Lead(IV) Oxide Formation and Stability in Drinking Water Distribution Systems

Report #4211
Lead(IV) Oxide Formation and Stability in Drinking Water Distribution Systems
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Lead(IV) Oxide Formation and Stability in Drinking Water Distribution Systems

Prepared by:
Yin Wang, Yanjiao Xie, and Daniel E. Giammar
Department of Energy, Environmental and Chemical Engineering
Washington University, 1 Brookings Drive, St. Louis, MO 63130

Sponsored by:
Water Research Foundation
6666 West Quincy Avenue, Denver, CO 80235

Published by:

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FOREWORD

The Water Research Foundation (Foundation) is a nonprofit corporation dedicated to the development and implementation of scientifically sound research designed to help drinking water utilities respond to regulatory requirements and address high-priority concerns. The Foundation’s research agenda is developed through a process of consultation with Foundation subscribers and other drinking water professionals. The Foundation’s Board of Trustees and other professional volunteers help prioritize and select research projects for funding based upon current and future industry needs, applicability, and past work. The Foundation sponsors research projects through the Focus Area, Emerging Opportunities, and Tailored Collaboration programs, as well as various joint research efforts with organizations such as the U.S. Environmental Protection Agency and the U.S. Bureau of Reclamation.

This publication is a result of a research project fully funded or funded in part by Foundation subscribers. The Foundation’s subscription program provides a cost-effective and collaborative method for funding research in the public interest. The research investment that underpins this report will intrinsically increase in value as the findings are applied in communities throughout the world. Foundation research projects are managed closely from their inception to the final report by the staff and a large cadre of volunteers who willingly contribute their time and expertise. The Foundation provides planning, management, and technical oversight and awards contracts to other institutions such as water utilities, universities, and engineering firms to conduct the research.

A broad spectrum of water supply issues is addressed by the Foundation's research agenda, including resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide a reliable supply of safe and affordable drinking water to consumers. The true benefits of the Foundation’s research are realized when the results are implemented at the utility level. The Foundation's staff and Board of Trustees are pleased to offer this publication as a contribution toward that end.

Roy L. Wolfe, Ph.D.  Robert C. Renner, P.E.
Chair, Board of Trustees  Executive Director
Water Research Foundation  Water Research Foundation
ACKNOWLEDGMENTS

The authors appreciate the advice and guidance of the Project Advisory Committee (PAC) – France Lemieux, Health Canada and Becki Rosenfeldt, Hazen and Sawyer - and the Water Research Foundation Project Manager, Traci Case. Windsor Sung of the Massachusetts Water Resources Authority also provided helpful input over the course of this project. The authors acknowledge the assistance of Wenlu Li, Zimeng Wang, and Jiewei Wu in conducting selected experiments and associated analyses.
EXECUTIVE SUMMARY

OBJECTIVES

The primary objective of this project was to advance our understanding of the dynamic processes that form PbO₂ solids in drinking water distribution systems and that control their subsequent stability and dissolution. Three specific objectives were pursued.

1. Identify threshold values of water chemistry parameters that govern the formation of PbO₂ and control which PbO₂ solid (plattnerite vs. scrutinyite) is produced.
2. Establish the equilibrium solubility of PbO₂ solids at conditions for which lead remains in the +IV oxidation state.
3. Elucidate the mechanisms and quantify the rates of the coupled processes of PbO₂ reduction and dissolution.

BACKGROUND

Lead release from pipes in distribution systems is a serious threat to public health. The observations of extremely high lead levels in Washington D.C. tap water in 2000-2004 illustrate the importance of this problem (Edwards and Dudi 2004; Renner 2004; U.S. Environmental Protection Agency 2007b). Research can contribute to the scientific basis for corrosion control strategies and help the water supply community meet the challenge of an aging infrastructure.

Lead concentrations in drinking water are affected by chemical reactions that occur within the distribution system. Of particular relevance to management of lead concentrations are the reactions that control the formation and stability of lead(IV) oxides (PbO₂ solid phases of scrutinyite and plattnerite). PbO₂ solids form at the high oxidation-reduction potential induced by residual free chlorine, and such solids have been observed as constituents of scales of lead corrosion products that develop on lead pipes (Schock et al. 2001; Edwards and Dudi 2004; Lytle and Schock 2005). The PbO₂ solids have low solubility. As long as a sufficiently high oxidation-reduction potential is maintained, dissolved lead concentrations remain at low levels. However, when the oxidation-reduction potential is lowered, as can occur when switching to chloramine as a residual disinfectant, the PbO₂ is no longer stable and its reduction releases lead to the water. Even when oxidizing conditions are present, the actual solubility of PbO₂ phases is imprecisely known.

Information on the dissolution rates of PbO₂ is particularly valuable as water suppliers consider process changes that affect water chemistry such as switching disinfectant type or dose, adjusting pH, or adding a corrosion inhibitor. Recent research linked the high lead concentrations in the Washington D.C. service area from 2000-2004 to the breakdown of PbO₂ solids following a change in the residual disinfectant from free chlorine to chloramine (Edwards and Dudi 2004; Renner 2004; U.S. Environmental Protection Agency 2007b). For other utilities that are considering switching from free chlorine to chloramine, information is needed on the rates and mechanisms of PbO₂ dissolution as a function of water chemistry. Orthophosphate has been demonstrated to decrease dissolved lead concentrations for systems using chloramine (Edwards and McNeill 2002; U.S. Environmental Protection Agency 2007b). Strategies that
inhibit PbO₂ dissolution and minimize lead release can be optimized based on an understanding of the effects of water chemistry on lead release rates.

**APPROACH**

The project was divided into three integrated tasks that corresponded to the three research objectives (Figure ES.1). The tasks progressed from (1) the formation of PbO₂, to (2) the stability of PbO₂ in equilibrated systems, and finally to (3) the rates of dissolution of PbO₂. All tasks integrated dissolved phase analysis with characterization of the structures and compositions of the solid phases; this approach facilitated observation of macroscopic precipitation and dissolution processes while developing a mechanistic basis for those processes.

