The adsorption of Pb(II) altered the distribution of the surface Pb(IV) species, thus affecting the dissolution rate. The presence of free chlorine significantly inhibited the dissolution of PbO\(_2\) at pH 3.5 to 8.5 due to the re-oxidation of the aqueous Pb(II) species.

Surface complexation modeling provided a useful tool for elucidating the mechanisms of the reductive dissolution of PbO\(_2\). The present work also suggested that the adsorption of the reaction products to the surface may affect the reductive and possibly oxidative dissolution rates of metal oxides.

**Acknowledgements**

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# Chapter 4 Supporting Information

Contents: Two Tables (4-S1 – 4-S2)

Ten figures (4-S1 – 4-S10)

**Table 4-S1.** Calculated steady-state surface site concentrations of PbO$_2$ (1 g/L) in the flow-through experiments in the absence of free chlorine with the consideration of potential Pb(II) adsorption to PbO$_2$.

<table>
<thead>
<tr>
<th>pH</th>
<th>Steady state effluent lead (nM)</th>
<th>$&gt;\text{Pb(IV)OH}_2^+$ (µM)</th>
<th>$&gt;\text{Pb(IV)OH}$ (µM)</th>
<th>$&gt;\text{Pb(IV)O}^-$ (µM)</th>
<th>$&gt;\text{Pb(IV)OPb(II)}^+$ (µM)</th>
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</thead>
<tbody>
<tr>
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<td>41.60</td>
<td>1.39</td>
<td>0.00</td>
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**Table 4-S2.** Calculated steady-state surface site concentrations of PbO$_2$ (1 g/L) in the flow-through experiments in the absence of free chlorine without considering Pb(II) adsorption to PbO$_2$.

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<th>pH</th>
<th>Steady state effluent lead (nM)</th>
<th>$&gt;\text{Pb(IV)OH}_2^+$ (µM)</th>
<th>$&gt;\text{Pb(IV)OH}$ (µM)</th>
<th>$&gt;\text{Pb(IV)O}^-$ (µM)</th>
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<td>0.94</td>
<td>40.20</td>
<td>6.88</td>
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Figure 4-S1. X-ray diffraction pattern of the commercial PbO₂ used in the present study. The reference powder diffraction file pattern of plattnerite (01-071-4820 from the International Centre for Diffraction Data database) is included.
Figure 4-S2. Electron micrograph showing the morphology of the plattnerite used in the present study.

Figure 4-S3. Zeta-potential of the PbO₂ used in the present study as a function of pH.
**Figure 4-S4.** Acid-base titration of 50 g/L PbO$_2$ in the presence of 0.01 M NaNO$_3$. The solid line represents the predicted pH based on equilibrium calculations that include surface protonation-deprotonation reactions.
Figure 4-S5. Effluent lead concentrations (■ and ▲) from completely mixed flow reactors (CMFRs) as a function of the number of hydraulic residence times ($t_{res} = 30$ min) in the absence of free chlorine at pH from 2.5 to 8.5. Duplicate experiments (represented by rectangles and squares) were conducted for each condition.
Figure 4-S6. Effluent lead concentrations (■ and ▲) from CMFRs as a function of the number of hydraulic residence times ($t_{res} = 30$ min) in the presence of $1.4 \times 10^{-5}$ M free chlorine at pH from 2.5 to 8.5. Duplicate experiments (represented by rectangles and squares) were conducted for each condition.
Figure 4-S7. Oxidation-reduction potential of different redox couples as a function of pH. The diagram is constructed for a total lead(II) concentration of 15 µg/L (7.2·10^{-8} M), a total free chlorine concentration of 1.4·10^{-5} M, a chloride concentration of 1.4·10^{-5} M, an oxygen partial pressure of 0.21 atm, and a dissolved inorganic carbon concentration of 50 mg C/L (4.2·10^{-3} M).
Figure 4-S8. Relationship between the dissolution rate of PbO$_2$ (1g/L) and the calculated concentrations of the surface species (a) >Pb(IV)OH and (b) >Pb(IV)O$^\cdot$. 
Figure 4-S9. The dissolution rate of PbO$_2$ in the absence of free chlorine. Error bars represent one standard deviation. The solid line represents the dissolution rate predicted by the fully developed model assuming that the dissolution rate was affected by all three Pb(IV) surface species. The dashed line represents the dissolution rate predicted by the simplified model assuming that the dissolution rate was solely dependent on $>$Pb(IV)OH$_2^+$. 
Chapter 5. Impact of Galvanic Corrosion on Lead Release from Aged Lead Service Lines

Results of this chapter have been published in Water Research, 2012, 46 (16), 5049 - 5060.

Abstract

Partial lead service line replacement (PLSLR) may be performed when tap water lead concentrations exceed the action level and in association with water main replacement or other maintenance. Partially replacing lead pipes with copper tubing can create a galvanic couple if the lead and copper are connected by a metal coupling, which can potentially enhance lead release by galvanic corrosion. The effect of two types of couplings, brass and plastic, on lead release after a simulated PLSLR was investigated in a set of laboratory-scale experiments. Experiments were conducted in a recirculation flow mode with intermittent stagnation periods using aged lead pipes harvested from Providence, RI. Release of both dissolved and particulate lead was higher for the brass-coupled systems than for the plastic-coupled systems, and galvanic corrosion was the primary cause of significant particulate lead release from the brass-coupled systems. For brass-coupled systems, longer stagnation times resulted in dramatically more release of particulate lead. Sampling of different volumes following stagnation showed that lead release for the brass-coupled systems was locally much higher in the region closest to the coupling. The impact of galvanic corrosion persisted for the six weeks of the experiment.
Keywords:
Lead, Drinking water, Galvanic corrosion, Partial lead service line replacement

5.1 Introduction

Lead-containing materials that include lead pipes, solder, fittings, and fixtures are widely found in household water supply plumbing in North America and Europe (Britton and Richards, 1981; Triantafyllidou and Edwards, 2011b). To protect consumers from lead exposure, the US Environmental Protection Agency (EPA) requires water supply utilities to optimize water treatment to minimize lead release from these customer plumbing components. The Lead and Copper Rule (LCR) requires a program of monitoring for lead in water samples taken inside customer homes and set a “lead action level” of 15 μg/L for a 1-L first-draw sample of tap water (USEPA, 1991). Lead concentrations that exceed the action level can be found for systems with distribution system water chemistry compositions that are aggressive for lead release, and excessive lead release can also occur in response to changes in water chemistry that accompany treatment process changes. A dramatic example is the period of high lead concentrations observed in Washington D.C. drinking water from 2001 to 2004 following a switch of the disinfectant from free chlorine to chloramines (Edwards and Dudi, 2004; Edwards et al., 2009).

Lead service line replacement (LSLR) is a strategy to control lead concentrations in drinking water distribution systems. Utilities typically have ownership of the lead service line only up to the property line, and the remainder of the service line is privately owned. Due to the cost of replacement, most customers choose not to replace their portion of the service lines.
Therefore, the lead service line is only partially replaced and the new connection of a building to the water main has both lead pipe and copper tubing.

After partial lead service line replacement (PLSLR), transient periods of elevated lead release have been observed for some systems, which lasted from a few days to even several months (Muylwyk et al., 2011; Sandvig et al., 2009; Swertfeger et al., 2006; USEPA, 2011). The enhanced lead release after PLSLRs may be attributed to the mechanical disturbance of the corrosion scales (Boyd et al., 2004; Deshommes et al., 2010; Hulsmann, 1990) and also to galvanic corrosion (Edwards and Triantafyllidou, 2007). While the former might be expected to only have a short-term effect, galvanic corrosion might result in an elevated lead level over a longer time.

The basic principle of galvanic corrosion is that when dissimilar metals with different electrochemical potentials are electrically connected and immersed in an electrolyte, a galvanic couple is set up that creates a driving force for oxidation-reduction reactions. In the PLSLR process, if a metal coupling like a brass compression fitting is used, then the lead pipe and copper tubing can be a galvanic couple with the lead serving as the anode. Galvanic corrosion is also possible for connections in which direct lead-copper contact occurs either deliberately (e.g., in some older connection) or inadvertently inside of plastic or dielectric fittings and for lead and copper sections with external wires providing a connection. Half reactions occur at the anode (Pb) and cathode (Cu) (Equations 5.1 and 5.2):

$$\text{Pb}_{(s)} = \text{Pb}^{2+} + 2e^- \quad (5.1)$$

$$\text{O}_2_{(aq)} + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O} \quad (5.2)$$

The net reaction is shown in Equation 5.3.

$$2\text{Pb}_{(s)} + \text{O}_2_{(aq)} + 4\text{H}^+ = 2\text{Pb}^{2+} + 2\text{H}_2\text{O} \quad (5.3)$$
The water in the pipe serves as the electrolyte for the galvanic cell and provides a pathway for ion migration between copper and lead pipe surfaces.

Several lab-scale studies have been conducted to evaluate the effect of galvanic corrosion on lead release following PLSLRs, and results suggested that the extent and duration of galvanic corrosion may be affected by the flow regimes. While galvanic corrosion was observed as a transient effect under continuous-flow conditions (Boyd et al., 2012; Kirmeyer et al., 2006; Reiber and Dufresne, 2006) it may last longer and cause significant lead release during stagnation (Arnold, 2011a; Triantafyllidou and Edwards, 2011a). Boyd and co-workers determined lead release after connecting lead pipes directly to copper tubing in a laboratory pipe loop with continuous recirculating flow, and based on measurements of water from the recirculation line they concluded that the galvanic corrosion was short-lived under various water chemistry conditions (Boyd et al., 2012). The total lead that accumulated in the reservoirs used for recirculation was not measured in this study, but other research with the same experimental system found total lead concentrations in the reservoirs that were up to 4-5 times higher than in the recirculating water (Nguyen et al., 2010a). In contrast, Triantafyllidou and Edwards (2011a) observed that a significant amount of lead was released after electrically connecting lead pipes to copper tubing in stagnant water, and the galvanic effect persisted for months or longer. They emphasized the importance of flow regimes on galvanic corrosion and suggested that stagnation represented the worst case scenario for lead release, while continuous flow may represent an optimal scenario due to pipe surface passivation. In a recent study, Cartier et al. (2012) investigated the galvanic impact on lead release using once-through flow with intermittent stagnation periods. They found that the lead release in the flowing water after stagnation strongly depended on the flow rate: while lead release was not enhanced by galvanic corrosion at
a low flow rate (1.3 L/min), moderate (8 L/min) and higher (32 L/min) flow rates resulted in much greater lead release.

The different conclusions reached in previous studies and unresolved issues regarding the impact of galvanic corrosion following PLSLRs motivated further research to clarify the extent, mechanisms, and duration of galvanic effects on lead release. New or cleaned lead pipes were commonly used in previous studies, and few studies have evaluated lead release using aged lead pipes with intact pipe scales. Due to the presence of the scales and their potential passivating effect, aged lead pipes may behave differently than new or cleaned lead pipes. The method of connecting lead pipe and copper tubing may affect galvanic corrosion, and experiments were needed that used the actual couplings used for PLSLRs. The present study aimed to investigate the extent and duration of galvanic corrosion on lead release after simulated PLSLRs. To best represent the flow regimes in real service lines, bench-scale experiments were conducted in a recirculation flow mode with intermittent stagnation. Experiments connected aged lead pipes harvested from an actual distribution system to new copper tubing using two different couplings, and water with chemistry that matched that in the distribution system was used.

5.2 Materials and Methods

5.2.1 Materials

Eight aged lead pipes that had been harvested from the Providence, RI, distribution system after 80-110 years of use were received and used in laboratory experiments. At the time of pipe harvesting, moist sponges were inserted into the pipes before their ends were tightly sealed with
tape to prevent the dehydration of the pipe scales. The pipes had inner diameters of 0.625 inch and outer diameters of 1.188 inch and were cut to 24-inch sections for use in experiments.

Type K copper tubing (1-inch inner diameter and 1.125-inch outer diameter) was cut to 24-inch sections (McMaster-Carr). Polyvinyl chloride (PVC) pipe sections (McMaster-Carr) with 24-inch lengths were used in place of lead pipes in control experiments; control experiments with brass couplings used 0.75-inch inner diameter PVC pipe and those with plastic couplings used 1-inch inner diameter PVC pipe. Connections were made with brass compression fittings (A.Y. McDonald) and all-plastic polypropylene fittings (Harco/Philmac). Reagent grade CaCl₂, MgCl₂, MgSO₄, NaCl, NaHCO₃, NaOCl solution, NaOH, and HNO₃ were purchased for use in experiments (Fisher Scientific). Ultrapure water (resistivity > 18.2 MΩ-cm) was used to prepare solutions.

5.2.2 Pipe Experiments

The eight harvested lead pipes were first conditioned in a static mode for eight weeks, and then four pipes were selected for conditioning in a recirculation mode with intermittent stagnation periods for an additional five weeks. After conditioning was completed, two lead pipes were connected to copper tubing with the brass compression couplings and two were connected with the plastic couplings. Experiments were conducted for six weeks in a recirculation mode with intermittent stagnation. Lead release directly from the couplings was also evaluated in separate control experiments in which PVC pipes were connected to copper tubing. All experiments were conducted at ambient laboratory temperature (21 ± 1 °C).

5.2.2.1 Conditioning
Before connecting the lead pipes to copper tubing, they were reconditioned with water prepared to simulate the chemistry of the Providence distribution system (Table 5.1). The goal of conditioning was to achieve stable lead release from the pipes prior to making the connections to the copper tubing so that any effects of the connections could be clearly seen. The pipes were first conditioned in a static “dump-and-fill” mode for eight weeks, and then four pipes were selected for five weeks of conditioning in the same operation cycle that was then used in experiments with connections of the lead pipes to the copper tubing. The details of the conditioning procedure are provided in the Supplementary Material.

**Table 5.1. Water composition of synthetic Providence water**

<table>
<thead>
<tr>
<th>Water composition parameter</th>
<th>Target range</th>
<th>Actual value¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.5 to 9.9¹</td>
<td>9.6 to 9.8</td>
</tr>
<tr>
<td>Free residual chlorine, mg/L as Cl₂</td>
<td>0.16 to 0.50</td>
<td>0.42</td>
</tr>
<tr>
<td>Total alkalinity, mg/L as CaCO₃</td>
<td>9.3 to 16.3</td>
<td>12.0</td>
</tr>
<tr>
<td>TDS, mg/L</td>
<td>97 to 113</td>
<td>113</td>
</tr>
<tr>
<td>Total hardness, mg/L as CaCO₃</td>
<td>34.3 to 44</td>
<td>38.5</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>17.3 to 22.4</td>
<td>19.4</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>20.0 to 24.0</td>
<td>21.8</td>
</tr>
</tbody>
</table>

¹The actual value of the pH was determined from daily measurements, and the values for the other parameters were determined from the recipe used to prepare the synthetic Providence Water.

### 5.2.2.2 Connecting Lead Pipes to Copper Tubing

After the lead pipes were conditioned in the recirculation flow mode, they were connected to copper tubing using the two different coupling types. A handheld multimeter (Fluke) was used to measure the resistance of the plastic-coupled and brass-coupled lead-copper pipe assemblies. Resistance higher than 3 MΩ was measured between the lead pipes and copper tubing connected by the plastic coupling, while essentially no resistance (less than 4 Ω) was detected when they were connected by the brass coupling. These observations confirmed that
only the brass compression couplings allow the electrical connection of the copper to lead that is necessary for galvanic corrosion to occur. The internal volumes of the lead pipe and copper tubing sections were 120 mL and 310 mL, respectively.

Experiments were operated in a recirculation mode with intermittent stagnation periods for six weeks (Figure 5.1). Recirculating flow has been used to investigate the galvanic corrosion in previous studies (Arnold, 2011a; Boyd et al., 2012). A once-through flow mode was not adopted due to the large volumes of synthetic Providence water that would have been needed. A peristaltic pump (Cole-Parmer) provided periodically recirculating flow through the pipe assemblies from a 10-L polyethylene reservoir. A variable area flow meter (Cole-Parmer) was used to monitor the flow rate. Three-way valves were positioned at the upstream and downstream ends of the pipes for collection of samples.

![Diagram of experimental system](image)

**Figure 5.1.** Experimental system with lead pipes and copper tubing connected with plastic or brass couplings.

The system was operated on a daily cycle during weekdays (Figure 5-S2 of the Supplementary Material). On each Monday morning, freshly prepared water was fed into the
pipes from the reservoirs. The weekday cycle for Monday-Thursday began with a 6-h stagnation time that was followed by 15 minutes of flow, a 17.25-h stagnation period, and finally 30 minutes of flow. On Fridays, the 17.25-h stagnation period was replaced with a 65.25-h stagnation period (over the weekend), hereafter referred to as the 65-h stagnation period. The reservoirs were then replaced with cleaned ones with freshly made feed solutions to start the next week’s cycle. The flow velocity during recirculation was 1 ft/s (3.6 L/min). The free chlorine concentration in the reservoir was monitored and adjusted to the target value on every weekday.