![Figure ES.1 Integrated approach to investigate dynamics of PbO₂ in distribution](https://example.com/figure_es1.png)

**Task 1: Critical Water Chemistry Thresholds for the Formation of PbO₂**

The impact of water chemistry on the extent of PbO₂ formation and the identity of the PbO₂ phases formed was evaluated in a series of bench-scale laboratory experiments. The formation of PbO₂ by the oxidation of different lead(II) and lead(0) precursors in water was investigated as a function of free chlorine concentration, pH, dissolved inorganic carbon (DIC), and time. Experiments were performed with five different precursor materials: elemental lead(0) powder, dissolved lead(II) chloride (PbCl₂), the lead(II) oxide massicot (β-PbO), the lead(II) carbonate cerussite (PbCO₃), and the lead(II) hydroxy carbonate hydrocerussite (Pb(OH)₂(CO₃)₂). Aqueous and solid phase samples were collected over reaction times up to 28 days. The presence of PbO₂ in the products of the reaction was identified using scanning electron microscopy (SEM) and X-ray diffraction (XRD). These methods were also used to identify intermediate products of the reaction that could influence the rate of PbO₂ formation and the identity of the specific PbO₂ solid that formed (scrutinyite versus plattnerite).

**Task 2: Determination of Equilibrium Solubility of PbO₂**

The dissolved lead concentrations achieved in aqueous solutions equilibrated with the two PbO₂ polymorphs, scrutinyite and plattnerite, were measured as a function of pH at free
chlorine concentrations designed to keep lead in the +IV oxidation state. Batch experiments were conducted with pure forms of plattnerite and scrutinyite. Filtered samples were collected over time to determine the concentration at which dissolved lead stabilized and the time to reach that stable state. Solids were also collected and characterized by XRD and SEM to probe for any transformations of the solids that might have occurred during the equilibrations.

**Task 3: Coupled Reduction-Detachment Processes During Dissolution of PbO₂**

The dissolution rates of plattnerite were examined as a function of water chemistry parameters that included pH, DIC, iodide, free chlorine, and orthophosphate. Because PbO₂ is often found in systems that are not at equilibrium, information about rates and not equilibrium solubility may be more important for predicting lead concentrations in water that has been in contact with corrosion scales that contain PbO₂. Dissolution rates were quantified using continuously-stirred tank reactors loaded with plattnerite and fed influents of controlled composition. Four sets of experiments probed different impacts of water chemistry on the plattnerite dissolution rate.

- Baseline experiments with DIC over a range of pH to determine the rates in the absence of any oxidants, reductants, or corrosion inhibitors.
- Experiments with iodide as a chemical reductant and carbonate from DIC as a Pb(II)-complexing ligand to probe the mechanisms of the reductive dissolution of PbO₂ as a process involving chemical reduction and detachment.
- Experiments with free chlorine present to quantify its inhibitory effect on PbO₂ dissolution and to probe for a critical concentration required to limit lead release.
- Experiments with orthophosphate present as a potential corrosion inhibitor.

**RESULTS AND CONCLUSIONS**

The research project made significant findings regarding the formation and stability of lead(IV) oxides at conditions relevant to drinking water distribution systems. Key findings with respect to formation, equilibrium dissolved lead concentrations, and PbO₂ dissolution rates are outlined below.

**Formation of Lead(IV) Oxides**

- PbO₂ can only form in the presence of free chlorine, and the threshold free chlorine concentration for producing PbO₂ is less than 4 mg Cl₂/L.
- The formation of PbO₂ is accelerated by the presence of dissolved inorganic carbon.
- Both polymorphs of PbO₂ (plattnerite and scrutinyite) can form, and most conditions resulted in a mixture of the two phases. The identity of the Pb(II)-containing precursor could control the identity of the specific PbO₂ phase that formed.

**Dissolved Lead Concentrations in Equilibrated Solutions**

- Dissolved lead concentrations from equilibration of PbO₂ in water with free chlorine were orders of magnitude higher than predicted from published thermodynamic data.
• Low dissolved lead concentrations in chlorinated solutions were still maintained over long periods of time. It was only after long stagnation times of 4 days or longer that the action level was reached at pH 7.5 and 8.5, and the action level was never reached at pH 6.0.
• The final dissolved lead concentrations achieved upon long-term contact of plattnerite and scrutinyite with water were similar.
• Dissolved lead concentrations increased with increasing pH above pH 6 and were unaffected by the presence of DIC.

Dissolution Rates of PbO₂

• The dissolution rate and not the equilibrium solubility of PbO₂ will control dissolved lead concentrations in waters that are in contact with PbO₂ as a corrosion product for most relevant stagnation times.
• The rate of PbO₂ dissolution rate decreased with increasing pH. This is in contrast to the dissolved lead concentrations after multi-day equilibration that increased with increasing pH.
• Dissolution was strongly inhibited by free chlorine even at concentrations as low as 0.2 mg Cl₂/L.
• Orthophosphate inhibited PbO₂ dissolution with its effects limited to near-neutral pH.
• The presence of chemical reductants can significantly accelerate the dissolution of PbO₂. Dissolution of PbO₂ is a two-step process that involves chemical reduction of Pb(IV) to Pb(II) followed by detachment of Pb(II) and release to solution. For most conditions the chemical reduction steps will be rate-limiting.

APPLICATIONS AND RECOMMENDATIONS

Lead(IV) oxides (PbO₂) can be an important component of corrosion products on pipe scales for utilities that have lead service lines in their distribution systems and that currently use or have used free chlorine as the secondary disinfectant. PbO₂ can only form in systems with free chlorine present; however, because of the low solubility of this phase and the complexity of pipe scales, PbO₂ may persist well after a switch from free chlorine to chloramine. The rate of PbO₂ formation and consequently the likely extent of PbO₂ formation on lead service lines is strongly affected by the water chemistry of the distribution system. The susceptibility of PbO₂ to reductive dissolution and its likely enrichment at the surface of the pipe scale can make it a major contributor to lead release to water even when it is only present as a minor constituent of a pipe scale. The presence of PbO₂ is a more important finding than the exact identity of the form of PbO₂ (plattnerite versus scrutinyite) that is present. Both plattnerite and scrutinyite can form on lead pipes in the presence of free chlorine, but similar dissolved lead concentrations were achieved in aqueous solutions equilibrated with the two solids. When free chlorine is present, low dissolved lead concentrations below the action level can be achieved even for stagnation times of several days.

For PbO₂-containing systems without free chlorine or for which free chlorine has been depleted, dissolved lead concentrations will be controlled by the rate of the dissolution reaction and not by equilibrium solubility. The dissolution rate of PbO₂ is a very strong function of the water chemistry, and orders of magnitude differences can occur in the rates depending on the
Utilities should be aware of conditions that could accelerate the dissolution of PbO\(_2\) and the release of lead from this potential reservoir of unstable lead in scales on lead service lines. This is particularly important for systems that have recently switched from using free chlorine to chloramine as the secondary disinfectant. Dissolution rates of PbO\(_2\) will increase in response to process changes that lower the pH of the water in the distribution system. The most significant parameter affecting PbO\(_2\) dissolution rates is the concentration and identity of species that can act as chemical reductants to accelerate PbO\(_2\) dissolution. These species include natural organic matter, dissolved iron(II) and manganese(II), and iodide. The impacts of water chemistry on the dissolution rate of PbO\(_2\) can also be used to promote conditions with the slowest dissolution rates and consequently the best abilities to maintain low lead concentrations in distribution systems. Free chlorine is an excellent inhibitor of the reductive dissolution of PbO\(_2\) even at concentrations as low as 0.2 mg/L as Cl\(_2\). Orthophosphate can also be effective at limiting the release of lead to water in systems that contain PbO\(_2\) for systems with pH values near neutral.
SIGNIFICANCE OF LEAD(IV) OXIDES TO LEAD IN DRINKING WATER

Lead release from pipes in distribution systems is a serious threat to public health. The observations of extremely high lead levels in Washington D.C. tap water early in the last decade illustrate the importance of this problem (Edwards and Dudi 2004; Renner 2004; U.S. Environmental Protection Agency 2007b). While advances in water treatment, supply, and distribution were ranked fourth on the list of 20th Century engineering achievements compiled by the National Academy of Engineering, management of our water treatment and supply infrastructure has been identified as a great engineering challenge for the 21st century, and corrosion control plays a leading role in this challenge (Edwards 2004). The American Society of Civil Engineers gave drinking water a D- in its 2004 report card for infrastructure (American Society of Civil Engineers 2005). As the water supply community meets the challenge of an aging infrastructure, there is an increasing need for research to provide a scientific basis for corrosion control.

Lead concentrations in drinking water are affected by chemical reactions that occur within the distribution system. Of particular relevance to management of lead concentrations are the reactions that control the formation and stability of lead(IV) oxides (PbO₂ solid phases of scrutinyeite and plattnerite). PbO₂ solids form at the high oxidation-reduction potential induced by residual free chlorine, and such solids have been observed as constituents of scales of lead corrosion products that develop on lead pipes (Edwards and Dudi 2004; Lytle and Schock 2005). The PbO₂ solids have low solubility, and as long as a sufficiently high oxidation-reduction potential is maintained, dissolved lead concentrations remain at low levels. However, when the oxidation-reduction potential is lowered, as can occur when switching to chloramine as a residual disinfectant, the PbO₂ is no longer stable and its reduction releases lead to the water. Even when highly oxidizing conditions are present, the actual solubility of PbO₂ phases is imprecisely known.

Information on the dissolution rates of PbO₂ is particularly valuable as water suppliers consider process changes that affect water chemistry such as switching disinfectant type or dose, adjusting pH, or adding a corrosion inhibitor. Recent research linked the high lead concentrations in the Washington D.C. service area from 2000-2004 to the breakdown of PbO₂ solids following a change in the residual disinfectant from free chlorine to chloramine (Edwards and Dudi 2004; Renner 2004; U.S. Environmental Protection Agency 2007b). For other utilities that are considering switching from free chlorine to chloramine, information is needed on the rates and mechanisms of PbO₂ dissolution as a function of water chemistry. Orthophosphate has been demonstrated to decrease dissolved lead concentrations for systems using chloramine (Edwards and McNeill 2002; U.S. Environmental Protection Agency 2007b). For other utilities that are considering switching from free chlorine to chloramine, information is needed on the rates and mechanisms of PbO₂ dissolution as a function of water chemistry. Orthophosphate has been demonstrated to decrease dissolved lead concentrations for systems using chloramine (Edwards and McNeill 2002; U.S. Environmental Protection Agency 2007b). Decreases occur through the precipitation of low solubility Pb(II) phosphate solids, but the identity of these solids and the rates and mechanisms of their formation have not been established. This research project examined the mechanisms through which PbO₂ dissolves and the potential for orthophosphate and low levels of free chlorine to mitigate lead release. An improved understanding of the effects of water chemistry on lead release rates can be used to identify strategies that inhibit PbO₂ dissolution and minimize lead release when dissolution occurs.
PROJECT OBJECTIVES, HYPOTHESES, AND STRUCTURE OF THE REPORT

Project Objectives

The project objective is to advance our understanding of the dynamic processes that form PbO₂ solids in drinking water distribution systems and that control their subsequent stability and dissolution. Three specific objectives and associated hypotheses are described below. The research approach is organized into three tasks to achieve these objectives.

Objective 1: Identify threshold values of water chemistry parameters that govern the formation of PbO₂ and control which PbO₂ solid (plattnerite vs. scrutinyite) is produced.

Hypothesis 1A: A threshold concentration of free chlorine must be exceeded for the formation of PbO₂, and the presence of dissolved inorganic carbon will favor the formation of Pb(II) carbonate solids that are intermediate phases in PbO₂ formation.

Hypothesis 1B: Plattnerite and scrutinyite will both form upon reaction of Pb(0) and Pb(II) solids with free chlorine, and the specific phase formed will be governed by the initial nucleation rate and the Pb(0) or Pb(II) precursor.

Significance: Many drinking water utilities use a free chlorine disinfectant residual, but not all of their distribution systems may contain PbO₂ solids. Knowledge of the extent of PbO₂ formation and the identity of the PbO₂ phases present is essential to predicting the potential for lead release upon changes to the water chemistry.

Objective 2: Establish the equilibrium solubility of PbO₂ solids at conditions for which lead remains in the +IV oxidation state.

Hypothesis 2A: The equilibrium solubility of PbO₂ at highly oxidizing conditions will increase with decreasing pH and will be below the drinking water standard for the relevant pH range.

Hypothesis 2B: The equilibrium solubility of scrutinyite and plattnerite will be similar (within an order of magnitude).

Significance: In distribution systems with PbO₂ and a sustained free chlorine residual, the dissolved lead concentrations will be controlled by the solubility of this phase. Measurement of the equilibrium solubility of PbO₂ will fill an important gap in our ability to predict dissolved lead concentrations in distribution systems.

Objective 3: Elucidate the mechanisms and quantify the rates of the coupled processes of PbO₂ reduction and dissolution.
**Hypothesis 3A:** The net release of lead from PbO$_2$ solids will be governed by coupled steps of (1) Pb(IV) reduction to Pb(II) and (2) detachment of Pb(II) from the surface. The water chemistry will govern which of these two steps is rate-limiting.