Pre-stagnation samples of 50 mL were collected at a flow rate of 1 L/min on each Monday and Thursday before the 6-h stagnation period and on Friday before the 65-h stagnation period. Post-stagnation samples of approximately 500 mL were collected at a flow rate of 1 L/min following the Monday and Thursday 6-h stagnation periods and the weekend 65-h stagnation period (Figure 5-S2 of the Supplementary Material). In Week 2 the post-stagnation samples were collected in a slightly different way: the first 50 mL of the post-stagnation water was sampled and represented the lead release far from the coupling, since it comes only from the downstream third of the lead pipe; then an additional 400-mL sample was collected, which included lead release near the coupling. After replacing the old reservoir with a new one each Monday, the solution in the old reservoir was acidified to pH < 2 by addition of concentrated HNO₃ and allowed to sit at this low pH for at least 24 hours before collecting a 10-mL sample for total lead and copper analysis.

5.2.2.3 Control Experiments (No Lead Pipe)

To test for lead release from the couplings and potential unexpected sources, control experiments were performed using PVC pipes connected to copper tubing with the brass and
plastic couplings. Because these experiments did not include a lead pipe section, the only significant source of lead should be the brass couplings. Experiments were operated for four weeks using the same weekly cycle used for the experiments with connected lead pipes and copper tubing.

### 5.2.3 Characterization of the Corrosion Products

The as-received pipes were characterized with respect to the composition and structure of the corrosion products. A portion of the pipes were cut longitudinally and scales were scraped from the inner surface of the pipes using a small stainless steel spatula. The scales were analyzed by X-ray diffraction (XRD) to identify crystalline solid phases present in the pipe scales. The morphology and semi-quantitative elemental composition of the corrosion products were determined by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). The elemental composition was further quantified by digesting 0.03 g of the scale in a mixture of 10-mL concentrated HNO₃ and 2.5-mL concentrated HCl that was heated at 100°C for 4 hours (Environmental Express Hot Block). The digestate was then diluted to 50-mL with ultrapure water and centrifuged for 10 min at 15000 relative centrifugal force (RCF). A 10-mL aliquot of the supernatant was collected, filtered using a 0.22 µm PES syringe filter, and preserved for elemental analysis.

### 5.2.4 Analysis Methods

Total and dissolved concentrations of lead and copper were measured by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7500ce). The samples were acidified to 2% HNO₃ prior to analysis. XRD was performed on a Rigaku Geigerflex D-MAX/A diffractometer.
using Cu-Kα radiation. Electron microscopy was performed on a JEOL 7001LVF field emission scanning electron microscope. Free chlorine concentrations were determined by the standard DPD colorimetric method (4500-Cl Chlorine G) with a spectrophotometer (PerkinElmer Lambda XLS+ or ThermoSpectronic Genesys 8) (Clesceri et al., 1999). Solution pH was measured with a glass pH electrode and pH meter (Accumet).

5.3 Results and Discussion

5.3.1 Characterization of Corrosion Products

The pipe scales scraped from Pipes 1A and 2B prior to conditioning were white powders. XRD patterns (Figure 5.2) showed that the dominant crystalline phase in the scales of both pipes was the lead(II) hydroxycarbonate plumbonacrite (Pb$_{10}$(CO$_3$)$_6$(OH)$_{10}$O). Lead(II) oxides, lead(II) carbonates, and lead(IV) oxides are widely observed as corrosion products in distribution systems (Hozalski et al., 2005; Kim and Herrera, 2010; Schock, 1999; Schock et al., 2008). The formation of lead(II) carbonates depends on the pH and alkalinity. Water with a high alkalinity favors the lead(II) carbonate cerussite (PbCO$_3$) and the hydroxycarbonate hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$) (Kim and Herrera, 2010); while more hydroxide-rich solids would form in a water with high pH and low alkalinity. The Providence water has a high pH (~9.8) and a relatively low alkalinity (12 mg /L as CaCO$_3$) and therefore the formation of plumbonacrite is not surprising. Although free chlorine was used as the disinfectant, a strong enough oxidant to produce lead(IV) oxides (PbO$_2$) (Wang et al., 2010), no lead(IV) oxide was observed in the Providence pipes. The lack of PbO$_2$ formation may be related to the low free chlorine concentration (0.4 mg/L) and the high pH since OCl$^-$ is a less potent oxidant than HOCl.
Acid digestion suggested that the dominant element of the scale was indeed lead (~62%). Trace amounts of manganese (7 µg/g), iron (9 µg/g), and vanadium (0.7 µg/g) were also observed. The corrosion products may simply scavenge these elements from the water and allow them to accumulate in the pipe scales; vanadium, which is likely present as vanadate, can behave similarly to phosphate and have an affinity for associating with lead (Gerke et al., 2009). No calcium, magnesium, or other common cations were detected.

5.3.2 Conditioning
The total lead concentrations over the eight weeks of static conditioning were highest during the first week with an average concentration around 16000 µg/L, and they dropped in the second week and primarily stayed within the range of 200-2000 µg/L (Figure 5-S4 of the Supplementary Material). Dissolved lead concentrations were much less variable than the total lead concentrations, and mostly stayed in the range of 60-200 µg/L (Figure 5-S5 of the Supplementary Material). Four pipes (1A, 9A, 1B, 2B) from the original eight were selected for further conditioning based on their similar average dissolved lead concentrations and low variations in dissolved lead.

The total and dissolved lead concentrations were similar and stable when the four pipes were conditioned in the recirculation flow mode. The dissolved lead concentrations in the post-stagnation water after the 6-h stagnation periods were stable in the range of 50-100 µg/L (Figure 5.3). The average post-stagnation dissolved lead concentrations for the four pipes were similar (1A = 84.1 ± 13.1 µg/L, 9A = 74.9 ± 8.3 µg/L, 1B = 79.7 ± 9.2 µg/L, 2B = 67.4 ± 10.2 µg/L). Based on the published thermodynamic data, the dissolved lead concentration in equilibrium with plumbonacrite is estimated as 50 - 60 µg/L at pH 9.4 to 9.8 (Benjamin, 2002; Taylor and Lopata, 1984). These results suggest that the stagnant water in the pipes was at or close to equilibrium with the plumbonacrite in the pipe scale. The total lead concentration profile was quite similar to the dissolved lead concentration profile (Figure 5-S6 of the Supplementary Material), which suggested that only limited particulate lead (i.e. the difference between total and dissolved lead) was released during the 6-h stagnation periods. Relative to the earlier static conditioning phase, the conditioning phase with recirculating flow yielded much more stable total lead concentrations, which might be due to the fact that greater volumes of freshly prepared water contacted the pipe scales during recirculating flow and helped to stabilize the pipe scales.
Figure 5.3. Dissolved lead concentration profile of the aged lead pipes during conditioning in the recirculating flow mode from Weeks 2 to 5. Panel a shows the post-stagnation lead concentration after 6 hours of stagnation; panel b shows the average post-stagnation lead concentration after 6-h stagnation periods. Error bars represent one standard deviation. The pipe labels are those that were assigned at the time the pipes were harvested.
5.3.3 Lead Release from Control Experiments without Lead Pipes

Lead release from the couplings was evaluated by connecting PVC pipes to copper tubing with the two types of couplings. For 6-h stagnation periods little lead (<7 µg/L) was released from the plastic coupled PVC-copper pipes, while greater amounts of dissolved lead were released from the brass-coupled systems (Figure 5.4). In the brass-coupled systems, the lead release is probably due to direct leaching from the brass coupling, since leaded brass is considered as a source of lead to drinking water (Edwards and Dudi, 2004; Zhang and Edwards, 2011). Lead concentrations in the post-stagnation water decreased over time, dropping from ~40 µg/L in Week 1 to ~20 µg/L in Week 4, which was consistent with a previous observation that lead leaching from brass decreased with time (Zhang and Edwards, 2011). High lead release in Week 1 in the present study might be due to the disturbance of the system after making the connections and the initial flushing, although this disturbance was probably mild compared to that in actual PSLRs. In the later comparisons of the copper-PVC control experiments with the copper-lead experiments, only the data from Weeks 2 to 4 of the control experiments will be emphasized.

Very limited particulate lead was released during stagnation in the control experiments. The total lead concentration profiles after 6-h stagnation were similar to those of the dissolved lead (Figure 5-S7 of the Supplementary Material). Increasing the stagnation time from 6 hours to 65 hours only slightly increased the dissolved and total lead concentrations, which was in accordance with a previous study that found that most lead was released from brass plumbing during the first 4 hours of stagnation (Tam and Elefsiniotis, 2009). Lead leaching from brass may be affected by water chemistry through the influence of the pH, alkalinity, type and
Figure 5.4. Post-stagnation dissolved lead concentrations of the control experiment from Weeks 1 to 4 after making connections of copper tubing to PVC pipes after (a) 6-h stagnation periods (average and standard deviation shown) and (b) the 65-h stagnation period. Error bars represent one standard deviation.
concentration of disinfectant, and the presence of natural organic matter (Edwards and Dudi, 2004; Korshin et al., 2000; Tam and Elefsiniotis, 2009). Tam and Elefsiniotis (2009) observed that total lead release increased with increasing alkalinity and decreasing pH; at pH 9 and 20 mg/L as CaCO$_3$ alkalinity, 50 µg/L total lead was released after 72 hours stagnation. In the present study around 20 µg/L total lead was released after 65 hours stagnation. The lower lead release may be attributed to the higher pH (9.8) and lower alkalinity (12 mg/L as CaCO$_3$) in the present study.

5.3.4 Lead and Copper Release Following Connection to Copper Tubing

5.3.4.1 Release of Dissolved Lead after Stagnation

After connecting lead pipes to copper tubing, dissolved lead concentrations in the post-stagnation water were much higher in the brass-coupled systems than in the plastic-coupled systems (Figure 5.5). For 6-h stagnation, the post-stagnation lead concentrations were quite stable with the average value of 45 µg/L over Weeks 2 to 6 for the plastic-coupled pipe assemblies. In contrast, when using brass couplings, lead concentrations increased to 90 – 135 µg/L after 6 hours of stagnation. Although the post-stagnation lead concentrations from brass-1 were higher than from brass-2, the lead release from both brass-coupled systems was still significantly higher than that from pipes with plastic couplings. The lead release from the brass-coupled systems was also much higher than that during conditioning. On average 45 – 67.5 µg dissolved lead was released from the brass-coupled pipe assemblies, while only 8.4 – 10.2 µg dissolved lead was released after 6-h stagnation from the lead pipes during conditioning. Increasing stagnation time to 65 hours slightly increased dissolved lead concentrations from both
the plastic-coupled and brass-coupled systems, which suggests that the water may be approaching but not quite reaching equilibrium with the corrosion products.

![Figure 5.5](image)

**Figure 5.5.** Average post-stagnation dissolved lead concentration with different stagnation time from Weeks 2 to 6 of the experiment with lead pipes connected to copper tubing (plastic-1 and -2 and brass-1 and -2) and Weeks 2 to 4 of the control experiment with copper tubing connected to PVC pipes (plastic-c and brass-c). Brass-1 and -2 represent Pipe 1B and 2B, and plastic-1 and -2 represent Pipe 1A and 9A hereafter. Error bars represent one standard deviation.

The enhancement of dissolved lead release may be at least partially due to galvanic corrosion. Both galvanic corrosion and direct leaching from the brass couplings can increase the lead concentrations in the brass-coupled systems. The control experiments with only the brass fitting had release of 20-30 µg/L of dissolved lead. This value is lower than the difference of 45-90 µg/L between the dissolved lead concentrations for the brass-coupled and plastic-coupled systems. Consequently, galvanic corrosion may slightly enhance dissolved lead release.
5.3.4.2 Release of Total Lead after Stagnation

Galvanic corrosion significantly enhanced total lead release. The post-stagnation total lead concentrations from the pipes with brass couplings were much higher than those from pipes with plastic couplings (Figure 5.6). For pipes with brass couplings the total lead concentrations after the 6-h stagnation period were 200-300 µg/L, while only about 50 µg/L total lead was released from the plastic-coupled pipes. Increasing the stagnation time to 65 hours increased the total lead release by a factor of seven for the brass-coupled systems, but stagnation time had a much smaller effect for the plastic-coupled systems. Considering that less than 30 µg/L total lead was released from the brass itself, the greater amount of total lead released from the brass-coupled systems is attributed to the galvanic reaction between the lead pipes and copper tubing. However, since lead and brass can also be a galvanic couple, the enhancement of lead release may partially be attributed to the galvanic reaction between the lead pipes and brass coupling as well. On average, compared to those from the plastic-coupled systems, galvanic reactions resulted in 4-6 times more total lead release from the brass-coupled systems after 6-h stagnation, and 15-30 times more after 65-h stagnation.

Particulate lead has been reported to contribute a large fraction of the lead in tap water (Britton and Richards, 1981; McNeill and Edwards, 2004). Consistent with previous studies, present results suggest that galvanic corrosion’s largest impacts are on particulate lead release. Triantafyllidou and Edwards (2011a) reported that in stagnant water 70 – 99 % of total lead released from the galvanically connected pipe assemblies was particulate lead. Cartier and colleagues (2012) investigated the impact of galvanic corrosion on lead release using once-through flow with intermittent stagnation periods. They observed that 75% of the total lead
Figure 5.6. Average post-stagnation total lead concentration with different stagnation time from Weeks 2 to 6 of the experiment with lead pipes connected to copper tubing (plastic-1 and -2 and brass-1 and -2) and Weeks 2 to 4 of the control experiment with copper tubing connected to PVC pipes (plastic-c and brass-c). Panel a shows the y-axis with the full range of concentrations measured, while panel b shows the y-axis range to 500 µg/L. Error bars represent one standard deviation.
released was particulate lead with flow rates of 8 and 32 L/min. In the present study, while little particulate lead (less than 10%) was observed in the plastic-coupled systems, it was more abundant in the brass-coupled systems for all six weeks of the experiment, especially after longer stagnation times (Figure 5.7). For the brass-coupled systems 55 – 93 % of the total lead was particulate.

The high level of particulate lead in the pipes with brass couplings may be due to two reasons. The first is that the accelerated release of lead due to the galvanic connection may have created local dissolved lead concentrations high enough to exceed the saturation of some lead(II) minerals, thus causing the precipitation of secondary solids and increasing particulate lead. The dissolved lead concentrations after 6 hours of stagnation were 90 – 135 µg/L, conditions that are oversaturated with respect to hydrocerussite and plumbonacrite, so the formation of these secondary lead(II) precipitates was possible. A second reason may be that galvanically driven corrosion of the lead pipe underlying the scales may have caused portions of the scales to break off and be released to the water as particulate, thus enhancing particulate lead release. This second mechanism would be expected to result in large variability of total lead concentrations with time as it would be impacted by episodic detachment of particulate lead. Cartier and colleagues (2012) collected samples at different flow rates and concluded that portions of the particulate lead scales were more likely to be released at moderate and high flow rates (8 and 32 L/min) but not low flow (1.3 L/min). In the present study the sampling flow rate was 1 L/min and the total lead concentrations were actually quite stable. Consequently, the accelerated release of dissolved lead and subsequent precipitation of lead-containing solids may be the primary cause of the high particulate lead concentrations for the galvanically coupled system.
Figure 5.7. Distribution of lead between dissolved and particulate forms for effluents from Weeks 1 to 6 of experiments with lead pipes connected to copper tubing for plastic couplings (panel a for plastic-1 and panel b for plastic-2) and brass couplings (panel c for brass-1 and panel d for brass-2). The labels on the x-axis indicate the day of the week and the week of the experiment. Weekend (Wknd) samples had 65 hours of stagnation and all other samples were after 6 hours of stagnation.
5.3.4.3 Total Lead Mobilized during Recirculation Cycle

In recirculating pipe loop systems, particulate lead may accumulate in the reservoirs by adsorption to the walls or deposition to the bottom of the reservoirs during the recirculation periods and following stagnation periods for which samples were not collected and cannot be mobilized. The water in the reservoir after 1 week of recirculation was acidified and its lead concentration was compared with that of the pre-stagnation water for the last stagnation period of the week. This last pre-stagnation water includes the total lead that was sufficiently mobile to be recirculated, and a comparison of its concentration with that in the acidified reservoir yields information on the total lead that had accumulated in the reservoir. For the pipes using plastic couplings, the total lead concentrations in the acidified reservoir were a little bit higher than those prior to acidification, indicating that some particulate lead had accumulated (Figure 5.8). However, for the pipes using brass couplings, the total lead concentrations in the acidified reservoir were 2.5 times higher than those prior to acidification, which indicated that significant amounts of particulate lead had been released during the recirculation periods and had accumulated in the reservoir. Results were consistent with previous studies observing the accumulation of lead in the reservoir (Arnold, 2011a; Nguyen et al., 2010a). Arnold (2011a) determined the lead release from lead pipes coupled with copper tubing by external wires in a recirculating flow system and found that the total lead concentrations in the acidified reservoir were generally 2 to 7 times higher than the those in the water that was recirculated from the reservoir. Investigating lead release in a similar pipe loop set-up, another study showed that the lead concentrations in the acidified reservoir were 4 – 5 times those in the unacidified reservoir (Nguyen et al., 2010a).
The total lead release over one week of recirculation and stagnation cycles may be estimated as the sum of the lead in all samples that were collected and the lead in the acidified reservoir. Using this approach, the total weekly lead release from the lead pipes with plastic couplings was sufficient to yield 50 to 70 µg/L for the 10 L of water used in the recirculation loop (Figure 5-S8 of the Supplementary Material). Based on the lead pipe-free control experiments, the brass fittings and other unexpected lead sources could yield an additional 30 µg/L (Figure 5-S9 of the Supplementary Material). Therefore, up to 100 µg/L lead would be released from the lead pipes with brass fittings if there was no effect of galvanic corrosion.