**Hypothesis 3B:** Phosphate will effectively mitigate lead release from PbO$_2$ by sequestering Pb(II) in low solubility Pb(II) phosphate solid phases in the pyromorphite group of minerals.

**Significance:** The breakdown of PbO$_2$ present in pipe scales has caused elevated lead concentrations. Knowledge of the specific processes responsible for PbO$_2$ breakdown and the associated rates of those processes can be used to design mitigation strategies. The addition of phosphate has been demonstrated to limit Pb release by forming Pb(II) phosphates, but the rates and mechanisms of their formation are not currently known.

**Structure of the Report**

The project was organized into three tasks (Figure 1.1). Each task corresponds to one of the three research objectives just presented. All tasks integrated dissolved phase analysis with characterization of the structures and compositions of the solid phases; this approach facilitated observation of macroscopic precipitation and dissolution processes while developing a mechanistic basis for those processes. In Task 1 we determined the impact of water chemistry on the extent of PbO$_2$ formation and the identity of the PbO$_2$ phases formed. The formation of PbO$_2$ from different Pb(II) precursors was investigated as a function of pH, time, and the concentrations of free chlorine and dissolved inorganic carbon. The results of Task 1 are presented in Chapter 2 of this report. Chapter 3 reports the results of Task 2, a task in which we quantified the dissolved lead concentrations that are maintained when chlorinated water equilibrated with scrutinyite or plattnerite. Dissolved lead concentrations were measured as a function of pH at free chlorine concentrations that help to keep lead in the Pb(IV) oxidation state. In Task 3, presented in Chapter 4, we determined the rate of lead release from PbO$_2$ when dissolution occurs by coupled processes of Pb(IV) reduction and detachment of Pb(II) from the solid surface. A series of experiments investigated the influence of water chemistry on the rates...
of dissolution and the mitigation of lead release.

Following the presentation of the results from the three tasks in Chapters 2-4, a research summary and conclusions are included as Chapter 5. Chapter 6 then presents a summary of recommendations to utilities based on the findings of this project.

BACKGROUND ON LEAD(IV) OXIDES AND RELEVANCE TO DRINKING WATER

Lead is a toxic heavy metal and the adverse effects of lead consumption are a public health concern. While water leaving treatment plants has very low concentrations of lead, internal corrosion of lead-containing pipe, fittings, and solder in water distribution systems can contribute lead to drinking water. While new construction does not use lead pipe, many older buildings retain the original lead service lines and internal plumbing. Concern for lead concentrations in water distribution systems motivated the passage of the Lead and Copper Rule in 1991. Controlling lead concentrations can be particularly challenging for drinking water utilities with older distribution system infrastructure and source waters with neutral pH and low alkalinity. The recent observations of high lead levels in Washington D.C. tap water demonstrate the magnitude of this challenge (Edwards and Dudi 2004; Renner 2004), and other North American cities face similar challenges (Nour et al. 2007; Renner 2006; 2007).

Chemical reactions that occur within the distribution system govern the dissolved lead concentrations in drinking water. Lead release can occur within components owned by the utility or in the plumbing of individual connections. Developing a better understanding of responses of premise plumbing to water quality changes was identified as one of three primary goals in the Water Research Foundation’s 2007 Distribution System Water Quality Strategic Initiative Plan (Awwa Research Foundation 2007). The release of lead from metal pipes and fittings is controlled by both the water composition and the properties of the pipe surface. Lead may be released directly from the pipe or from lead-containing corrosion products on the pipe surface. Corrosion products that develop in scales on pipe surfaces include lead(II) carbonates, phosphates, and oxides (Schock and Lytle 2010). More recently lead(IV) oxides (PbO₂), which are the focus of this project, have been recognized as important components in pipe scales (Lytle and Schock 2005; Schock et al. 2008).

Information on the formation and stability of PbO₂ is important as water suppliers consider process changes that affect water chemistry (AWWA 2005). Knowledge of the conditions favorable for the development of PbO₂ can provide estimates of the extent and identity of these solid phases within a distribution system. As long as the water chemistry remains sufficiently oxidizing (e.g., from a sufficient free chlorine residual), dissolved lead concentrations in equilibrium with PbO₂ will be kept at low levels. However, changes in water chemistry that lower the oxidation-reduction potential can destabilize the PbO₂ solids and cause release of lead to the water. In addition to releasing lead, the breakdown of lead corrosion products can also mobilize other contaminants that are enriched in the corrosion products (Schock et al. 2008).

The increase in lead concentrations in the Washington D.C. Water and Sewer Authority service area in 2000-2004 provide a dramatic example of the impacts of water chemistry on PbO₂ formation and dissolution. Lead(IV) oxides developed on pipe scales when free chlorine was used as the residual disinfectant. When residual disinfection was switched to chloramination, lead release from the pipe resulted in high lead concentrations (Edwards and Dudi 2004; Renner 2004; U.S. Environmental Protection Agency 2007b). The lead
concentrations have ultimately been controlled by increasing the pH and adding orthophosphate (Edwards and McNeill 2002; U.S. Environmental Protection Agency 2007b), which further illustrates the influence of water chemistry on rates of lead release from pipe surfaces.

**Lead(IV) Oxide Occurrence and Stability in Distribution Systems**

*Occurrence of Lead(IV) Oxides*

Lead(IV) oxides have been observed as a component of the scales on lead pipe from distribution systems (Lytle and Schock 2005; Schock et al. 2008; Vasquez et al. 2006). Two polymorphs of PbO₂ can be formed: scrutinyite (α-PbO₂) and plattnerite (β-PbO₂) (Lytle and Schock 2005). In a study of pipe sections removed from 34 different distribution systems that represented a range of water chemistries, 26% of the systems had samples that included PbO₂. Investigation of these pipe scales as a function of depth observed three different modes of PbO₂ occurrence: uniform scales, patchy coverage with coexistence with hydrocerussite (Pb₃(CO₃)₂(OH)₂), and a layered structure with plattnerite (β-PbO₂) on top of cerussite (PbCO₃) (Schock et al. 2005b). In a laboratory study that contacted new lead pipe with chlorinated water (3.5 mg/L as Cl₂) at a relatively high pH of 9.5-10, both plattnerite and scrutinyite formed in scales of corrosion products on the pipe surface. They only formed after longer overall contact times than were necessary for the formation of lead(II) carbonate corrosion products, and even when the PbO₂ solids were observed, they were present together with lead(II) carbonates (Xie and Giammar 2011).

Although lead is not stable in the +IV oxidation state in oxygenated water, this oxidation state is stable at the high oxidation-reduction potential (ORP) provided by free chlorine. The formation of PbO₂ was observed upon reaction of dissolved lead with sodium hypochlorite, and Pb(II) carbonate phases were observed as intermediate products that can co-exist with PbO₂. The formation of PbO₂ is reversible, with PbO₂ disappearing when a residual hypochlorite concentration is not maintained. Hydrocerussite can be transformed to scrutinyite following a lag period when reacted with free chlorine (Liu et al. 2006). In contrast to the facilitated formation of PbO₂ by carbonate, the presence of orthophosphate inhibited PbO₂ formation in chlorinated solutions (Lytle et al. 2009).

*Solubility of Lead(IV) Oxides*

In the presence of strong oxidants, HOCl/OCl⁻ in particular, lead can be oxidized from the +II oxidation state to the +IV oxidation state. Figure 1.2 illustrates the dominant solid and dissolved species as a function of both pH and ORP. The reduction half-reaction is given as Equation 1.1.

\[
Pb^{4+} + 2e^- = Pb^{2+}, E_H^o = 0.845 \text{ V} \tag{1.1}
\]

A complete reaction for the oxidation of dissolved lead(II) by HOCl to form PbO₂(s) is given as Equation 1.2.

\[
Pb^{2+} + HOCl + H_2O = PbO_2(s) + Cl^- + 3H^+ \tag{1.2}
\]
For this case, the divalent free lead ion concentration is determined by the oxidation-reduction potential (ORP) set by the concentrations of chloride and hypochlorous acid and by the pH. When lead(IV) is the dominant oxidation state, as controlled by free chlorine, the dissolved
lead concentrations can be very low (Figure 1.3a). The lead(IV) oxide (PbO$_2$) that forms has a very low solubility given by the reaction and solubility product in Equations 1.3 and 1.4.

$$\text{PbO}_2(s) + 4\text{H}^+ = \text{Pb}^{4+} + 2\text{H}_2\text{O} \quad (1.3)$$

$$K_{sp,\text{ scrutinyite}} = \frac{[\text{Pb}^{4+}]}{[\text{H}^+]^4} = 10^{-8.26} \quad (1.4)$$

The total dissolved lead(IV) is the sum of the concentrations of the free metal ion Pb$^{4+}$ as well as the hydrolysis complexes PbO$_3^{2-}$ and PbO$_4^{4-}$; however, these complexes are only significant at very high pH (>$12$) and are negligible over the pH range of interest in water supply and treatment (Pourbaix 1974). While free chlorine is sufficiently oxidizing to promote the formation of lead(IV), monochloramine can oxidize metallic lead(0) to lead(II) but not to lead(IV) (Switzer et al. 2006). Direct electrochemical measurement of the ORP values of monochloramine and free chlorine confirmed the inability of monochloramine to stabilize lead(IV) oxides (Rajasekharan et al. 2007).

**Stability of Lead(IV) Oxides**

If a strong oxidant like HOCl/OCl$^-$ is no longer present, then the lead(IV) in PbO$_2$ can be reduced to lead(II). The dissolved lead concentrations in equilibrium with lead(II) carbonates and phosphates are significantly higher than those in equilibrium with lead(IV) oxides (Figure 1.3b). While recent studies have established the ability of natural organic matter (Dryer and Korshin 2007; Lin and Valentine 2008a; Lin and Valentine 2009; Shi and Stone 2009b), iodide (Lin et al. 2008), bromide at acidic conditions (Lin and Valentine 2010), and iron(II) and manganese(II) (Shi and Stone 2009a) to reduce PbO$_2$. These studies and others (Switzer et al. 2006) have also shown that PbO$_2$ can undergo reduction even in solutions without strong reductants. PbO$_2$ is such a strong oxidant, that its reduction by water is even energetically favorable (Equation 1.5).

$$\text{PbO}_2(s) + 2\text{H}^+ = \text{Pb}^{2+} + 0.5\text{O}_2 + \text{H}_2\text{O} \quad (1.5)$$

Maintaining the low solubility of PbO$_2$ requires that the water chemistry be sufficiently oxidizing to maintain lead in the +IV oxidation state. This has been observed by the requirement of free chlorine in contact with lead pipes to provide a low dissolved lead concentration (Boyd et al. 2007). Changes in ORP that result from changes in the residual disinfectant or in disinfectant demand in the distribution system can lead to transformations from low solubility PbO$_2(s)$ to higher solubility lead(II) carbonate and phosphate phases (Schock and Giani 2004). A study of lead release from pipes that included PbO$_2$ as a constituent of the pipe scale observed lead concentrations below $20 \mu\text{g L}^{-1}$ in chlorinated water held stagnant in the pipes until the free chlorine was depleted, and after that depletion the lead concentrations increased markedly (Xie and Giammar 2011). The decrease in the ORP that occurs when chloramine is used instead of free chlorine causes the PbO$_2$ to breakdown and release lead back to solution (Vasquez et al. 2006). Laboratory and pilot-scale studies have observed higher dissolved lead levels with chloramine than with free chlorine, which can be explained by the differences in solubility of Pb(IV) and Pb(II) phases (Edwards and Dudi 2004; Vasquez et al. 2006).
Dissolution Rates of Lead Corrosion Products

Information on the dissolution rates of lead-containing solids is necessary to complement knowledge of the equilibrium solubility. The water present in a drinking water distribution will often not be in equilibrium with the solid phases present in the pipe. Estimates of lead concentrations in distribution systems based on equilibrium solubility are qualitatively good, but they are usually not quantitatively accurate. Equilibrium-based models tend to overpredict lead concentrations. Such models are limited by the accuracy of available equilibrium constants, transitions between scale types, by-product release, and reaction kinetics (Edwards et al. 1999; Vasquez et al. 2006). For systems without equilibrium between the solid and dissolved phase, the rate of dissolution and the contact time between the water and the lead-containing solid will determine the dissolved lead concentration. Differences between lead concentrations during times of flowing water and during stagnation periods can be significant. For example, lead concentrations in new pipe were low during flowing conditions but exceeded 15 μg/L after 8 hours of stagnation, even in the presence of inhibitors (Hozalski et al. 2005). During stagnant periods, dissolved lead concentrations in lead pipe approach equilibrium exponentially with time. The largest increases occur within the first 24 hours (Lytle and Schock 2000).