Figure 5.8. Average total lead concentration in the reservoir before and after acidification from Week 2 to Week 6 of the experiments with lead pipes connected to copper tubing (plastic-1 and -2 and brass-1 and -2), and from Weeks 2 to 4 of the control experiment with coupled copper tubing and PVC pipes (plastic-c and brass-c). The acidified reservoir concentrations provide information on the particulate lead accumulation in the reservoir over one week. “Pre-acidification” indicates the samples collected from the reservoir after one-week operation before acidification, and “post-acidification” denotes the samples collected in the acidified reservoir after one-week operation. Error bars represent one standard deviation.
However, the experimental pipe assemblies with lead pipe and brass couplings yielded total lead concentrations of 300 to 1000 µg/L per week. The 3 – 10 times increase in total lead by galvanic corrosion is in the range of previous observations (Cartier, 2012; Cartier et al., 2012; Triantafyllidou and Edwards, 2011a). These results confirm that galvanic corrosion can significantly increase the release of lead, especially particulate lead, for at least the six weeks of study. Boyd and co-workers (2012) investigated lead release under continuously recirculating flow conditions and observed that the galvanic effect was short-lived and typically lasted no more than 2 weeks. In contrast, Triantafyllidou and Edwards (2011a) found that galvanic corrosion increased lead release for at least 25 weeks and that lead concentrations were not decreasing with time in a static lead-copper pipe rig system. The difference between these studies may be attributed to the very different experimental approaches, especially with respect to continuously recirculating flow versus exclusively stagnant “dump-and-fill” as well as to the study of Boyd et al. not accounting for the potential accumulation of lead in the reservoirs used for recirculation.

The enhanced lead release from galvanic corrosion may be related to the specific water chemistry of Providence. Galvanic corrosion was found to have a higher impact in systems with low alkalinity than those with high alkalinity (Arnold, 2011a; Nguyen et al., 2011a). High alkalinity can buffer the pH drop caused by the release of Pb$^{2+}$, which is a Lewis acid, in the microlayer of water closest to the lead pipe’s surface (Nguyen et al., 2011a). In addition to alkalinity, increasing chloride-to-sulfate mass ratio (CSMR) has been found to increase lead release from galvanic reactions and the threshold value above which lead release would be accelerated was around 0.6 – 0.77 (Edwards et al., 1999; Nguyen et al., 2011a). A previous study found that increasing the CSMR from 0.2 to 16 increased lead release by 3 to 12 times from
galvanically connected lead-copper rigs (Triantafyllidou and Edwards, 2011a). The low alkalinity (12 mg/L as CaCO₃) of Providence water and the CSMR of 0.89 make this water one in which galvanic corrosion may have considerable effects on lead release. Different results would be expected for different water chemistries and pipe scale compositions.

**5.3.4.4 Localization of Lead Release**

Localized lead release caused by galvanic corrosion was evaluated during Week 2 of the experiment by a sampling approach that collected water from different zones of the pipe assemblies. The flow during sampling was laminar, and although ideal plug flow in a pipe is better achieved at turbulent than laminar conditions, the velocity was still sufficiently high that advection and not longitudinal dispersion was the dominant transport process (Van Der Leer et al., 2002) so that sequential volumes of water collected will correspond to different zones within the pipe assembly. The dissolved lead concentrations were very similar for the brass- and plastic-coupled systems for the first 50-mL samples; while the 400-mL samples had much higher dissolved lead concentrations for the brass-coupled systems than for the plastic-coupled pipe assemblies, suggesting that more lead was released near the brass coupling (Figure 5.9). The total lead concentration profile had a similar trend to that of the dissolved lead, although a higher lead release from brass-1 than brass-2 was observed.

The greater amount of lead released near the brass coupling may be attributed to galvanic corrosion. Less than 30 μg/L dissolved and total lead was released directly from brass fittings after 6-h stagnation periods in the control experiments, which was much lower than the difference between the lead concentrations from the brass-coupled and the plastic-coupled systems, especially for total lead. The actual lead concentration in the portion of the pipe closest
Figure 5.9. Average (a) dissolved and (b) total lead concentration after 6 hours of stagnation in different sampling regimes from Week 2 of the experiment with coupled lead pipes and copper tubing. The 50-mL sample represents the lead release far from the coupling and the 400-mL sample includes lead release near the coupling as well as water from the copper tubing section. Error bars represent one standard deviation.
to the brass coupling could be much higher than those in the overall 400-mL sample since the 400-mL sample included water that had been stagnant in the copper tubing, which would have diluted the lead concentration in the water nearest to the couplings.

Previous studies also found that galvanic corrosion was localized in the region of lead pipe nearest to the copper (Triantafyllidou and Edwards, 2011a) and decreased with increasing distance between the lead pipes and copper tubing (Clark et al., 2011). By measuring the open circuit potential of the lead pipes and copper tubing which were directly connected, Boyd and colleagues also found that the galvanic effect was highly localized (Boyd et al., 2012). An investigation of galvanically connected joints collected from actual distribution systems and premise plumbing observed that the extent of galvanic corrosion depended on water chemistry, and for the joints having galvanic corrosion, the lead pipe was significantly corroded within the first few cm next to the joint with brass (DeSantis et al., 2009). By the traditional sampling approach the lead concentration is only measured in the 1-L first-draw sample (USEPA, 1991). Therefore after a PLSLR is conducted, it will be difficult to capture the high lead concentrations near the coupling by the traditional sampling approach. If the 1-L sample that is collected does not include the water near the junction, then the highest lead concentrations to which a consumer might be exposed could be significantly underestimated. Sampling at low flow rates may not be able to capture all the particulate lead, thus also resulting in an underestimation of exposure to lead in tap water (Cartier et al., 2012).

5.3.4.5 Release of Copper

Both the dissolved and total copper concentrations were low in the post-stagnation water (Figure 5-S10 of the Supplementary Material), well below the copper action level of 1300 µg/L
(USEPA, 1991). The dissolved and total copper concentrations were similar for each sample, so most copper was dissolved. The copper concentration was higher in the first week, which might be due to the initial flush of the new copper pipes after making the connections. Copper concentrations for the brass-coupled pipe assemblies were lower than those for the plastic-coupled systems based on the paired-t test (p < 0.01). On average copper concentration was 24% less for the brass-coupled systems than for the plastic-coupled systems. The result was expected since copper would be acting as the cathode in galvanic corrosion, and the cathode is protected from corrosion by its connection to the anode in a galvanic cell.

5.4 Conclusions

The effect of galvanic corrosion on lead release was investigated using aged lead pipes from Providence with synthetic Providence water. Conditioning of harvested pipes was sufficient to generate a set of four pipes with similar behavior before making connections of the lead pipes to copper tubing. For lead pipes connected to copper tubing, lead release was significantly higher in brass-coupled systems than in plastic-coupled systems. This difference can primarily be attributed to galvanic corrosion. If galvanic corrosion is a transient effect, then more than six weeks are required for the effect to subside. Galvanic corrosion slightly increased the concentrations of dissolved lead, and it markedly increased the concentrations of particulate lead. The release of particulate lead caused by galvanic corrosion increased significantly with increasing stagnation time from 6 hours to 65 hours. Total lead release was 4-6 times higher after 6-h stagnation and 15-30 times higher after 65-h stagnation for systems with galvanic corrosion. Given the localized nature of the lead release, sampling protocols need to be sure to capture the lead from this localized region if they are to assess the total lead loading to the tap.
from the service line. With respect to preventing galvanic corrosion and limiting lead release, plastic couplings are preferable to brass couplings for PLSLRs.

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Chapter 5 Supporting Information

Contents: Ten figures (5-S1 – 5-S10)

**Figure 5-S1.** System for pipe conditioning in the recirculation flow mode.

**Figure 5-S2.** Sampling times each week after connecting lead pipes to copper tubing and PVC pipes. ‘6 h’, ’17 h and 15 min’ and ’65 h and 15 min’ means the water is in stagnant mode; while ’15 min’ and ’30 min’ suggests the water is in the recirculating flow mode. ‘Pre-stagnation’ denotes the sample collected in the influent sampling port before stagnation, and ‘Post-stagnation’ denotes the sample collected in the effluent sampling port after stagnation.
Figure 5-S3. Electron micrographs of the corrosion scales from Pipe 1A. Panel b is a higher magnification image of a section from panel a.
Figure 5-S4. Total lead in static conditioning. Total lead concentration profile of the aged lead pipes in the static conditioning mode from Weeks 1 to 8. Panel a shows the y-axis with the full range of concentrations measured, while panel b shows the y-axis range to 10000 µg/L.
Figure 5-S5. Dissolved lead in static conditioning (Weeks 6-8). Dissolved lead concentration profile of the aged lead pipes in the static conditioning phase from Weeks 6 to 8. Panel a shows the post-stagnation lead concentration after 6 hours of stagnation over time; panel b shows the average lead concentration of different pipes from Weeks 6 to 8. Error bars represent one standard deviation.
Figure 5-S6. Total lead in recirculating conditioning (Weeks 2-5). Total lead concentration profile during conditioning of the aged lead pipes in the recirculating flow mode from Weeks 2 to 5. Panel a shows the post-stagnation lead concentration after 6 hours of stagnation over time; panel b shows the average effluent lead concentration after the 6-h stagnation periods. Error bars represent one standard deviation.
Figure 5-S7. Total lead in control experiments (no lead pipe). Post-stagnation total lead concentrations of the control experiment from Weeks 1 to 4 after making connections of copper tubing to PVC pipes after (a) 6-h stagnation periods (average and standard deviation shown) and (b) the 65-h stagnation period.
Figure 5-S8. Total lead release from each weekly operating cycle. Total lead mobilized during one-week operation of recirculation with intermittent stagnation periods from Weeks 1 to 6 after connecting lead pipes to copper tubing, which is estimated as the sum of the lead in the post-stagnation samples after stagnation and the lead in the acidified reservoir.
Figure 5-S9. Lead in acidified reservoirs in control experiments (no lead pipe). Total lead concentration in the acidified reservoir of the control experiment from Weeks 1 to 4 after making connections of copper tubing to PVC pipes.
Figure 5-S10. Copper in coupling experiments. Post-stagnation (a) dissolved and (b) total copper concentrations after the 6-h and 65-h stagnation periods over Weeks 1 to 6 of the experiments with connected lead pipes and copper tubing. The water in the reservoir was changed every week, which caused the concentrations dropping at the beginning of each week. Three samples were collected each week, and the one with the highest copper concentration was for the 65-h stagnation period.
Chapter 6. Effect of Connection Methods on Lead Release from Galvanic Corrosion

Results of this Chapter have been submitted to Journal – American Water Works Association

Abstract

Laboratory experiments were performed to evaluate the impact of galvanic corrosion on lead release following simulated partial lead service line replacements (PLSLRs). Experiments were conducted in a recirculating flow mode with intermittent stagnation periods using aged lead pipes harvested from Washington DC. Lead pipe and copper tubing were connected by brass, brass dielectric, and plastic couplings and additional experiments were performed with plastic couplings and an external wire to connect the lead and copper. Lead release increased in the order of systems connected with plastic, plastic with external wires, brass dielectric, and brass couplings. The trends are consistent with galvanic reactions between lead and copper and between lead and brass. For systems with galvanic corrosion, the increased lead release was primarily in a particulate form. Increasing the chloride-to-sulfate mass ratio (CSMR) from 0.7 to 7 did not increase the dissolved or total lead release.

6.1 Background
Lead service line replacement (LSLR) may be required when the tap water lead concentrations exceed the action level, which has been set as 15 µg/L for a 1-L first draw sample of tap water, and cannot be lowered by corrosion control methods (USEPA, 1991). In many instances only partial lead service line replacements (PLSLRs) are conducted since utilities can replace only the publicly owned portion of the service line and the private side of the service line is not replaced (Swertfeger et al., 2006). Often PLSLRs are implemented by replacing the old lead pipe with new copper tubing and connecting the remaining lead pipe with a brass fitting.

In the PLSLR process, a galvanic couple can be created if the lead pipe and copper tubing are electrically connected either by direct contact or by a metal coupling. This can result in an acceleration of the corrosion and release of lead, as shown in Reaction 6.1:

\[
2\text{Pb}_{(s)} + \text{O}_2^{(aq)} + 4\text{H}^+ = 2\text{Pb}^{2+} + 2\text{H}_2\text{O}
\]  

(6.1)

Significant corrosion has been observed in the field for the lead pipes next to the joint with brass, which was probably due to galvanic reactions (DeSantis et al., 2009). Recent studies found that lead concentrations did not decrease following PLSLRs; instead, higher lead concentrations were observed for some utilities even several months after PLSLRs (Muylwyk et al., 2011; Sandvig et al., 2009; Swertfeger et al., 2006; USEPA, 2011). Galvanic corrosion has been proposed as a reason that may result in elevated long-term lead release (Edwards and Triantafyllidou, 2007; Triantafyllidou and Edwards, 2011a; USEPA, 2011).

The impact of galvanic corrosion on lead release following PLSLRs can be affected by the methods used to connect the lead pipes and copper tubing. Connecting lead pipes and copper tubing using external electrical wires triggered galvanic corrosion and increased lead release by 1.5 – 75 times in stagnant water (Cartier et al., 2012; Triantafyllidou and Edwards, 2011a). While this connection method allows direct measurement of galvanic currents, actual
connections in PLSLRs use couplings such as brass compression fittings, brass dielectric compression fittings, and brass valves. Recent studies have found that lead release was significantly enhanced by connecting lead pipes and copper tubing with brass compression fittings, and the enhancement was primarily attributed to galvanic corrosion (Cartier, 2012; Wang et al., 2012a). Clark et al (2011) measured lead release after connecting lead pipes and copper tubing using different methods and found that the lead concentrations increased in the order of systems connected by direct end-to-end connection, brass compression fittings, and brass valves.

Water chemistry can affect galvanic corrosion. Several studies have reported that increasing the chloride-to-sulfate mass ratio (CSMR) accelerated lead release due to galvanic corrosion (Edwards and Triantafyllidou, 2007; Gregory, 1990; Nguyen et al., 2010b; Triantafyllidou and Edwards, 2011a), and the critical value above which lead release was enhanced was 0.6 – 0.77 (Edwards et al., 1999; Nguyen et al., 2011a). Triantafyllidou and Edwards (2011a) quantified lead release in externally wired pipe assemblies and found that 3 – 12 times more lead was released from the system with a CSMR of 16 than from one with a CSMR of 0.2. Cartier (2012) observed that lowering the CSMR from 0.9 to 0.3 significantly decreased lead release from lead pipes connected to copper tubing with brass compression fittings. Decreasing the pH (Gregory, 1990) or increasing the nitrate concentration (Nguyen et al., 2011c) were also found to increase lead release due to galvanic corrosion. In contrast increasing bicarbonate, zinc, or silicate concentrations could inhibit galvanic corrosion (Gregory, 1990; Nguyen et al., 2011a). Orthophosphate is often added to inhibit lead corrosion (McNeill and Edwards, 2002), but it was not found to decrease lead release from galvanic corrosion (Arnold, 2011b; Cartier, 2012).
The corrosion products that constitute pipe scales can potentially passivate the pipe surface and have an impact on galvanic corrosion. By measuring the surface potential, Reiber and Dufresne (2006) found that while galvanic corrosion was significant on new lead pipe surfaces, it was minimal and highly transient on aged lead pipes. For a system in which new lead pipe and copper tubing were galvanically connected, Arnold (2011a) observed that lead(IV) oxides formed on lead pipes after around 2 months of continuously recirculation with chlorinated water and that the presence of the lead(IV) oxides protected the lead pipes from galvanic corrosion. Although corrosion products may passivate the pipe surface, they may break off and be released as particulate lead at high flow rates (Cartier et al., 2012). While new or cleaned lead pipes were commonly used in previous work to simulate PLSLRs (Boyd et al., 2012; Cartier et al., 2012; Clark et al., 2011; Triantafyllidou and Edwards, 2011a), only a few studies have used lead pipes harvested from actual distribution systems (Cartier, 2012; Wang et al., 2012a).

The extent and duration of galvanic corrosion can be affected by the flow regime as well. Trantafyllidou and Edwards (2011a) observed that lead concentrations were significantly increased in stagnant water due to galvanic corrosion and suggested that stagnation represented a worst case for lead release. In determining lead release from galvanically connected lead-copper pipe assemblies, Arnold (2011a) found that greater amounts of lead were released in intermittent flow than during continuous flow. Flow rates also affected lead release from galvanic corrosion with medium (8 L/min) and high (32 L/min) flow rates having much higher lead release than at a low flow rate (1.3 L/min) (Cartier et al., 2012).

The primary objectives of the present study were to (1) determine the effect of connection methods on lead release due to galvanic corrosion and (2) evaluate the effect of CSMR on lead
release. To best represent actual PLSLRs, aged lead pipes were connected with new copper tubing by commercially available couplings.