Dissolution rates of precipitated solids are functions of properties of both the dissolving solid and the solution in which it is dissolving. Dissolution rates generally increase with decreasing pH, with this effect becoming most pronounced at neutral pH and below. Rates can be affected by inhibiting or enhancing dissolved species that include orthophosphate, carbonate, other complexing ligands, and reductants. Reductants will accelerate the dissolution of PbO₂. The rapid release of lead from distribution systems following switches from free chlorine to chloramine indicates the large energetic driving force for reductive dissolution of PbO₂.

The dissolution rates of lead(II) carbonate and phosphate solids have been examined in previous research as a function of water chemistry, in particular as a function of pH. However, very little was known about the rates of PbO₂ dissolution and the factors controlling those rates. With previous WaterRF support, we prepared a thorough review of the literature of dissolution rates of lead corrosion products and measured the dissolution rates of different lead(II) solids (Giammar et al. 2010). Carbonate solids are among the most rapidly soluble minerals (Stumm and Morgan 1996), and their dissolution rates increase significantly with decreasing pH at acidic conditions. Dissolution rates of PbCO₃(s) were on the order of 10⁻⁴ mol m⁻² h⁻¹ at pH 7 (Pokrovsky and Schott 2002), and our recent work measured rates of 1.2·10⁻⁶ mol m⁻² h⁻¹ at pH 7.5 in water with no added alkalinity, orthophosphate, or disinfectant (Giammar et al. 2010). For lead(II) phosphates, a recent study on the dissolution rates of chloropyromorphite (Pb₅(PO₄)₃Cl(s)) observed that dissolution rates increase with decreasing pH and decreasing solution saturation; at a pH of 7 and a highly undersaturated solution, the dissolution rate is 1.1·10⁻⁷ mol m⁻² h⁻¹ (Xie and Giammar 2007), and for hydroxylpyromorphite a dissolution rate of 1.2·10⁻⁸ mol m⁻² h⁻¹ was measured at pH 7.5 in a simple aqueous solution (Giammar et al. 2010).

Only recently have dissolution rate measurements of lead(IV) oxides been made. Because the reductive dissolution of PbO₂ in pure water is energetically favorable, extensive dissolution was measured for plattnerite (Lin and Valentine 2008a) and scrutinyite (Dryer and Korshin 2007). The dissolution of both materials was significantly accelerated by the presence of natural organic matter (NOM), which served as a reductant for the PbO₂. NOM may also inhibit the development of Pb(II) precipitates that would limit further dissolution. The dissolution of PbO₂ increased with decreasing pH. At pH 7, the data of Lin and Valentine...
(2008a) can be used to extract a dissolution rate of $6.5 \times 10^{-9}$ mol m$^{-2}$ h$^{-1}$. This study also verified that the lead released was lead(II) and not lead(IV).

Mitigation of Lead Release from Corrosion Products on Lead Pipe

Many water utilities must implement a corrosion control strategy to minimize dissolved lead concentrations in their distribution systems. Recommended strategies for controlling lead corrosion include pH and/or alkalinity adjustment and addition of orthophosphate (Edwards et al. 1999). The general strategy of corrosion control is to promote the formation of low solubility lead-containing solids that passivate the surface. These solids include lead(IV) oxides at sufficiently oxidizing conditions; however, when lead(IV) oxides are no longer stable, then the impact of water chemistry on the stability of lead(II) phases becomes important.

Dissolved lead concentrations can respond significantly to changes in pH and alkalinity. Based on a survey of utilities, large decreases in soluble lead levels are observed with increasing alkalinity (Edwards et al. 1999). The effect of increasing alkalinity is consistent with lead concentrations being determined by the solubility of lead carbonate (cerussite and hydrocerussite) solids. The stability of these carbonate solids is determined by the activity of the carbonate ion, which is determined by both the DIC (or alternatively alkalinity) and pH. Consequently, increasing pH without also increasing carbonate alkalinity will not be as effective. In fact, without sufficient alkalinity (less than 20-30 mg/L as CaCO$_3$), increasing pH can actually exacerbate lead release (Dodrill and Edwards 1995). Large variations in the pH of the water of the Washington D.C. service area have been identified as a contributing factor to the high lead concentrations from 2000-2004 (U.S. Environmental Protection Agency 2007a).

Orthophosphate inhibitors can effectively mitigate lead concentrations in distribution systems. The form in which the phosphate is added is vitally important. Orthophosphate and associated forms (e.g., zinc orthophosphate) are the most effective inhibitors (Cantor et al. 2003; Churchill et al. 2000; Edwards et al. 1999; Schock and Lytle 2010). Orthophosphate inhibitors can result in the precipitation of insoluble lead phosphate solids that limit lead release to solution. The dissolution rate of the lead carbonate hydrocerussite was significantly decreased by the addition of orthophosphate in a study conducted over a pH range of 7.5-10 and various dissolved inorganic carbon concentrations, and electron microscopy imaging confirmed the formation of a low solubility lead(II) phosphate solid (Giammar et al. 2010). Orthophosphate was also found to mitigate the release of dissolved lead from pipes during stagnant conditions (Xie and Giammar 2011). In contrast to orthophosphate, polyphosphates form dissolved complexes with lead and can increase dissolved lead concentrations in distribution systems (Cantor 2006; Dodrill and Edwards 1995; Edwards and McNeil 2002; McNeill and Edwards 2002; Schock et al. 2005a).

The benefits of orthophosphate as a corrosion inhibitor are most significant for systems with relatively low alkalinity or pH, conditions at which lead concentrations are not controlled by lead carbonate solids. In a survey of utilities, the most pronounced benefits of orthophosphate addition were seen in waters with less than 30 mg/L alkalinity as CaCO$_3$ (Dodrill and Edwards 1995). Recommended orthophosphate doses can range from less than 1 mg/L to as much as 4.5 mg/L as P (Edwards et al. 1999). The addition of orthophosphate to the treated water in Washington D.C. has effectively lowered dissolved lead concentrations to below the action level (U.S. Environmental Protection Agency 2007a, b).
CHAPTER 2
FACTORS CONTROLLING THE FORMATION OF LEAD(IV) OXIDES

OVERVIEW OF RESEARCH ON LEAD(IV) OXIDE FORMATION

The two polymorphs of lead(IV) oxide (PbO$_2$), scrutinyite ($\alpha$-PbO$_2$) and plattnerite ($\beta$-PbO$_2$), have been widely observed as corrosion products in drinking water distribution systems (Schock and Giani 2004; Schock et al. 2005b). The formation of lead(IV) oxide (PbO$_2$) from lead pipes is a two-step process. First, lead(0) metal is oxidized to lead(II) corrosion products, like lead(II) oxides and carbonates. In the presence of free chlorine, these lead(II) compounds are further oxidized to lead(IV) oxide. Figure 2.1 shows the possible formation pathways of PbO$_2$ from lead(II) species. Water chemistry parameters that include pH, dissolved inorganic carbon (DIC), and free chlorine, as well as the identities of the precursors can affect the formation of PbO$_2$. The primary aims of the task presented in this chapter were to (1) investigate the effect of water chemistry on the extent and identity of PbO$_2$ formation and (2) determine the pathways of PbO$_2$ formation from various precursors.