### 6.2 Materials and Methods

#### 6.2.1 Materials

Laboratory experiments were conducted with aged lead pipes that were harvested from the Washington DC distribution system after use for over 100 years. The pipes had inner diameters of 0.75 inches and outer diameters of 1.18 to 1.2 inches. All pipes were cut to generate 24-inch sections for use in experiments.

Type K copper tubing (1 inch inner diameter and 1.125 inches outer diameter) was cut to 24-inch sections (Mcmaster-Carr). Polyvinyl chloride (PVC) pipe sections (Mcmaster-Carr) with inner diameters of 1 inch were cut to 24-inch sections and used in lead-free control experiments. Couplings used in the experiments were brass compression fittings (A.Y. McDonald), brass dielectric fittings (A.Y. McDonald) and all-plastic polypropylene fittings (Harco – Philmac).

All solutions were prepared using ultrapure water (resistivity > 18.2 MΩ-cm). Reagent grade CaCl₂, MgCl₂, MgSO₄, Na₂HPO₄, NaF, NaCl, NaHCO₃, NaOCl, NaOH, and HNO₃ were purchased (Fisher Scientific) and used for preparing synthetic tap water.

#### 6.2.2 Pipe Conditioning

Six harvested lead pipes were conditioned with water prepared to simulate the chemistry of the Washington DC distribution system (Table 6.1) before being connected to copper tubing.
The pipes were first conditioned in a static “dump-and-fill” mode for at least 8 weeks; different “dump-and-fill” conditioning times were used for different pipes because pipes were maintained in this mode until their use in specific experiments. This “dump-and-fill” mode was operated following the procedures described in Wang et al (2012a). Samples were collected periodically and preserved for dissolved (filtered with 0.45 µm polyethersulfone (PES) syringe filters) and total lead analysis.

Table 6.1. Water composition of synthetic DC water with original and elevated CSMR.

<table>
<thead>
<tr>
<th>Water composition parameter</th>
<th>Range for DC water(^\d)</th>
<th>Synthetic water (Original CSMR)</th>
<th>Synthetic water (elevated CSMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7 to 7.8</td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Combined chlorine, mg/L as Cl(_2)</td>
<td>3.6 to 3.8</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Total alkalinity, mg/L as CaCO(_3)</td>
<td>49 to 99</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>TDS, mg/L</td>
<td>126 to 261</td>
<td>310</td>
<td>310</td>
</tr>
<tr>
<td>Total hardness, mg/L as CaCO(_3)</td>
<td>114 to 155</td>
<td>128</td>
<td>128</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>30 to 56</td>
<td>34</td>
<td>77</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>40 to 71</td>
<td>50</td>
<td>11</td>
</tr>
<tr>
<td>Orthophosphate, mg/L as PO(_4)</td>
<td>2.4 to 2.8</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\(^\d\) The ranges are for the Dalecarlia Water Treatment Plant

After being conditioned in the static mode, the pipes were conditioned in a recirculating flow mode for 4 weeks. A similar protocol was then used when the lead pipes were connected to the copper tubing. Briefly, the system was operated on a daily cycle during weekdays. On each Monday morning, freshly made synthetic DC water was fed into the pipes from a 10-L polyethylene reservoir. The weekday cycle for Monday-Thursday started with a 6-h stagnation period, then 15 minutes of flow, a 17.25-h stagnation period, and finally 30 minutes of flow. On Fridays, the 17.25-h stagnation period was replaced with a 65.25-h stagnation period (over the weekend), hereafter just referred to as the 65-h stagnation period, as the last phase of the weekly
cycle. The reservoirs were then replaced with cleaned ones with freshly made solutions to begin the next week’s cycle. A peristaltic pump (Cole Parmer) provided a flow rate of 5.2 L/min, which corresponded to water velocity of 1 ft/s in the lead pipes. The chlorine concentrations in the reservoir were regularly monitored and adjusted to the target value.

A 50-mL water sample was collected each Monday, Wednesday, and Friday prior to the 6-h stagnation period and on Friday prior to the 65-h stagnation period. Following the corresponding stagnation periods, 50-mL post-stagnation samples were collected from which 10 mL were used for total lead analysis, 10 mL for dissolved lead analysis, and the remaining 30 mL for pH and combined chlorine measurement. The orthophosphate concentration was also determined for selected samples.

### 6.2.3 Experiments with Couplings

After being conditioned in the recirculating flow mode for four weeks, the lead pipes were connected to copper tubing using the different couplings and placed in the recirculation system (Figure 6.1) and operated for at least six weeks. The overall timeline of all experiments conducted is listed in Table 6.2. Two pipes were connected to copper tubing using the plastic couplings (plastic-1 and plastic-2), two using the brass couplings (brass-1 and brass-2), and two using the brass-dielectric couplings (brass-die-1 and brass-die-2). The electrical resistance between the lead and copper was measured by a handheld multimeter (BK Precision). For the plastic-coupled and brass dielectric-coupled systems, the resistance was high (larger than 1 MΩ) between the lead pipes and copper tubing, indicating no electrical connection; little resistance (less than 4 Ω) was observed for the brass-coupled pipe assemblies. The brass dielectric
couplings still have the potential for dissimilar metal couples of copper/brass and brass/lead.

The internal volumes of the lead pipe and copper tubing sections were 180 mL and 310 mL,

Figure 6.1. (a) Schematic view of the recirculating flow system with lead pipes and copper tubing connected with different couplings (Adapted from Wang et al. (2012a)) and (b) photograph of the couplings used to connect lead pipe and copper tubing.
respectively. Experiments were operated in a recirculation mode with intermittent stagnation periods according to the same cycle used for condition and described in the preceding section.

**Table 6.2.** Timeline of the experiments conducted in the recirculating flow mode.

<table>
<thead>
<tr>
<th>Connection Methods(^1)</th>
<th>Experimental Dates</th>
<th>Condition of lead pipe</th>
<th>CSMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic with and without external wires</td>
<td>8/29/2011 – 9/26/2011 (4 weeks)</td>
<td>no wire</td>
<td>CSMR = 0.7</td>
</tr>
<tr>
<td></td>
<td>9/26/2011 – 11/07/2011 (6 weeks)</td>
<td>no wire</td>
<td>CSMR = 7</td>
</tr>
<tr>
<td></td>
<td>11/07/2011 – 12/05/2011 (4 weeks)</td>
<td>no wire</td>
<td>CSMR = 0.7</td>
</tr>
<tr>
<td></td>
<td>12/05/2011 – 1/02/2012 (4 weeks)</td>
<td>with wire</td>
<td>CSMR = 0.7</td>
</tr>
<tr>
<td></td>
<td>1/02/2012 – 2/13/2012 (6 weeks)</td>
<td>no wire</td>
<td>CSMR = 0.7</td>
</tr>
<tr>
<td></td>
<td>2/13/2012 – 2/20/2012 (1 week)</td>
<td>no wire</td>
<td>CSMR = 0.7</td>
</tr>
<tr>
<td>Brass Conditioning of lead pipe</td>
<td>11/07/2011 – 12/05/2011 (4 weeks)</td>
<td>CSMR = 0.7</td>
<td></td>
</tr>
<tr>
<td>Brass Dielectric Conditioning of lead pipe</td>
<td>1/02/2012 – 2/13/2012 (6 weeks)</td>
<td>CSMR = 0.7</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)Experiments were conducted in duplicates.

To determine whether the chloride-to-sulfate-mass-ratio (CSMR) would affect galvanic corrosion, after six weeks of the experiment, for pipes with plastic and brass couplings, the CSMR was increased from its original value of 0.7 to an elevated value of 7.0 for four weeks (Table 6.1). The value of 0.7 is near the boundary of where CSMR was found to result in enhanced galvanic corrosion in previous research (Nguyen et al., 2011b).

The opportunity for galvanic corrosion to occur was also introduced for the copper-lead assemblies with the plastic couplings by electrically connecting them with an external wire as has been done in previous work (Triantafyllidou and Edwards, 2011). This connection allows for the measurement of galvanic current by placing a multimeter (BK Precision) in the externally-wired connection. These systems are referred to as plastic-ex-1 and plastic-ex-2. This connection was made for the same pipes that had been studied with the plastic couplings (without the externally wired connection) at first with the original CSMR and then at the elevated value. Before making the connection with the external wires, the copper-lead assemblies were operated using the water with the original CSMR for four weeks. After then
operating the pipe assemblies with the external connection for six weeks, the wires were disconnected and lead release was monitored for one more week.

To test for lead release from the couplings themselves, control experiments were performed using PVC pipes connected to copper tubing. Because no lead pipe section was present in these experiments, the brass couplings were the only significant source of lead, although it is possible that lead-containing plasticizers in the PVC may also contribute some lead. Experiments were operated for four weeks using the same weekly cycle used for the experiments with connected lead pipes and copper tubing.

In both the experimental lead-copper and control PVC-copper experiments, influent samples of 50 mL were collected at a flow rate of 1 L/min on each Monday and Thursday before the 6-h stagnation period and on Friday before the 65-h stagnation period. Post-stagnation samples of approximately 500 mL were collected directly from the pipe assemblies at a flow rate of 1 L/min following the Monday and Thursday 6-h stagnation periods and the weekend 65-h stagnation period. A profile sampling approach was performed once for each lead-copper pipe assembly using the synthetic DC water with the original CSMR. Seven consecutive 70-mL samples were collected for each lead-copper pipe assembly after 6 hours of stagnation in an effort to identify possible localization of lead release along the pipe sections. Dissolved and total concentrations of lead and copper were measured.

After replacing the old reservoir with a new one each Monday, the solution in the old reservoir was acidified to pH < 3 by addition of concentrated HNO₃ and allowed to sit at this low pH for at least 24 hours before collecting a 10-mL sample for total lead and copper analysis. This acidification was intended to mobilize and dissolve particulate or adsorbed lead that may have accumulated in the reservoirs during the previous week.
6.2.4 Characterization of Lead Pipe Scales

The cross-sections and interior walls of the as-received pipes were prepared to characterize the structure and composition of the corrosion products. For imaging, a 1-inch section of the pipe was filled with epoxy. Then the cross-section was cut and the thickness of the pipe scales was observed using scanning electron microscopy (SEM). For X-ray diffraction (XRD), 6-inch portions of the as-received pipes were cut longitudinally and scales were scraped from the inner surfaces of the pipes using a metal spatula. XRD was performed to identify the crystalline phases of the solids present in the scales. The elemental composition of the scales was quantified by digesting 0.01 g of the scale in a mixture of 2.5 mL concentrated HCl and 10 mL concentrated HNO₃ that was heated to 100°C for 4 hours. The digestate was then diluted to 50-mL with ultrapure water, filtered through a 0.22 µm PES syringe filter, and preserved for elemental analysis.

6.2.5 Analysis Methods

Concentrations of lead and copper were measured by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7500ce). The samples were acidified to 2% HNO₃ before analysis. XRD was conducted on a Rigaku Geigerflex D-MAX/A diffractometer using Cu-Ka radiation. Electron microscopy images were acquired on a JEOL 7001LVF field emission scanning electron microscope. Total chlorine and orthophosphate concentrations were determined by the standard DPD and ascorbic acid colorimetric methods (4500-Cl G and 4500-P).
E) with a spectrophotometer (PerkinElmer Lambda XLS+). Solution pH was measured with a glass pH electrode and pH meter.

6.3 Results and Discussion

6.3.1 Pipe Scale Characterization

Using XRD the lead(II) phosphate hydroxylpyromorphite (Pb₅(PO₄)₃OH) was observed as the dominant solid phase in the scales of the two pipes examined (Figure 6.2). Hydroxylpyromorphite has been observed in distribution systems using phosphate as corrosion inhibitors (Davidson et al., 2004; Schock et al., 2005a). Orthophosphate has been added in DC water treatment plants to mitigate lead release to tap water since 2005. Lytle et al. (2009) found that hydroxylpyromorphite formed from Pb(II) aqueous species even in the presence of free chlorine, where the formation of PbO₂ is favored. In addition, characteristic peaks of scrutinyite (α-PbO₂) at 2θ of 28° and of plattnerite (β-PbO₂) at 2θ of 25° were also observed. PbO₂ has been found in distribution systems with a consistent use of free chlorine as their disinfectant (Kim and Herrera, 2010; Schock and Giani, 2004; Schock et al., 2005b). Washington DC used free chlorine as the disinfectant persistently before 2001 and now still runs with free chlorine for about 1 month per year to limit the growth of biofilms.

The dominant solids present in the pipe scales were aggregates of small roughly spherical particles with primary sizes less than 100 nm (Figure 6.3a). The shape observed in the present work was consistent with that of lead(IV) oxide or hydroxylpyromorphite, both of which have been previously observed as small roughly spherical particles or aggregates (Giammar et al., 2008; Wang et al., 2010). The thickness of the scale was around 40 μm. Xie and Giammar (2011)
conditioned new lead pipes for 8 months in the lab and observed development of a pipe scale with a similar thickness of 24 µm; while a 300-µm thick pipe scale was observed for the pipe harvested from water utilities in Illinois (Nadagouda et al., 2011).

![Figure 6.2. X-ray diffraction patterns of the crystalline phases in the scales from DC pipes. Powder diffraction file patterns for hydroxylpyromorphite (04-012-9459), scrutinyite (04-008-7674), and plattnerite (01-071-4820) from the International Centre for Diffraction Data are shown for reference. The pipe labels 3A and 4A are identification codes based on their harvesting address. Pipes that have the same first digit in their codes were from the same location.]

Completely digesting the scales determined that trace amounts of aluminum (15 mg/g), manganese (5 mg/g), vanadium (4 mg/g), and copper (6 mg/g) were present. Manganese and vanadium have been observed in the scales of the lead pipes in the distribution system of Providence, RI (Wang et al., 2012a). Gerke et al. (2009) analyzed the scales of 15 lead pipes from 8 different distribution systems and found that most scales contained vanadium with a concentration of 2 – 8 mg/g scale. They suggested that vanadium can be present in the form of
vanadinite \((\text{Pb}_5(\text{VO}_4)_3\text{Cl})\). Due to the similarity of \(\text{VO}_4^{3-}\) to \(\text{PO}_4^{3-}\), \(\text{VO}_4^{3-}\) may even partially substitute for \(\text{PO}_4^{3-}\) in the lead phosphate solids in the pipe scales.

**Figure 6.3.** Electron micrographs of (a) the morphology of the scales from Pipe 4A and (b) a cross-section of Pipe 4C after filling with epoxy and polishing. The pipe labels 4A and 4C are identification codes of the pipes based on their harvesting address. Pipes that have the same first digit in their codes were from the same location.

### 6.3.2 Lead Release from Pipe Conditioning

In the recirculating flow mode, the average dissolved lead concentrations following 6-h stagnation periods were quite similar for the six pipes, with the average value around 15 \(\mu\text{g/L}\) (Figure 6.4a). Increasing the stagnation time to 65 hours did not affect the dissolved lead concentrations except for one pipe, suggesting that the water in the pipes may have reached equilibrium with respect to the corrosion products within 6 hours. Based on available thermodynamic data (Benjamin, 2002; Schecher and McAvoy, 1998), the dissolved lead concentration in equilibrium with hydroxylpyromorphite at the DC water chemistry is estimated to be 9 \(\mu\text{g/L}\), which was close to the measured value. The total lead concentrations were only slightly higher than the dissolved lead concentrations (Figure 6.4b), indicating only limited particulate lead release in the flow from the pipe after the prescribed stagnation periods during
condition. Further, the concentrations observed for the six pipes were similar prior to their connections to copper tubing by different methods.

![Figure 6.4](image)

**Figure 6.4.** Average (a) dissolved and (b) total lead concentrations in the effluent after 6-h and 65-h stagnation periods of the recirculating-flow conditioning mode. Error bars represent one standard deviation. The labels 2A, 2B, 3A, 4A, 4C, and 4E are identification codes of the pipes based on their harvesting address. Pipes that have the same first digit in their codes were from the same location.

### 6.3.3 Lead and Copper Release from the Experiments with Couplings

After connecting lead pipes to copper tubing using the different types of test couplings, dissolved and total lead concentrations were monitored regularly each week. The effluent lead concentrations after stagnation were lowest for the plastic-coupled systems, which is in accordance with the absence of a galvanic connection in the plastic-coupled pipe assemblies. Relative to the plastic-coupled systems, the total lead concentrations increased in the order of plastic with external wires, brass dielectric fittings, and conventional brass fittings after the 6-h stagnation period (Figure 6.5).
6.3.3.1 Effect of Coupling Types

Total lead and dissolved lead concentrations were quite similar for the plastic-coupled system, suggesting that lead was present primarily in the form of dissolved lead. The total lead concentrations in the plastic-coupled systems following 6-h stagnation periods were stable over the six weeks of experiments, with an average concentration around 10 µg/L (Figure 6.5). Increasing the stagnation time to 65 hours only slightly increased the total lead concentrations. These lead concentrations were close to the predicted equilibrium solubility of hydroxylpyromorphite and similar to values during pipe conditioning. Since lead pipes and copper tubing were not galvanically connected in the plastic-coupled systems, the lead concentrations provided a baseline for lead release in a system free of any galvanic corrosion.
Connecting the lead and copper with external wires in the plastic-coupled systems allowed galvanic corrosion. Enhanced lead release was only observed for one of the duplicates (plastic-ex-2) (Figure 6.6). On average the total lead concentrations for plastic-ex-2 were 8 times higher than without the wired connection (Figure 6.5). The enhancement of lead release for the externally wired connections can be attributed to galvanic reactions between lead and copper. Removing the wires immediately decreased the lead concentrations to the levels without the wired connection (Figure 6.6). Interestingly the duplicate pipe assemblies behaved almost identically before the external connection was made, but one of the pipes was much more susceptible to galvanic corrosion upon the connection. Differences in the structure and spatial distribution of scales of corrosion products on the pipes could be responsible for the observed differences.