![Figure 2.1 Potential pathways of PbO$_2$ formation from initial Pb(II) phases](https://example.com/fig21.png)

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Figure 2.1 Potential pathways of PbO$_2$ formation from initial Pb(II) phases

MATERIALS AND METHODS

**Materials**

Five different materials were studied as starting materials for PbO$_2$ formation. Elemental lead(0) powder was used to identify the formation pathways of PbO$_2$ through the Pb(0)-Pb(II)-Pb(IV) processes. To elucidate the formation pathways of PbO$_2$ from Pb(II) phases, four Pb(II) compounds were chosen as starting phases. Dissolved lead(II) chloride (PbCl$_2$) was used to study PbO$_2$ formation from the aqueous phase. The lead(II) solids massicot ($\beta$-PbO), cerussite
(PbCO₃), and hydrocerussite (Pb(OH)₂(CO₃)₂) were used to identify the formation of PbO₂ from lead(II) corrosion products that are frequently observed in distribution systems.

Lead(0) powder (99.9% purity) was purchased from Alfa-Aesar. Reagent grade massicot was purchased from Aldrich. A PbCl₂ solution was prepared using a reagent grade PbCl₂ salt from Fisher Scientific. Cerussite and hydrocerussite were synthesized in our lab using methods described before (Noel and Giammar 2007). Briefly, hydrocerussite was synthesized by simultaneous addition of 0.1 M NaHCO₃ and 0.15 M Pb(NO₃)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 NaHCO₃ and 0.1 M Pb(NO₃)₂ were simultaneously added to ultrapure water while maintaining pH 7.0 ± 0.5. The identities of the solids were confirmed by X-ray diffraction (XRD) (Figure 2.2), and the morphology of the solids was characterized using SEM (Figure 2.3). The specific surface areas of lead(0) powder, massicot, cerussite, and hydrocerussite were measured using BET-N₂ adsorption to be 0.05, 0.21, 1.09, and 4.77 m²/g, respectively. Reagent grade Pb(NO₃)₂, NaHCO₃, NaOH, NaOCl solution, and HNO₃ were purchased (Fisher Scientific). Ultrapure water (resistivity >18.2 MΩ·cm) was used to prepare solutions.

**PbO₂ Formation Experiments**

The conditions for PbO₂ formation were examined in batch experiments to determine the factors that resulted in pure scrutinite, pure plattnerite, neither phase, or mixtures of the two phases. Factors evaluated were the form in which lead was added (i.e., the precursor), the pH,
and the concentrations of free chlorine and DIC (Table 2.1). Experiments were performed at room temperature (21 ± 1 °C) using 500-mL polypropylene batch reactors. Lead precursors were added to the reactors to achieve a total lead concentration of 0.5 mM. The desired DIC concentration was provided by the addition of NaHCO₃. Then the pH was adjusted to the target value and maintained subsequently by the periodic addition of HNO₃ and NaOH. Finally, aliquots of a stock solution of sodium hypochlorite were added to provide the target free chlorine concentrations. For experiments with 4 and 20 mg Cl₂/L free chlorine, the free chlorine concentration was maintained at the initial value by periodic addition of sodium hypochlorite solution; while for experiments with 42 mg Cl₂/L free chlorine, the free chlorine concentration was allowed to decrease from its initial value. Two different approaches to providing the free chlorine were used because these experiments were initiated by different researchers at different times. For selected conditions both approaches were used, and there were no differences in the results. The relatively high free chlorine concentrations were used in order to generate sufficient amounts of products for characterization. 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. For experiments with no DIC, the experiments were conducted in an argon-filled glovebox with the atmosphere in contact with a 0.5 M NaOH solution to absorb any remaining CO₂. After 1, 7, and 28 days of reaction solid samples were collected and centrifuged prior to XRD and SEM analysis. Aqueous samples were taken periodically, filtered with 0.22 μm nitrocellulose membranes, and analyzed for free chlorine.

Figure 2.3. Electron micrographs showing the morphology of pure (a) cerussite, (b) hydrocerussite, (c) massicot and (d) lead(0) powder
Analytical Methods

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. BET-N₂ adsorption was performed on a BET-Autosorb instrument (Quantachrome Instruments). 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).

RESULTS AND DISCUSSION

Overview

The conditions of experiments completed and information on the solids present after reaction times are summarized in Table 2.2. PbO₂ only formed in the presence of free chlorine. Because the lowest free chlorine concentration studied was 4 mg Cl₂/L, any threshold value required for PbO₂ formation is below this concentration. This observation is expected since PbO₂ is a strong oxidant that is only stable in a system with high oxidation reduction potential (ORP). The pH and DIC affected the identity of the PbO₂ produced by forming lead(II) carbonate intermediate solid phases. The extent and identity of PbO₂ formation also depended on the starting phases.

Products of Reaction with Massicot

Effect of pH and DIC

The pH and DIC are important water chemistry parameters and determine the alkalinity of the water. A typical range of DIC in drinking water is 0 – 50 mg C/L (Schock 1989) and 0

Table 2.1

<table>
<thead>
<tr>
<th>Property</th>
<th>Selected Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting phase</td>
<td></td>
</tr>
<tr>
<td>Dissolved lead: PbCl₂ solution</td>
<td></td>
</tr>
<tr>
<td>Lead metal: Pb(0)(s)</td>
<td></td>
</tr>
<tr>
<td>Massicot: PbO(s)</td>
<td></td>
</tr>
<tr>
<td>Cerussite: PbCO₃</td>
<td></td>
</tr>
<tr>
<td>Hydrocerussite: Pb₃(CO₃)₂(OH)₂</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.5, 8.5, 10</td>
</tr>
<tr>
<td>DIC</td>
<td>0, 20 mg C/L</td>
</tr>
<tr>
<td>Free chlorine</td>
<td>0, 4, 20, 42 mg/L as Cl₂</td>
</tr>
<tr>
<td>Reaction time</td>
<td>1 day, 7 days, 28 days</td>
</tr>
</tbody>
</table>
Chapter 2: Factors Controlling the Formation of Lead(IV) Oxides