Galvanic current was detected in both of the externally-wired plastic-coupled systems, and the current did not decrease over the 6 weeks of the experiments. For plastic-ex-1, the

Figure 6.6. Total lead concentrations in the effluent after 6-h stagnation periods over a five month period in the plastic-coupled pipe assemblies that investigated the effects of chloride-to-sulfate mass ratio (CSMR) and the external electrical connection of the lead pipe and copper tubing.
average galvanic current during the stagnation periods was 18 \mu A, and plastic-ex-2 had a higher average galvanic current of 40 \mu A. These results suggested that there may be a threshold value of galvanic current that would enhance lead release from the aged lead pipes. Galvanic current has also been measured in previous studies of lead corrosion. By connecting lead pipes and copper tubing using external wires, Cartier et al (2012) found that the galvanic current persisted for seven months with an average value around 25 \mu A during stagnation. Using a similar connection method but completely different water chemistry, Triantafyllidou and Edwards (2011a) reported galvanic currents during stagnation as high as 87 \mu A. It should be noted that both in the present and previous work (Cartier et al, 2012; Triantafyllidou and Edwards, 2011), the observed lead release was much lower than the total amount of lead(0) oxidation to lead(II) that is predicted from the galvanic current using Faraday’s Law. The total electron transfer from the lead to the copper is measured in the galvanic current, and this can then be used to determine the amount of lead oxidation that occurred. Results indicated that a large amount of the lead(II) generated by galvanic corrosion may accumulate in the pipe scale and not be released to water. In the present work, the galvanic currents during recirculation were typically 50\% higher than those during stagnation periods, which was consistent with a previous observation that the galvanic current was 25 – 50 \% higher during flow than during stagnation (Cartier et al., 2012). For galvanic corrosion to occur, transport of solutes from the anode to the cathode must occur; for stagnant water this transport is controlled by diffusion, but for conditions with flow the transport can be provided much more rapidly by convection.

Greater amounts of total lead were released from the brass dielectric-coupled systems than from the plastic-coupled ones (Figure 6.5). The total lead concentrations continuously decreased for one of the duplicate assemblies (brass-die-1) but were stable for the other (brass-
die-2). As with the externally-wired plastic connections, the difference in the behavior of the duplicate assemblies with brass dielectric couplings may be attributed to microscale differences in the composition and distribution of the pipe scales. On average the total lead concentrations following 6-h stagnation periods were an order of magnitude higher for the brass dielectric-coupled systems than for the plastic-coupled ones. Increasing the stagnation time to 65-h further enhanced the total lead release. The brass dielectric couplings themselves may be a source of lead; however, lead pipe-free control experiments suggested that less than 20 µg/L lead was released from the couplings following 6-h stagnation periods (Figure 6.7). Therefore the majority of the lead release in the brass dielectric-coupled systems may be attributed to galvanic corrosion. With the brass dielectric couplings, the lead and copper are not galvanically connected, but brass and lead can act as a galvanic couple with lead serving as the anode.

The highest lead release was observed in the brass-coupled pipe assemblies (Figure 6.5). Compared with those in plastic-coupled systems, the total lead concentrations in the brass-
coupled systems were about 20 times higher following 6-h stagnation periods. Increasing the stagnation time from 6-h to 65-h doubled the total lead concentrations. The brass couplings themselves would release less than 20 µg/L total lead (Figure 6.7), and therefore the much greater lead release was primarily due to galvanic corrosion. For both stagnation times, the duplicate brass-coupled assemblies were in agreement over the entire experiment duration. Clark et al (2011) also observed that more lead was released from brass-coupled systems than from systems in which the lead and copper were directly connected.

Copper release was monitored for the systems with different couplings and can provide complementary data to lead release regarding galvanic corrosion. Dissolved and total copper concentrations were similar for all of the systems, so most copper was dissolved. While copper concentrations were similar for all the pipe assemblies after 6 hours of stagnation, increasing the

![Figure 6.8. Copper in the experiments with lead pipes connected to copper tubing. Average total copper concentration after two stagnation times. Error bars represent one standard deviation.](image)
stagnation time to 65 hours resulted in a different trend of copper release (Figure 6.8). The highest copper release was observed for the plastic-coupled systems in which no galvanic corrosion could occur. Relative to the plastic-coupled systems, the copper concentrations decreased in the order of systems coupled with brass dielectric, externally wired plastic, and brass. These results are consistent with copper acting as the cathode that is protected against corrosion in a galvanic interaction with lead or brass. It should be noted that for plastic-ex-1, although lead release was not enhanced due to galvanic corrosion, copper concentrations after 65 hours of stagnation were decreased relative to those prior to making the external galvanic connections (plastic) and were comparable to those for plastic-ex-2 (Figure 6.8). Combined with the measurements of galvanic current, these results regarding copper concentrations confirm that although lead release was not increased a galvanic interaction did still take place in the plastic-ex-1 system.

6.3.3.2 Distribution of Released Lead between Dissolved and Particulate

The distribution of total lead between particulate and dissolved was examined for all of the pipe assemblies (Figure 6.9). Dissolved lead was more abundant than particulate lead for the plastic-coupled systems. When the externally wired connection was made for plastic-ex-2, the increased lead concentration was primarily in the form of particulate lead, and more than 80% of the total lead was particulate (Figure 6.9b). Triantafyllidou and Edwards (2011a) determined lead release by connecting lead pipes and copper tubing with external galvanic wires. They observed that in stagnant water 70 – 99 % of total lead was in particulate forms.

Compared to the plastic-coupled systems, both dissolved and particulate lead concentrations increased significantly for the brass-coupled and brass dielectric-coupled systems.
For the brass-coupled systems, particulate lead became more dominant, and typically 52 – 72% of the total lead was particulate in the water following 6 hours of stagnation. By examining the lead release from a similar pipe loop with a different water chemistry, Wang et al (2012a)

Figure 6.9. Distribution of lead between dissolved and particulate forms for Weeks 1 to 6 of experiments with lead pipes connected to copper tubing following 6-h stagnation periods using (a-b) plastic (with and without externally wired connections), (c-d) brass dielectric, and (e-f) brass compression couplings. The labels on the x-axis indicate the day of the week and the week of the experiment.
reported that 55 – 93% of the total lead was in particulate form in brass-coupled pipe assemblies. For the systems with brass dielectric couplings, the concentrations of dissolved and particulate lead were comparable.

Lead particles may also be released during flow periods. Cartier et al (2012) found that significant amounts of particulate lead were released at flow rates of 8 and 32 L/min. In the recirculating flow experiments, the particulate lead released during recirculation can accumulate in the reservoir (Arnold, 2011a; Nguyen et al., 2010a). To evaluate the amount of particulate lead that had accumulated in the reservoir, the water in the reservoir after a 1 week cycle of stagnation and recirculation was acidified. In all cases a significant increase (2.5 – 4.5 times) in lead concentrations was observed following acidification of reservoirs that served pipe assemblies in which galvanic corrosion occurred. The total lead that had accumulated in the reservoirs followed the same trend as the stagnation samples with concentrations increasing in the order of plastic, externally-wired plastic, brass dielectric, and brass (Figure 6.10). By quantifying lead release in a similar experimental set-up but with a different water chemistry, Wang et al (2012a) found that for the brass-coupled pipe assemblies, the total lead concentrations in the reservoir increased by 3.5 times after acidification. In previous work with systems that had lead and copper connected by external wires, the total lead concentrations in the acidified reservoir were 3 – 8 times those prior to acidification (Arnold, 2011a; Nguyen et al., 2010a).

The total mass of lead released over one-week recirculation and stagnation cycles can be calculated as the sum of the lead in the samples and in the acidified reservoir. On average 0.16·10³ µg, 1.17·10³ µg, 2.14·10³ µg, and 4.12·10³ µg total lead was released over one week for plastic-coupled, plastic-ex-2, brass dielectric-coupled, and brass-coupled pipe assemblies, respectively. Assuming that similar amounts of lead were released from the 17.25-h and 65-h
stagnation periods, the total stagnation periods for a week contributed approximately 33%, 51%, 29%, and 40% of the total lead released for plastic-coupled, plastic-ex-2, brass dielectric-coupled, and brass-coupled pipe assemblies, respectively. Significant amounts of lead release, consequently, were released during stagnation as well as during flow.

Results of lead release from both stagnation and flow suggested that galvanic corrosion enhanced total lead release for at least six weeks. Triantafyllidou and Edwards (2011a) observed that lead concentrations were increased for several months in stagnant water in a system where lead and copper were galvanically connected by external wires and suggested that the enhancement was attributed to galvanic corrosion. Cartier (2012) monitored lead release in a once-through flow system following connecting lead pipes to copper tubing with brass couplings.
and found that galvanic corrosion enhanced lead release for at least eight weeks. Muylwyk et al. (2011) measured lead concentrations in tap water in Guelph, Ontario following PLSLRs (94 replacements tracked) and found that for some places high lead concentrations persisted for at least 18 months. Further studies focused on lead release over a long term are needed to better evaluate the duration of galvanic corrosion in the future.

6.3.3.3 Localized Nature of Galvanic Corrosion

Localized lead release caused by galvanic corrosion was evaluated by a sampling approach that collected water from different zones of the pipe assemblies after a 6-h stagnation period (Figure 6.11). For the plastic-coupled systems, lead concentrations were highest near the end of the lead pipe and they decreased along the portion to the copper tubing. For the brass-coupled, brass dielectric-coupled, and one of the externally-wired plastic-coupled systems, the highest lead concentrations were observed in the zones near the coupling connections, indicating that galvanic reactions were most dramatic in the regions near the couplings. Previous observations also concluded that galvanic corrosion was a localized phenomenon by using various techniques. Boyd et al. (2012) measured the open circuit potential of the directly connected lead pipe and copper tubing, and observed that the galvanic effect was localized in the region of lead pipes closest to the copper. Several studies measured the galvanic currents between the lead pipes and copper and found that the galvanic currents were highest within the first few inches next to the junctions and decreased with increasing distance (Clark et al., 2011; Triantafyllidou and Edwards, 2011a). By measuring lead release from brass-coupled pipe assemblies, Wang and colleagues observed higher lead release near the brass couplings due to galvanic corrosion (Wang et al., 2012a). In the present work, the lead concentrations near the
couplings were 5–8 times higher than at the lead-ends of the systems in which galvanic corrosion occurred. Although these high local lead concentrations may not increase the overall lead exposure at the tap for systems where a large portion of the lead service line was replaced, the maximum lead concentration that a consumer might be exposed to could be increased significantly. Further, depending on the relative amounts of lead pipe remaining after a PLSLR,
the increased local release of lead due to galvanic corrosion may outweigh the decrease in lead associated with the removal of a portion of the lead pipe.

6.3.3.4 Effect of CSMR

For both the plastic-coupled and the brass-coupled systems, increasing the CSMR from 0.7 to 7.0 did not increase the total lead release following either 6-h or 65-h stagnation periods (Figure 6.12). This observation is expected for the plastic-coupled pipe assemblies since no galvanic corrosion would occur in that system. However, for the systems having galvanic connections, CSMR was previously found to be an important parameter that affected the extent of galvanic corrosion (Edwards and Triantafyllidou, 2007; Gregory, 1990; Nguyen et al., 2010b; Triantafyllidou and Edwards, 2011a). Previous studies suggested that the threshold value of the CSMR above which lead release from galvanic corrosion could be accelerated was around 0.6 to 0.77 (Edwards et al., 1999; Nguyen et al., 2011a). Based on chloride and sulfate concentrations that are representative of those in the water in the DC Water distribution system, the original CSMR was selected as 0.7 for the present study, which was within this critical range. It is possible that lower lead release would have occurred for the pipe assemblies if the CSMR were decreased to a lower value. Cartier (2012) determined lead release from galvanic corrosion in a once-through flow system by connecting lead pipes and copper tubing using brass couplings. They found that decreasing the CSMR from 0.9 to 0.3 decreased lead release. In a system where lead pipes and copper tubing were connected using external wires, the lead release increased by 3-12 times when the CSMR was increased from 0.2 to 16. However, the authors pointed out that even when the CSMR was low (0.2), lead release from galvanic corrosion was still significant (Triantafyllidou and Edwards, 2011a). In the present study, the relatively high alkalinity (76
mg/L as CaCO$_3$), combined with the presence of orthophosphate, may have helped mitigate any enhanced lead release that could have been caused by increased galvanic corrosion at the elevated CSMR.
6.4 Conclusions

The effect of coupling types and CSMR on lead release following simulated PLSLRs with copper was investigated using aged lead pipes harvested from Washington DC. Before conducting the experiments, the pipes were conditioned for a total of at least 12 weeks. Experiments with lead-copper pipe assemblies conducted for six weeks in a recirculation flow mode with intermittent stagnation periods yielded the following conclusions.

- The lowest lead release was observed for the plastic-coupled pipe assemblies, which served as a galvanic-free control. Relative to the plastic-coupled systems, the total lead release following stagnation increased in the order of systems coupled with plastic fittings with external wires, brass dielectric fittings, and brass fittings.

- The copper concentrations following 65 hours of stagnation decreased in the order of systems coupled with plastic, brass dielectric, externally wired plastic, and brass, which was consistent with copper acting as the cathode in a galvanic interaction with lead.

- For the plastic-coupled systems with external wires, lead and copper can serve as a galvanic couple with lead serving as the anode, resulting in an increase of lead release and decrease of copper release, especially after 65 hours of stagnation. Galvanic currents between lead and copper were detected, which confirmed the occurrence of galvanic corrosion. However, different pipes had different susceptibility to galvanic corrosion and a threshold value of galvanic current may be present above which lead release would be enhanced.

- For the brass dielectric-coupled system, since brass itself only released limited lead, the enhanced lead release was probably due to the galvanic reaction between lead and brass.
• For the systems with enhanced lead release, the increased lead amounts were primarily in particulate forms. Increasing the stagnation time from 6 hours to 65 hours further increased the release of particulate lead, especially for the brass-coupled pipe assemblies.

• For the systems with enhanced lead release caused by a connection to copper tubing, lead concentrations were locally much higher in the regions closest to the couplings.

• For both the brass-coupled and plastic-coupled pipe assemblies, increasing the CSMR from 0.7 to 7 did not increase lead release.

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Chapter 7. Conclusions and Recommendations

7.1 Conclusions

The present work investigated lead release from two types of oxidation-reduction processes that affect lead concentrations in drinking water. Task 1 determined the effect of water chemistry and lead(II) precursors on the extent and identity of the formation of the lead corrosion product PbO$_2$. Task 2 quantified the dissolution rates of PbO$_2$ at a variety of water chemistry conditions and proposed pathways for the reductive dissolution of PbO$_2$. Task 3 investigated the impact of galvanic corrosion on lead release following simulated PLSLRs by connecting aged lead pipes harvested from two distribution systems to copper tubing using different connection methods.

Task 1: Investigate the effect of water chemistry and precursors on the formation of PbO$_2$

In the first task, the extent and identity of PbO$_2$ formation was determined as a function of pH, the presence of DIC, and free chlorine concentrations. Experiments were conducted for 28 days using batch reactors with four lead(II) compounds that are precursors of PbO$_2$ formation: dissolved lead(II) chloride, massicot (β-PbO$_2$), cerussite (PbCO$_3$), and hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$). Samples were taken periodically and the solids were characterized using XRD and SEM to identify secondary phases and observe changes in particle morphology.
PbO$_2$ formed both in the absence and presence of DIC. When starting with massicot, the presence of DIC accelerated PbO$_2$ formation and changed the identity of the PbO$_2$ product (scrutinyite (α-PbO$_2$) versus plattnerite (β-PbO$_2$)). In the presence of DIC, lower pH favored plattnerite and higher pH resulted in scrutinyite formation. This trend was not observed in the absence of DIC, and mixtures of scrutinyite and plattnerite formed at both pH 7.5 and 10.

PbO$_2$ could form through either an aqueous phase oxidation pathway or a solid-phase mediated oxidation pathway. Water chemistry parameters affected the formation pathways by promoting the precipitation of different intermediate solids, thus changing the identity of the PbO$_2$ product. When no intermediate solids formed, hydrocerussite led to the formation of pure scrutinyite, and massicot and PbCl$_2$ led to mixtures of scrutinyite and plattnerite.

**Task 2: Establish the rate-controlling processes and quantify associated kinetic parameters of PbO$_2$ reductive dissolution**

Task 2 quantified the dissolution rates of PbO$_2$ at a variety of pH and concentrations of DIC, free chlorine, and iodide. Experiments were performed using continuously stirred tank reactors (CSTRs) and the steady-state concentrations of dissolved lead were used to calculate the dissolution rate.

The dissolution rate of PbO$_2$ increased with decreasing pH. The presence of free chlorine inhibited the dissolution of PbO$_2$, especially at pH 6.7 to 8.5 where the addition of 1 mg/L as Cl$_2$ free chlorine decreased the dissolution rate by an order of magnitude. Iodide acted as a reductant to accelerate PbO$_2$ dissolution, and the dissolution rate increased with increasing iodide concentrations. In the presence of iodide, addition of 10 mg C/L DIC accelerate PbO$_2$ dissolution, but further increases in DIC concentration did not affect the dissolution rate.
The reductive dissolution of PbO$_2$ was proposed to be a coupled process involving chemical reduction of Pb(IV) to Pb(II) at the PbO$_2$ surface followed by detachment of Pb(II) to solution. The dissolution rate was directly correlated with the surface species of PbO$_2$ that participated in the reaction. In the absence of iodide and free chlorine, the dissolution rate was predominantly controlled by >Pb(IV)OH$_2^+$ for acidic conditions and by >Pb(IV)OH and >Pb(IV)O$^-$ at neutral to basic conditions. Surface complexation models were able to predict the concentrations of the Pb(IV) surface species. In the presence of iodide, chemical reduction was the rate-limiting step for PbO$_2$ dissolution and the dissolution followed Langmuir-Hinshelwood kinetics.

Task 3: Determine the impact of connection methods and water chemistry on lead release following simulated PLSLRs

In task 3, the extent of galvanic corrosion following simulated partial lead service line replacements (PLSLRs) were investigated in bench-scale experiments with aged lead pipes harvested from two different distribution systems. The lead pipes were connected to copper tubing by different types of couplings that are used in practice. Test couplings studied were brass compression, brass compression with a dielectric insert, plastic, and plastic with an external wire to provide electrical connectivity between the lead and brass. To simulate the flow regimes in real service lines, experiments were performed in a recirculating flow mode with intermittent stagnation periods. The aged lead pipes were conditioned using the water to simulate the chemistry of the Washington DC or Providence, RI distribution system before they were connected to the copper tubing.
For the experiments with both the DC and Providence pipes and corresponding water compositions, lead release was significantly higher in the brass-coupled pipe assemblies than in the plastic-coupled pipe assemblies, and the difference was primarily attributed to galvanic corrosion. Galvanic corrosion slightly increased the concentrations of dissolved lead but dramatically enhanced particulate lead release. Galvanic corrosion primarily occurred in the regions next to the coupling connections and it persisted for six weeks of the experiments.

The effect of external wired plastic and brass dielectric couplings was determined using synthetic DC water. The lead release increased in the order of the systems coupled with plastic, plastic with external wires, brass dielectric, and brass. Enhancement of lead release was observed for one of the plastic-coupled systems with external electric wires but not for the other, suggesting that a threshold value of galvanic current may be present above which lead release would be increased. The enhancement was attributed to the galvanic reactions between lead and copper. For the brass dielectric-coupled pipe assemblies, the lead concentration was increased due to the galvanic reactions between lead and brass. The duplicates behaved differently with one having stable elevated concentrations over six weeks and the other having concentrations that consistently decreased with time. The divergent behavior of the duplicate experiments for both the plastic with the external wire and the brass dielectric connecton methods suggest that pipes that otherwise behave similarly can have very different susceptibility to galvanic corrosion. For both the plastic- and brass-coupled pipe assemblies, increasing CSMR from 0.7 to 7 did not increase lead release.

7.2 Recommendations for Future Work
Free chlorine has been widely used as a disinfectant in distribution systems but only some systems have observed PbO\textsubscript{2}. The present work demonstrated that PbO\textsubscript{2} formed in the presence of 4 mg/L as Cl\textsubscript{2} free chlorine, which is a higher value than is used in distribution systems. Further research to investigate the formation of PbO\textsubscript{2} at lower free chlorine concentrations can be helpful to determine whether a threshold value of free chlorine concentrations would be present above which PbO\textsubscript{2} formation is favored.

The dissolution rate of PbO\textsubscript{2} can directly be correlated with the PbO\textsubscript{2} surface speciation. The presence of foreign ions may react with the PbO\textsubscript{2} surface species, thus affecting the dissolution rate of PbO\textsubscript{2}. To build a comprehensive reaction-based framework for PbO\textsubscript{2} dissolution, further experiments are needed to determine the effect of common ions present in tap water, especially silicate and phosphate, on PbO\textsubscript{2} dissolution rates and the associated kinetic parameters. In addition, direct measurements of the oxidation states of the lead at the surface and in the solution using electrochemical methods or solid phase characterization techniques such as X-ray photoelectron spectroscopy (XPS) could provide supporting evidence for understanding the pathways of the reductive dissolution of PbO\textsubscript{2}.

Bacteria are ubiquitous in the environment and biofilms can form in lead service lines. Investigation of the interactions between the biofilm and lead corrosion products will provide a better understanding of the lead release in actual distribution systems. Further experiments are needed to determine the impact of biofilm on the formation and dissolution of lead corrosion products including PbO\textsubscript{2} and to quantify the kinetic parameters of the PbO\textsubscript{2} dissolution in the presence of a biofilm.

Galvanic corrosion can be present following PLSLRs and its impact strongly depends on the presence of the corrosion products and the water chemistry. Characterization of the
composition and spatial distribution of the corrosion products in the pipe scales will be important to understand and predict the susceptibility of the pipes to galvanic corrosion. To best represent actual field PLSLRs, long-term experiments with actual waters from distribution systems are required to evaluate the extent and duration of galvanic corrosion. In addition, to extend the results obtained from the present study to different distribution systems, future experiments are needed to quantify the impact of galvanic corrosion over a wider variety of water chemistry parameters including pH, alkalinity, and total dissolved solids.
Appendix A. Effect of Cations on the Dissolution of PbO₂

A.1 Introduction

Lead(IV) oxide (PbO₂) has been widely found as a corrosion product in U.S. drinking water distribution systems, and its dissolution can control lead concentrations in tap water (Schock and Giani, 2004; Switzer et al., 2006). PbO₂ is a strong oxidant and reductant found in drinking water (natural organic matter (NOM), Mn²⁺, and Fe²⁺) can dramatically accelerate its dissolution (Dryer and Korshin, 2007; Lin and Valentine, 2008a; Shi and Stone, 2009a). Like other metal oxides, the dissolution of PbO₂ is surface-controlled and the dissolution rates strongly depend on the surface species that participate in the reaction.

Divalent and trivalent cations are ubiquitous and their presence may inhibit the dissolution of metal oxides. Bondietti et al. (1993) found that Cr³⁺ greatly inhibited the proton-promoted dissolution of hematite (α-Fe₂O₃) at acidic conditions, and they attributed the inhibition to strong adsorption of Cr³⁺ that blocked the surface sites of hematite from being protonated. Shi and Stone (2009b) observed that the presence of 0.1 mM Ca²⁺ decreased the rate of reductive dissolution of PbO₂ by hydroquinone by about 20%. In a recent study Cerrato et al. (2012) observed that Ca²⁺ and Zn²⁺ decreased the dissolution rate of UO₂ by orders of magnitude, and they proposed that the inhibition was due to the formation of secondary precipitates on the UO₂ surface.

Until now the role of cations on the reductive dissolution of PbO₂ was not well understood, especially at conditions relevant to drinking water distribution. Divalent cations including Cu²⁺,
Zn$^{2+}$, and Pb$^{2+}$ can strongly adsorb to metal oxide surfaces (Stumm and Morgan, 1996). Dissolved copper, much of which is present as Cu$^{2+}$, is present in the systems containing copper service lines, and Zn$^{2+}$ can be released to tap water by brass-containing materials. The primary objective of the present study was to evaluate the effect of strongly adsorbing divalent cations on the kinetics of PbO$_2$ dissolution at conditions relevant to drinking water distribution.

A.2 Materials and Methods

A.2.1 Materials

Ultrapure water (resistivity $>$18.2 MΩ·cm) was used to prepare the solutions. PbO$_2$ was purchased (Acros), and X-ray diffraction (XRD) patterns confirmed that it was pure plattnerite (β-PbO$_2$). The specific surface area of the plattnerite was 3.6 m$^2$/g as measured by BET-N$_2$ adsorption. The PbO$_2$ has three major isotopes, $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb, with quite stable relative abundance as determined by the counts for each isotope as measured by inductively coupled plasma mass spectrometry (ICP-MS) ($^{206}$Pb counts/$^{208}$Pb counts = 0.48 ± 0.01, $^{207}$Pb counts/$^{208}$Pb counts = 0.41 ± 0.01). While the isotopic composition of lead materials can vary depending on the source and the ICP-MS sensitivity may not be identical for each isotope, these ratios are similar to those of the average natural abundance of lead isotopes ($^{206}$Pb/$^{208}$Pb = 0.46 and $^{207}$Pb/$^{208}$Pb = 0.42). Reagent grade CuCl$_2$, KI, NaNO$_3$, NaHCO$_3$, NaOH, ZnCl$_2$, NaOCl solution, $^{206}$Pb standard solution, Pb standard solution (mixture of $^{206}$Pb, $^{207}$Pb and $^{208}$Pb), and concentrated HNO$_3$ were purchased (Fisher Scientific). The ratios of $^{206}$Pb counts/$^{208}$Pb counts and $^{207}$Pb counts/$^{208}$Pb counts for the Pb standard solution were quite similar to those for the PbO$_2$ ($^{206}$Pb/$^{208}$Pb = 0.48 and $^{207}$Pb/$^{208}$Pb = 0.41 from data shown later in Table A.2).
A.2.2 PbO$_2$ Dissolution Experiments

The effect of different cations on the dissolution of PbO$_2$ was investigated at room temperature (21 ± 1 °C) using 125-mL well-mixed high-density polyethylene (HDPE) batch reactors. Four sets of experiments were performed to evaluate the effect of different parameters (Table A1). For Set A, PbO$_2$ dissolution was determined in the presence of two cations at two different pH values with a fixed cation concentration. Set B aimed to determine the effect of different cation concentrations at a fixed pH. A $^{206}$Pb standard solution was used in Set C to evaluate the impact of Pb(II) on the dissolution of PbO$_2$ and to distinguish the Pb(II) initially added in the solution from that released from PbO$_2$. A model reductant iodide was added in Set D to determine if the presence of cations would affect the reductive dissolution of PbO$_2$. Control experiments in the absence of cations were also conducted for all four sets of experiments.

For each experiment, a 0.5 M NaHCO$_3$ stock solution was added to provide a dissolved inorganic carbon (DIC) concentration of 50 mg C/L. Then an aliquot of a 1 g/L CuCl$_2$, 1 g/L ZnCl$_2$, or 0.01 g/L $^{206}$Pb stock solution was added to provide the desired cation concentrations. For the experiments with iodide, aliquots of a 10 mM KI stock solution were added to provide an iodide concentration of 0.1 mM. The ionic strength was fixed at 0.01 M by addition of a 1.0 M NaNO$_3$ solution. The pH was adjusted to the target value by addition of 2% HNO$_3$ or freshly prepared 0.5 M NaOH solutions. The PbO$_2$ solids were then added to the reactor to a concentration of 0.05 or 0.1 g/L. The reactor was then sealed with caps and run for 2 to 24 hours. Samples were taken periodically, filtered with 0.22-µm polyethersulfone (PES) syringe filters, acidified to 2% HNO$_3$, and preserved for dissolved lead analysis.
Table A.1. Experimental conditions studied for the PbO$_2$ dissolution

<table>
<thead>
<tr>
<th>Set</th>
<th>pH</th>
<th>Cation Conc. (µg/L)</th>
<th>PbO$_2$ Conc. (g/L)</th>
<th>Reductant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.6, 8.5</td>
<td>Cu(II): 400 Zn(II): 400</td>
<td>0.1</td>
<td>N.A.</td>
</tr>
<tr>
<td>B</td>
<td>8.5</td>
<td>Cu(II): 100, 200, 400, 600</td>
<td>0.1</td>
<td>N.A.</td>
</tr>
<tr>
<td>C</td>
<td>8.5</td>
<td>$^{206}$Pb (II): 100, 200</td>
<td>0.05</td>
<td>N.A.</td>
</tr>
<tr>
<td>D</td>
<td>8.5</td>
<td>Cu(II): 400 Zn(II): 400</td>
<td>0.1</td>
<td>$\Gamma$: 0.1 mM</td>
</tr>
</tbody>
</table>

Table A.2. Counts of one $^{206}$Pb and one Pb standard from a typical ICP-MS run.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{206}$Pb</th>
<th>$^{207}$Pb</th>
<th>$^{208}$Pb</th>
<th>Total Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1990</td>
<td>1709</td>
<td>4026</td>
<td>7725</td>
</tr>
<tr>
<td>Pb-standard (10 µg/L)</td>
<td>52110</td>
<td>43678</td>
<td>107466</td>
<td>203255</td>
</tr>
<tr>
<td>$^{206}$Pb-standard (10 µg/L)</td>
<td>200307</td>
<td>1752</td>
<td>3480</td>
<td>205538</td>
</tr>
</tbody>
</table>

$^1$Counts may vary for different ICP-MS runs, but the ratio of $^{206}$Pb counts/$^{208}$Pb counts and $^{207}$Pb counts/$^{208}$Pb counts were stable for different runs.

A.2.3 Analytical Methods

Dissolved lead (Pb) concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500ce instrument with a detection limit of 0.1 µg/L for Pb. The method allowed simultaneous measurement of the counts of $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb. Separate calibration standards were prepared with a $^{206}$Pb standard and a Pb standard (mixtures of $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb). For the Pb standard, since $^{208}$Pb was more dominant than $^{207}$Pb and $^{206}$Pb and the ratios of $^{206}$Pb counts/$^{208}$Pb counts and $^{207}$Pb counts/$^{208}$Pb counts were stable, the counts of $^{208}$Pb were used for making the calibration curve. For the $^{206}$Pb standard, it contained almost no $^{207}$Pb and $^{208}$Pb (Table A.2), and therefore the calibration curve was acquired by linear
regression of the $^{206}$Pb counts at different concentration levels. BET-N$_2$ adsorption for surface area measurement was performed on a BET-Autosorb instrument (Quantachrome Instruments). Solution pH was measured with a glass pH electrode and pH meter (Accumet).

**A.3 Results and Discussion**

**A.3.1 Effect of pH**

The presence of 400 µg/L (6.2 µM) Cu(II) or Zn(II) inhibited the initial dissolution of PbO$_2$ at both pH 7.6 and 8.5 (Figure A.1). At pH 7.6, the dissolved lead concentrations increased over time in the absence of Cu(II) and Zn(II) and reached about 60 µg/L after 96 hours of reaction. The lead concentrations in the presence of Cu(II) or Zn(II) also increased over time, but to a lesser extent. The lead concentrations were about 20 and 30 µg/L after 96 hours of reaction for experiments at pH 7.6 with Zn(II) and Cu(II), respectively (Figure A.1a). Employing linear regression to the data of the first 48 hours, the initial dissolution rates of PbO$_2$ were calculated as $0.9$, $0.6$, and $0.4 \cdot 10^{-10}$ mol·m$^{-2}$·min$^{-1}$ for the experiments without Zn(II) and Cu(II), with Cu(II), and with Zn(II), respectively.

In the absence of additional cations, the dissolution rate of PbO$_2$ was higher at pH 8.5 than at pH 7.6. To avoid the formation of any possible lead(II) solids, including cerussite (PbCO$_3$) and hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$), experiments at pH 8.5 were conducted for 6 hours. While about 50 µg/L dissolved lead was released after 6 hours of reaction in the experiments without Cu(II) and Zn(II), lead concentrations were only about 10 µg/L for the experiments with Cu(II) or Zn(II). The initial dissolution rates based on lead concentrations of the first 6 hours were 19.4, 0.8, and $1.3 \cdot 10^{-10}$ mol·m$^{-2}$·min$^{-1}$ for the experiments without Zn(II) and Cu(II), with Cu(II), and
with Zn(II), respectively. Even more dramatically than occurred at pH 7.6, the presence of Zn(II) and Cu(II) decreased the dissolution rate of PbO₂.

Figure A.1. Dissolution of 0.1 g/L PbO₂ with 50 mg C/L DIC in the absence and presence of 0.4 mg/L Cu(II) or Zn(II) at (a) pH 7.6 and (b) pH 8.5.

Figure A.2. Initial (points) and predicted equilibrium concentrations (lines) for Zn(II) and Cu(II) solids with 50 mg C/L DIC.
The inhibitory effect of Cu(II) and Zn(II) may be due to their adsorption to or precipitation on the PbO₂ surface. Both mechanisms would block the reactive surface sites of PbO₂ from dissolution. For experiments with Zn(II) the system is undersaturated with respect to any Zn(II) solids (i.e. Zn(OH)₂ and ZnCO₃) (Figure A.2), and it is unlikely that any precipitate formed. Therefore the inhibitory effect of Zn(II) may be due to adsorption. For experiments with Cu(II) the system is supersaturated with respect to the Cu(II) solid Cu₂(OH)₂CO₃ at both pH 7.6 and 8.5 (Figure A.2). However, no precipitation was observed in the PbO₂-free control experiments. Since adsorption is a rapid process that would drive dissolved Cu(II) concentration below saturation and the effect of Cu(II) was so similar to that of Zn(II), the inhibitory effect of Cu(II) may also be attributed to adsorption.

A.3.2 Effect of Cu(II) Concentration

The dissolution of PbO₂ in the presence of various initial Cu(II) concentrations was evaluated at pH 8.5 (Figure A.3). The presence of 100 µg/L Cu(II) (1.6 µM) inhibited the extent of the dissolution for 6 hours by an order of magnitude. Increasing the Cu(II) concentration did not further inhibit PbO₂ dissolution. For the experiment with 100 µg/L Cu(II) the system was undersaturated with respect to the Cu(II) solid Cu₂(OH)₂CO₃, and the inhibitory effect was due to adsorption of Cu(II). Because of the similar inhibitory effect for higher Cu(II) concentrations, and that no precipitation was observed in the PbO₂-free control experiments, results indicated that even for conditions initially favoring the formation of Cu₂(OH)₂CO₃, the inhibitory effect was probably due to Cu(II) adsorption.

Increasing the initial Cu(II) concentrations increased the adsorption density of Cu(II) by PbO₂. The equilibrium relationship between dissolved and adsorbed Cu(II) concentrations was
fitted using the Langmuir isotherm, and a maximum adsorption capacity of 57 µmol/g was determined (Figure A.4). Increasing the initial Cu(II) concentrations from 100 to 600 µg/L increased the adsorption density of Cu(II) by a factor of four, but this four-time enhancement did not further inhibit the dissolution of PbO₂. These results suggest that not all PbO₂ surface sites contribute equally to dissolution and that PbO₂ dissolution may be primarily controlled by some reactive surface sites that are the same ones to which Cu(II) adsorption occurred first. Cu(II) may primarily be adsorbed to these reactive surface sites, thus inhibiting the dissolution.

![Graph](image)

**Figure A.3.** Dissolution of 0.1 g/L PbO₂(s) with 50 mg C/L DIC in the presence of 0, 0.1, 0.2, 0.4, and 0.6 mg/L Cu(II) at pH 8.5.

### A.3.3 Effect of Pb(II)

The effect of different Pb(II) concentrations on the dissolution of PbO₂ was determined at pH 8.5. Unlike Cu(II) and Zn(II), Pb(II) may be released from the reductive dissolution of PbO₂. Since the Pb(II) released from PbO₂ is a mixture of three Pb isotopes (i.e. ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb)
with a stable relative abundance, a $^{206}$Pb-only stock solution was initially added to the reactors as a spike to determine the effect of Pb(II) adsorption on PbO$_2$ dissolution. $^{208}$Pb(II) was only released from PbO$_2$ and was not present in the $^{206}$Pb(II) spike, and therefore the concentrations obtained from the $^{208}$Pb calibration curve represented the amounts of Pb(II) released from PbO$_2$. Both the initial added Pb(II) spike and the Pb(II) released from PbO$_2$ contained $^{206}$Pb, and the ratio of $^{206}$Pb counts/$^{208}$Pb counts was 0.48 for the Pb(II) released from PbO$_2$. Therefore the counts of $^{206}$Pb from the initial $^{206}$Pb(II) spike can be calculated as:

$$\text{Counts of } ^{206}\text{Pb (spike)} = \text{Counts of } ^{206}\text{Pb (total)} - 0.48 \times \text{Counts of } ^{208}\text{Pb}$$  \hspace{1cm} (A.1)

The concentration of lead contributed by the $^{206}$Pb(II) spike can then be calculated using the calibration standards of $^{206}$Pb and the counts of $^{206}$Pb (spike) acquired from Equation A.1.

The addition of the $^{206}$Pb(II) spike inhibited the dissolution of PbO$_2$ at pH 8.5. After the

![Figure A.4. Adsorption of Cu(II) onto 0.1 g/L PbO$_2$(s) in the presence of 50 mg C/L DIC as a function of the equilibrium dissolved Pb(II) concentrations. The dash line represents the prediction from Langmuir isotherm.](image)
$^{206}\text{Pb(II)}$ spike was added to the solution, it adsorbed to the surface of PbO$_2$ rapidly, and almost 100% adsorption was achieved after 2 hours of reaction for experiments both with 100 µg/L (0.5 µM) and 200 µg/L (1.0 µM) $^{206}\text{Pb(II)}$ (Figure A.5). Compared to that in the absence of $^{206}\text{Pb(II)}$ spike, addition of 100 µg/L $^{206}\text{Pb(II)}$ decreased the extent of lead release from PbO$_2$ by roughly 50% after 6 hours of reaction; increasing the Pb(II) concentration to 200 µg/L decreased the extent by an order of magnitude. As with Cu(II) and Zn(II) the inhibitory effect is probably due to adsorption of Pb(II) to the PbO$_2$ surface to block reactive surface sites.

![Figure A.5](image)

**Figure A.5.** Dissolution of 0.05 g/L PbO$_2$(s) with 50 mg C/L DIC in the presence of (a) 0.1 and (b) 0.2 mg/L initially added $^{206}\text{Pb(II)}$ spike at pH 8.5. Diamond dots (♦) represent lead released from PbO$_2$ without the addition of the $^{206}\text{Pb(II)}$ spike, black square dots (■) represent lead release from PbO$_2$ in the presence of the $^{206}\text{Pb(II)}$ spike, and white square dots (□) denote the concentrations of the initially added $^{206}\text{Pb(II)}$ spike.

### A.3.4 Dissolution of PbO$_2$ with Iodide

The addition of Cu(II) or Zn(II) significantly inhibited the dissolution of PbO$_2$ by iodide at pH 8.5 (Figure A.6). Iodide has been proven as an effective reductant to accelerate the dissolution of PbO$_2$ (Lin et al., 2008; Wang et al., 2012b). In the absence of Cu(II) and Zn(II), lead concentrations increased to about 280 µg/L after 1 hour of reaction and then decreased. At
this condition dissolution was so extensive that the solution became oversaturated with respect to hydrocerussite and it is likely that hydrocerussite formed and resulted in the decrease of dissolved lead concentrations after 1 hour. Therefore only the data for the first hour were used to acquire the initial dissolution rate of PbO₂. Employing linear regression to the data of the first hour, the initial dissolution rate in the presence of 10 mM iodide was $4.5 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$. The steady-state dissolution rate of PbO₂ with 20 µM iodide was reported as $2.0 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$ for measurements made using a flow-through approach (Wang et al., 2012b). The initial dissolution rate can be much higher than the steady-state dissolution rate due to the presence of labile phases. In addition, the much higher iodide concentration in the present study would also result in a higher dissolution rate. Addition of 400 µg/L Cu(II) or Zn(II) decreased the dissolution rate of PbO₂ by more than an order of magnitude. The initial dissolution rates in the

![Figure A.6. Dissolution of 0.1 g/L PbO₂(s) with 50 mg C/L DIC and 10 mM iodide in the absence and presence of 0.4 mg/L Cu(II) and Zn(II) at pH 8.5.](image-url)
presence of Cu(II) and Zn(II) were 3.0 and 1.0 \cdot 10^{-9} \text{ mol \cdot m}^{-2} \cdot \text{min}^{-1}, respectively.

The inhibitory effect may be attributed to the adsorption of Zn(II) and Cu(II). It has been suggested that the first step in PbO_2 reduction by iodide is the adsorption of iodide onto the PbO_2 surface (Wang et al., 2012b). The presence of Zn(II) or Cu(II) would compete with iodide for the available surface sites of PbO_2. At pH 8.5, the PbO_2 surface is negatively charged and it is expected that the adsorption of Zn(II) and Cu(II) would be much stronger than that of iodide. Therefore Zn(II) and Cu(II) adsorption would passivate the surface and block the reactive surface sites.

A.4 Conclusions

Batch experiments were conducted to determine the effect of different cations (Pb(II), Cu(II), and Zn(II)) on the dissolution of PbO_2 at pH 7.6 and 8.5. The presence of cations inhibited the dissolution of PbO_2, and the effect was more dramatic at pH 8.5 than at pH 7.6. Increasing the Cu(II) concentrations from 100 to 600 \mu g/L did not further decrease the dissolution rate of PbO_2. Even in the presence of the potent reductant iodide, the presence of Cu(II) and Zn(II) decreased the dissolution rate by an order of magnitude. The inhibitory effect was primarily due to the adsorption of the cations to the surface of PbO_2 that blocked the reactive surface sites.
Appendix B. Effect of Low-Lead Brass and Orthophosphate on Lead Release following Simulated Partial Lead Service Line Replacement

B.1 Introduction

Brass transition couplings are typically used to connect aged lead pipes and new copper tubing in the partial lead service line replacement (PLSLR) process. In this approach lead and copper can be electrically connected, which may cause galvanic corrosion of the lead pipe and result in an enhancement of lead release to tap water. In addition, lead may also be released directly from the brass. Under recent federal legislation the lead content for water distribution and plumbing components in contact with drinking water will be limited to not more than 0.25% by weight for the wetted materials of components. This is a reduction from the current limit of 8.0% for water distribution system components, and 4.0% for plumbing components permitted under the Safe Drinking Water Act. This requirement will apply to the brass couplings used in PLSLRs and therefore the low-lead brass fittings will be used in future replacements instead of conventional brass couplings.

Orthophosphate has been widely added to tap water to inhibit lead corrosion (McNeill and Edwards, 2002). The effect of orthophosphate on lead release following PLSLRs has been evaluated in only a few lab experiments. Arnold et al. (2011b) determined lead release by connecting lead pipes and copper tubing with external electrical wires at various alkalinitities and concentrations of natural organic matter (NOM). They found that orthophosphate only mitigated
lead release at a high alkalinity without NOM. By connecting aged lead pipes and copper tubing with brass couplings, Cartier (2012) found that addition of orthophosphate did not decrease the lead concentrations. The impact of orthophosphate may greatly depend on the water chemistry of the distribution system. Until now the conditions over which the addition of orthophosphate could protect the lead pipes from galvanic corrosion are not known.

The primary objectives of the present study were to (1) determine the extent of galvanic corrosion following the connection of lead pipes to copper tubing with low-lead brass couplings and (2) determine whether orthophosphate could mitigate lead release from galvanic corrosion at one particular water chemistry. A secondary objective was to evaluate the lead release directly from the low-lead brass. Experiments were performed in a recirculating flow mode with intermittent stagnation periods. Lead pipes harvested from two distribution systems (Providence, RI and Washington, DC) were used in the experiments with aqueous solutions prepared to simulate the water chemistry of these two distribution systems.

**B.2 Materials and Methods**

**B.2.1 Materials**

Two aged lead pipes harvested from the DC distribution system and four from the Providence distribution system were received and used in laboratory experiments. These pipes have been used for over 100 years. For the DC pipes, the inner and outer diameters were 0.75 and 1.2 inches, respectively. The corrosion products in the pipe scales were hydroxylpyromorphite (Pb₅(PO₄)₃OH), scrutinyite (α-PbO₂), and plattnerite (β-PbO₂). These two pipes were given identification codes of 1 and 4b based on their harvested address. For the Providence pipes, the inner diameter was 0.625 inches and outer diameter was 1.188 inches.
Plumbonacrite ($\text{Pb}_{10}(\text{CO}_3)_6(\text{OH})_{10}\text{O}$) was observed as the dominant corrosion product in the pipe scales. These four pipes were used in a previous experiment that was described in Chapter 5 and were given identification codes of 1A, 9A, 1B, and 2B.

Type K copper tubing with inner diameters of 1 inch and outer diameters of 1.125 inches were cut to 24-inch sections (McMaster-Carr). Chlorinated polyvinyl chloride (CPVC) pipe sections (1 inch) (McMaster-Carr) with 24-inch lengths were used in lead pipe-free control experiments. Couplings donated for use in the experiments were low-lead brass compression fittings that would comply with the new requirements for lead in brass used in water system components (A.Y. McDonald). Flexible PVC couplings (Fernco), polyethylene tubing (Cole-Parmer), three-way polyethylene valves (Cole-Parmer), and 10-L polyethylene carboys (Cole-Parmer) were used in the test pipe-loop systems. Reagent grade chemicals $\text{CaCl}_2$, $\text{MgCl}_2$, $\text{MgSO}_4$, $\text{Na}_2\text{HPO}_4$, $\text{NaF}$, $\text{NaCl}$, $\text{NaHCO}_3$, $\text{NaOCl}$ solution, $\text{NaOH}$, and $\text{HNO}_3$ (Fisher Scientific) and ultrapure water (resistivity > 18.2 MΩ-cm) were used to prepare the synthetic tap waters used in the experiments.

**B.2.2 Conditioning**

Before being connected to the copper tubing, the DC and Providence lead pipes were conditioned with water prepared to simulate the DC and Providence distribution system water chemistry, respectively (Table B.1). The pipes were first conditioned in a static “dump-and-fill” mode for 12 (Providence pipes) and 31 weeks (DC pipes) using the procedures described in Chapter 5. Then the pipes were conditioned in a recirculating flow apparatus with intermittent periods of stagnation for three weeks. The pattern of flow during the recirculating flow mode is the same as that described in Chapter 5. Samples were collected periodically and concentrations
of total and dissolved (filtered through 0.45 µm polyethersulfone (PES) syringe filters) lead were analyzed.

**Table B.1. Water composition of synthetic DC and Providence water**

<table>
<thead>
<tr>
<th>Water Composition parameter</th>
<th>Washington DC Actual Range$^1$</th>
<th>Synthetic water</th>
<th>Providence, RI Actual Range</th>
<th>Synthetic water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7 to 7.8</td>
<td>7.7</td>
<td>9.5 to 9.9</td>
<td>9.6 to 9.8</td>
</tr>
<tr>
<td>Free chlorine, mg/L as Cl$_2$</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.16 to 0.50</td>
<td>0.42</td>
</tr>
<tr>
<td>Combined chlorine, mg/L as Cl$_2$</td>
<td>3.6 to 3.8</td>
<td>3.7</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Total alkalinity, mg/L as CaCO$_3$</td>
<td>49 to 99</td>
<td>76</td>
<td>9.3 to 16.3</td>
<td>12.0</td>
</tr>
<tr>
<td>TDS, mg/L</td>
<td>126 to 261</td>
<td>310</td>
<td>97 to 113</td>
<td>113</td>
</tr>
<tr>
<td>Total hardness, mg/L as CaCO$_3$</td>
<td>114 to 155</td>
<td>128</td>
<td>34.3 to 44</td>
<td>38.5</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>30 to 56</td>
<td>34</td>
<td>17.3 to 22.4</td>
<td>19.4</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>40 to 71</td>
<td>50</td>
<td>20.0 to 24.0</td>
<td>21.8</td>
</tr>
<tr>
<td>Orthophosphate, mg/L as PO$_4$</td>
<td>2.4 to 2.8</td>
<td>2.5</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

$^1$ The ranges are for the Dalecarlia Water Treatment Plant

**B.2.3 Coupling Experiments**

After being conditioned in the recirculating flow mode for three to four weeks, the lead pipes were connected to copper tubing using the low-lead brass couplings and placed in the recirculating flow system (Figure B.1). Electrical continuity between the lead pipe and copper tubing was tested by measuring the electrical resistance between the two metals with a digital multimeter (BK Precision). As expected little resistance was observed for the low-lead brass-coupled copper-lead pipe assemblies. Two sets of experiments were conducted and the timeline is listed in Table B.2. Each experiment was conducted for six weeks.

In the first set of experiments, synthetic DC water was used. The two DC pipes that were connected to copper tubing are referred to as DC-1 and DC-2. To test for lead release from the
couplings and potential unexpected sources, control experiments were performed using CPVC pipes connected to copper tubing with the low-lead brass couplings. To further distinguish lead release from the low-lead brass couplings from other unexpected sources, the low-lead brass couplings were bypassed during one week of the experiment.

**Table B.2.** Timeline of the experiments conducted in the recirculating flow mode

<table>
<thead>
<tr>
<th>Set (Water chemistry)</th>
<th>Connection methods(^1)</th>
<th>Experimental dates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(3 weeks)</td>
</tr>
<tr>
<td>Set 1 (DC)</td>
<td>Cu – PVC</td>
<td>Conditioning of lead pipe(^2)</td>
</tr>
<tr>
<td></td>
<td>Cu – Pb</td>
<td>Conditioning of lead pipe(^3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>w/ low-lead brass</td>
</tr>
<tr>
<td>Set 2 (Providence)</td>
<td>Cu – Pb</td>
<td>Conditioning of lead pipe(^3)</td>
</tr>
</tbody>
</table>

\(^1\)Duplicate experiments were conducted.

\(^2\)Conditioning was conducted in the recirculating flow mode. The lead pipes were conditioned in the “dump-and-fill” mode for 31 weeks before placed in the recirculating flow apparatus.

\(^3\)Conditioning was conducted in the recirculating flow mode. The pipes were used in the experiments in Chapter 5 in January-June, 2011, and then had been stored with water in them through April 2012. Then the pipes were conditioned in the “dump-and-fill” mode for 7 weeks before placed in the recirculating flow apparatus.

Synthetic Providence water was used in the second set of experiments. At the time of connecting the Providence lead pipes to copper tubing, for two pipes (1A and 2B) orthophosphate was added to the water to provide a concentration of 2.5 mg/L as PO\(_4\), and these two assemblies are referred to as Prov-P-1 and Prov-P-2. No orthophosphate was added to the other two pipe assemblies (Pipes 1B and 9A), which are referred to as Prov-C-1 and Prov-C-2. Pipes 1A and 9A were previously connected to copper tubing with plastic couplings and Pipes 1B and 2B were with brass couplings in the experiments in Chapter 5.
Figure B.1. Experimental system with lead pipes and copper tubing connected with low-lead brass couplings.

The same flow cycle and sampling sequence used in Chapter 5 were used. Samples after 6-h stagnation were collected on Mondays and Thursdays, and 65-h stagnation samples were collected after weekend stagnation. The water in the recirculating reservoirs was replaced each Monday morning with freshly prepared water. The old reservoir was then acidified to pH < 2 by addition of nitric acid for solubilization of any lead that had collected in the reservoir over the preceding week. A profile sampling approach was performed once for the copper-CPVC pipe assemblies during the six weeks of the experiments. In this approach, seven consecutive 70-mL samples were collected for each copper-CPVC pipe assembly after 6 hours of stagnation. This sampling approach investigated possible localization of lead release along the pipe sections. For each sample, 10 mL was used for total lead and copper analysis, 10 mL for dissolved lead and copper, and the remaining 30 mL for pH and total chlorine measurement. The concentration of orthophosphate was also measured for selected samples.
B.2.4 Analytical Methods

Concentrations of lead and copper were measured by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7500ce). The samples were acidified to 2% HNO₃ before analysis. Chlorine (free and combined chlorine) and orthophosphate concentrations were determined by the standard DPD and ascorbic acid colorimetric methods (4500-Cl G and 4500-P E) with a spectrophotometer (PerkinElmer Lambda XLS+). Solution pH was measured with a glass pH electrode and pH meter (Accumet).

B.3 Results and Discussion

B.3.1 Lead Release from Pipe Conditioning

Conditioning of the pipes was performed to allow the pipe scales to recover from any effects associated with harvesting and shipment prior to their connection to copper tubing. In the recirculating flow mode, the lead concentrations following the 6-h stagnation periods are shown in Figure B.2. For the Providence pipes, the total and dissolved lead concentrations were quite similar, suggesting that only limited amounts of particulate lead were released during conditioning (shown as Conditioning 2012 in Figure B.2a). The average dissolved lead concentrations were in the range of 40 – 50 µg/L; these values were close to the predicted dissolved lead concentrations in equilibrium with plumbonacrite, which were estimated as 50 – 60 µg/L at pH 9.4 to 9.8. For the two DC pipes (Pipe 1 and 4b), the dissolved lead concentrations were around 8 µg/L. Based on the available equilibrium constants (Benjamin, 2002), the predicted dissolved lead concentration in equilibrium with hydroxylpyromorphite was 9 µg/L.
Figure B.2. Lead in recirculating conditioning. Average dissolved and total lead concentrations in the effluent after 6-h stagnation in the recirculating-flow conditioning mode for (a) Providence and (b) DC pipes. Error bars represent one standard deviation. For the DC pipes, Pipes 2a, 2b, 3a, 4a, 4c, and 4e were conditioned in the “dump-and-fill” mode for 8 – 21 weeks; while Pipes 1 and 4b were conditioned in the “dump-and-fill” mode for 31 weeks.
Results suggested that for both DC and Providence pipes, the stagnant water in the pipes was close to equilibrium with respect to the dominant corrosion product in the pipe scales.

The time of conditioning in the “dump-and-fill” mode affected the lead concentrations in the recirculating conditioning mode. Longer conditioning time in the “dump-and-fill” mode decreased both the total and dissolved lead concentrations in the recirculating flow mode and made the dissolved lead concentrations closer to the predicted equilibrium solubility of the dominant corrosion products. The Providence pipes were previously conditioned in the recirculating flow mode (shown as Conditioning 2011 in Figure B.2a) and then used in the experiment in Chapter 5. Both the total and dissolved lead concentrations were stable with an average value around 80 µg/L during the conditioning for the experiments presented in Chapter 5.

Then the pipes were stored with synthetic Providence water for a year, and then conditioned in the “dump-and-fill” mode for 12 weeks before conducting the present experiments. The one-year of additional contact with the water and the 12 extra weeks of conditioning may further stabilize the pipe scales and result in a decrease of the lead concentrations in the recirculating flow conditioning in the present work. For the DC pipes, six pipes (2a, 2b, 3a, 4a, 4c, and 4e) were conditioned in the “dump-and-fill” mode for 8 to 21 weeks and then used in the experiments of Chapter 6. The total lead concentrations were about 15 – 20 µg/L in the recirculating flow mode for these pipes (Figure B.2b). The two pipes in the present experiment (1 and 4b) were conditioned in the “dump-and-fill” mode for 31 weeks and the total lead concentrations in the recirculating flow mode were lower at about 10 µg/L. Results were consistent with those acquired from the Providence pipes suggesting that longer stagnation time decreased lead concentrations.
B.3.2 Lead Release from the Low-lead Brass Coupling

In the copper-CPVC pipe assemblies with the water chemistry of the Washington DC distribution system, less than 5 µg/L dissolved lead was released after either 6-h or 65-h stagnation (Figure B.3). Previous experiments conducted in our lab observed that 10 – 30 µg/L dissolved lead was released from the conventional brass or brass-dielectric couplings (that is, brass couplings with the current permissible lead content). As anticipated much less lead was released from the low-lead brass couplings than from the conventional brass or brass dielectric couplings.

Lead concentrations in the low-lead brass-coupled systems were similar to those in the plastic-coupled systems (Figure B.3). Ideally the brass coupling would be the only source of lead; however, the approximately 5 µg/L lead concentration in the plastic-coupled copper-PVC systems suggested that sources other than the couplings may be present and contribute to the lead release. To distinguish lead release from the low-lead brass from release from other sources, the low-lead brass-coupled copper-CPVC pipe assemblies were bypassed for one week. In the bypassed systems the water was still circulated through the reservoir, tubing, and three-way sampling valves (Figure B.1). Both the dissolved and total lead concentrations for this bypassed system were lower than without bypassing the brass couplings, except for the total lead after 65 hours of stagnation (Figure B.3). Although lead release from the low-lead brass-coupled system was generally higher than from the bypassed system, the difference was not very large. By comparing the lead concentrations in the bypassed and un-bypassed systems, the low-lead brass coupling may be determined to at most release 1 µg/L total lead after 6 or 65 hours of stagnation. The three-way sampling valves were the most likely source of the lead in the bypassed systems, and these sampling values would also have been a source for the systems without the bypass.
Figure B.3. Lead in control experiments (no lead pipes). Average dissolved (a) and total (b) lead concentrations in the effluent after 6-h and 65-h stagnation after connecting CPVC pipes to copper tubing using low-lead brass and plastic couplings. ‘Bypass’ denotes that the pipe assemblies were bypassed. Error bars represent one standard deviation.
Some lead-containing particles may have accumulated in the three-way sampling valves in previous experiments and not been removed by the cleaning procedures performed between experiments.

A profile sampling approach was performed to evaluate lead release from the low-lead brass couplings. In this approach, samples from different zones of the pipe assemblies after one 6-h stagnation period were collected (Figure B.4). If significant lead was released from the low-lead brass coupling, then lead concentrations would be highest in Zones 4. However, the dissolved lead concentrations were similar for all zones. The total lead concentrations were more variable, but they were not consistently higher near the coupling. Results from the profile sampling indirectly indicated that little lead was released from the low-lead brass couplings.

B.3.3 Lead Release following Connection to Copper Tubing

B.3.3.1 Effect of Low-Lead Brass Coupling

Lead concentrations were monitored regularly following the connection of lead pipes to copper tubing using low-lead brass couplings for both the water chemistries of DC and Providence. Separate experiments had been conducted to determine the lead release from galvanic-free pipe assemblies by connecting lead pipes and copper tubing with plastic couplings (Providence in Chapter 5 and DC in Chapter 6). Compared to the plastic-coupled pipe assemblies, lead release was enhanced significantly for the low-lead brass-coupled pipe assemblies (Figure B.5). For the systems with DC water chemistry, about 10 µg/L total lead was released following 6-h stagnation periods for the plastic-coupled pipe assemblies; while 120 – 200 µg/L total lead was released in the low-lead brass-coupled pipe assemblies. Considering that little lead was released directly from the low-lead brass coupling, galvanic corrosion increased lead release by
Figure B.4. Profile sampling in control experiment (no lead pipe). Dissolved (a) and total (b) lead concentration after 6 hours of stagnation in different sampling regimes from experiments with CPVC pipes connected to copper tubing using low-lead brass couplings.
Figure B.5. Total lead in experiments with lead pipes connected to copper tubing. Average total lead concentrations for (a) DC pipes and (b) Providence pipes after 6-hour and 65-hour stagnation times. Error bars represent one standard deviation.
12 – 20 times. Increasing the stagnation time to 65 hours further enhanced lead release by 10% and 160% for the duplicates. For the system with Providence water chemistry, lead release from the low-lead brass-coupled pipe assemblies were 3 – 5 times and 6 – 12 times that from the plastic-coupled pipe assemblies following 6-h and 65-h stagnation, respectively. For both the systems with DC and Providence water chemistry, the lead concentrations were stable over the six weeks of the experiments, which suggested that galvanic corrosion could persist for at least six weeks.

The distribution of total lead between particulate and dissolved was determined for the low-lead brass-coupled pipe assemblies with both DC and Providence water chemistry (Figure B.6). Particulate lead was more abundant than dissolved lead following 6-h stagnation periods, except for Prov-C-2 where more dissolved lead was released. Increasing the stagnation time to 65 hours significantly increased the particulate lead release but only slightly enhanced the dissolved lead release. For all the pipe assemblies particulate lead was more dominant after 65 hours of stagnation. Results suggested that galvanic corrosion primarily enhanced particulate lead release, especially after longer stagnation time. The high level of particulate lead in the pipes may be due to two reasons. The first is the creation of local dissolved lead concentrations that were high enough to exceed the saturation of some lead(II) minerals, thus causing the precipitation of secondary solids and increasing particulate lead. The second is the destabilization of the pipe scales that could cause portions of the scales to break off and be released to the water.
Figure B.6. Distribution of lead between dissolved and particulate forms following stagnation periods during Weeks 1 to 6 of experiments with lead pipes connected to copper tubing using low-lead brass couplings. The labels on the x-axis indicate the day of the week and the week of the experiment. Weekend (Wknd) samples had 65 hours of stagnation and all other samples were after 6 hours of stagnation.
B.3.3.2 Effect of Orthophosphate

Addition of orthophosphate inhibited lead release from the low-lead brass-coupled pipe assemblies with Providence water chemistry (Figure B.7). Compared to that without orthophosphate, addition of 2.5 mg/L as PO$_4$ orthophosphate decreased the average dissolved and total lead concentrations by 55% and 60%, respectively, following 6-h stagnation periods. Addition of orthophosphate dropped both the dissolved and total lead concentrations to levels similar to those for the plastic-coupled pipe assemblies. It should be noted that the four pipes with low-lead brass fittings had been conditioned in the static “dump-and-fill” mode for much longer time than those with plastic couplings. Therefore the concentrations of the four pipes with low-lead brass fittings in the recirculating flow mode were actually lower than those of the pipes with plastic couplings (Figure B.2a). Although this difference may affect the direct comparison of the lead concentrations in the plastic-coupled and low-lead brass-coupled pipe assemblies, results still suggested that orthophosphate may be able to mitigate lead release due to galvanic corrosion, at least for the Providence water chemistry with a high pH (9.8) and low alkalinity (12.0 mg/L as CaCO$_3$).

Orthophosphate is often recommended for use at pH values closer to neutral where the reductions in solubility can be about two orders of magnitude, but based on equilibrium models, the calculated decrease in solubility is still about an order of magnitude at pH 9-10. Orthophosphate may limit lead release by forming the very low solubility lead(II) phosphate solid hydroxylpyromorphite. However, in the present study, even for the systems with orthophosphate, the dissolved lead concentrations were one order of magnitude above the equilibrium solubility of hydroxylpyromorphite, and were actually still close to the equilibrium solubility of plumbonacrite (Figure B.8). The formation of a lead(II) phosphate scale that could
Figure B.7. Lead concentrations in the absence and presence of orthophosphate. Average (a) dissolved and (b) total lead concentrations after both 6-hour and 65-hour stagnation times following the connection of Providence pipes to copper tubing. The pipes with low-lead brass fittings had been conditioned much longer than the pipes with plastic couplings. Error bars represent one standard deviation.
possibly control lead concentrations at even lower values may take longer than six weeks.

Washington DC added orthophosphate to control their lead concentrations in 2004 and observed that the lead concentrations started to drop below the action level after about four months of adding 3.5 mg/L as PO$_4$ orthophosphate. Further characterization of the corrosion products for the systems with orthophosphate would help in understanding the composition of the scales.

![Figure B.8](image)

**Figure B.8.** Predicted equilibrium solubility. Average dissolved lead concentrations in the experiments with Providence lead pipes connected to copper tubing (points) and predicted lead concentrations in equilibrium with different corrosion products (lines).

Although lead concentrations were higher than the predicted equilibrium solubility of hydroxylpyromorphite, the addition of orthophosphate still mitigated lead release due to galvanic corrosion in the present study. Two previous studies determined the effect of orthophosphate on the extent of galvanic corrosion and found that addition of orthophosphate did not protect the
lead pipes against galvanic corrosion (Arnold et al., 2011; Cartier, 2012). The different conclusions may be attributed to major differences between the water chemistry in the present study and in those previous studies. Experiments for both of the two previous studies were conducted at relatively neutral pH (7.3 for Arnold et al and 7.7 for Cartier); while the present experiments were performed at a higher pH of 9.8. Gregory (1990) suggested that galvanic corrosion could be more severe with decreasing pH. In addition, chloride-to-sulfate mass ratio (CSMR) has been reported as an important parameter for galvanic corrosion (Edwards and Triantafyllidou, 2007; Gregory, 1990; Nguyen et al., 2010b; Triantafyllidou and Edwards, 2011a). The CSMR was about 0.9 in both the present study and Cartier’s work; while Arnold et al. used a much higher CSMR of 2.5. Increasing the CSMR can accelerate lead release from galvanic corrosion (Edwards and Triantafyllidou, 2007; Gregory, 1990; Nguyen et al., 2010b; Triantafyllidou and Edwards, 2011a).

**B.4 Conclusions**

Lead release after connecting lead pipes to copper tubing with low-lead brass couplings was investigated using aged lead pipes harvested from Washington DC and Providence. By conducting the experiments for six weeks in a recirculating flow mode with intermittent stagnation periods, the following conclusions were acquired.

- For both the DC and Providence water chemistry, compared to the plastic-coupled pipe assemblies, lead release was greatly enhanced after lead pipes were connected to copper tubing with low-lead brass couplings. The enhancement of lead release can be attributed to galvanic reactions. Lead concentrations did not decrease over the six weeks of the
experiments, suggesting that galvanic reaction was not a transient effect and persisted at least for six weeks.

- For the systems with Providence water chemistry, addition of orthophosphate effectively decreased lead concentrations in the low-lead brass-coupled pipe assemblies. Results indicated that the presence of orthophosphate may mitigate lead release due to galvanic corrosion for a system with water chemistry similar to that of Providence.

- Very little lead was released directly from the low-lead brass couplings with lead concentrations of 1 µg/L or less being attributable to release from the coupling.
Appendix C. Dissolution Rate Equation

Derivation

During the flow-through experiments, the dissolution rate of PbO$_2$ can be quantified by performing a lead mass balance on the continuously stirred tank reactor (CSTR) (Equation 1),

\[
\frac{dm}{dt} = V_R \cdot \frac{dC}{dt} = QC_{in} - QC + r_{exp} \cdot A \cdot [\text{solids}] \cdot V_R
\]

where

- \( m \) = mass of lead (mol)
- \( t \) = time (min)
- \( V_R \) = reactor volume (L)
- \( Q \) = volumetric flow rate (L·min$^{-1}$)
- \( C \) = concentration of lead in the effluent (mol·L$^{-1}$)
- \( C_{in} \) = lead concentration in the influent (mol·L$^{-1}$)
- \( r_{exp} \) = dissolution rate (mol·m$^{-2}$·min$^{-1}$)
- \( A \) = specific surface area of the solid (m$^2$·g$^{-1}$)
- \([\text{solids}]\) = solid concentration in the reactor (g·L$^{-1}$)

From Equation 1, the experimental dissolution rate can be derived as a function of flow rate, reactor volume, and lead concentrations in the effluent and influent in the following equation when the reactor reaches steady state (i.e. \( \frac{dC}{dt} = 0 \)).

\[
r_{exp} = \frac{Q(C_{ss} - C_{in})}{V_R \cdot A \cdot [\text{solids}]}
\]

where

- \( C_{ss} \) = concentrations of lead in the effluent at steady state (mol·L$^{-1}$)
Since no lead is present in the influent, $C_{in}$ equals to 0. The hydraulic residence time $t_{res}$ can be defined as $V_R/Q$. The dissolution rate at steady state therefore can be simplified as:

$$r_{exp} = \frac{C_{ss}}{t_{res} \cdot A \cdot [solids]}$$

(3)
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