Table 2.2
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>
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<td>4</td>
<td>M/S/P</td>
<td>S/P</td>
<td>M/S/P</td>
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<td></td>
<td>20</td>
<td>M</td>
<td>M/C</td>
<td>C/M</td>
<td>M/H</td>
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<tr>
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<td>N</td>
<td>S/P</td>
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<tr>
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<td>N</td>
<td>S/P</td>
<td>S/P</td>
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<td>S/P</td>
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<tr>
<td></td>
<td>42*</td>
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<td>P/S</td>
<td>P/S</td>
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</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>Pb powder (0.5 mM)</td>
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<td>E/C</td>
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<tr>
<td></td>
<td>4</td>
<td>E</td>
<td>E/C/O</td>
<td>E</td>
<td>E/H</td>
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<tr>
<td></td>
<td>20</td>
<td>E</td>
<td>E/P/S</td>
<td>P/S</td>
<td></td>
</tr>
</tbody>
</table>

S: Scrutinyite, P: Plattnerite, H: Hydrocerussite, C: Cerussite, E: Elemental lead, M: Massicot; L: litharge; Cl: Pb₄O₃Cl₂·H₂O; O: PbO₂, which was only identified by SEM.
The phase identified in bold was the predominant solid phase in the mixture.* indicates the initial free chlorine concentration; in these experiments the free chlorine was allowed to decline from its initial value.

and 20 mg C/L was selected in the present study. In the absence of DIC, a mixture of scrutinyite and plattnerite formed with 20 mg Cl₂/L free chlorine (Figure 2.4). A peak at 20° of 28° that is characteristic of scrutinyite appeared in the XRD patterns after 28 days at both pH 7.5 and pH 10. The characteristic peaks of plattnerite at 20° of 25° and 32° also appeared. No intermediate solid was observed (Figure B1 in the Appendices). This result demonstrated that a mixture of scrutinyite and plattnerite formed directly from massicot in the absence of DIC. The higher intensity of the peaks at 20° of 25°, 28°, and 32° at pH 10 than pH 7.5 indicated that PbO₂ formation was faster at pH 10. The presence of DIC accelerated the formation of PbO₂. The peaks of massicot disappeared in the presence of DIC, but massicot still coexisted with PbO₂ in the absence of DIC after 28 days of reaction (Figure 2.4). The presence of DIC may accelerate PbO₂ formation by either forming solid intermediates or soluble Pb(II)-carbonate complexes that have been demonstrated to enhance the dissolution of lead(II) solids (Giammar et al. 2008).

The pH affected the identity of the PbO₂ formed in the presence but not the absence of DIC. In the absence of DIC, mixtures of plattnerite and scrutinyite formed with similar abundance after 28 days of reaction at both pH 7.5 and 10. In the presence of 20 mg C/L DIC after 28 days of reaction with 20 mg Cl₂/L free chlorine, mixtures of plattnerite and scrutinyite formed; plattnerite was more dominant at pH 7.5, while scrutinyite was dominant at pH 10 (Figure 2.4). A similar trend was observed using 4 mg Cl₂/L free chlorine (Figure B2 in the Appendices). A previous study showed that plattnerite formed at pH 7.5 and scrutinyite formed at pH 10 from PbCl₂ solution in the presence of DIC (Lytle and Schock 2005), which is consistent with the observation in the present study. The effect of DIC may be attributed to the formation of lead(II) carbonate intermediate solids (Figures B3 - 4 in Appendices). SEM images...
Figure 2.4 X-ray diffraction patterns of solids following reaction of massicot with 20 mg Cl₂/L free chlorine in the absence and presence of 20 mg C/L DIC after 28 days together with reference patterns from the ICDD database.

Figure 2.5 Electron micrographs of PbO₂ products from reaction of PbO (a) after 1 day at pH 7.5 with no DIC and 20 mg Cl₂/L free chlorine and (b) after 1 day at pH 10 with 20 mg/L DIC and 20 mg Cl₂/L free chlorine.
showed that PbO₂ (small spherical particles) grew on the surface of massicot in the absence of DIC; while in the presence of DIC, hydrocerussite intermediate solids (plate-like crystals) were observed, and PbO₂ formed on the edges of hydrocerussite (Figure 2.5). The formation of lead(II) carbonate intermediate solids may affect the PbO₂ formation pathways, thus affecting the phases of the PbO₂ formed.

**Effect of free chlorine**

Free chlorine concentration affected the extent of PbO₂ formation and its impact was strongly DIC-dependent (Figure 2.6). Higher free chlorine concentrations enhanced the formation of PbO₂ in the presence of DIC. After 7 days of reaction at pH 7.5 with 4 mg Cl₂/L free chlorine and 20 mg C/L DIC, a small XRD peak at 2θ of 32° appeared that indicated the formation of PbO₂. However, the dominant solids were still massicot and cerussite, which formed from the reaction of massicot with DIC. Increasing the free chlorine concentration to 20 mg Cl₂/L resulted in a complete transformation to scrutinyite and plattnerite after 7 days of reaction. In the absence of DIC, an opposite trend was observed with less PbO₂ formed at the higher free chlorine concentration. Even after 28 days of reaction with 20 mg Cl₂/L free

---

**Figure 2.6** 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 together with reference patterns from the ICDD database.
chlorine, the dominant solids were still massicot; while scrutinyite and plattnerite became dominant with 4 mg Cl₂/L free chlorine.

This impact of DIC on the effect of free chlorine on PbO₂ formation may be attributed to different formation mechanisms of PbO₂ from massicot in the absence and presence of DIC. PbO₂ may form through two parallel pathways (Figure 2.1):

1. Direct oxidation of PbO (s) to PbO₂(s) (reaction 3.1) and
2. Oxidation of dissolved lead that was released to solution from PbO(s) (reactions 3.2 – 3.3):

\[
\begin{align*}
PbO(s) + HOCl & = PbO_2(s) + H^+ + Cl^- \quad (3.1) \\
PbO(s) + 2H^+ & = Pb^{2+} + H_2O \quad (3.2) \\
Pb^{2+} + HOCl + H_2O & = PbO_2(s) + Cl^- + 3H^+ \quad (3.3)
\end{align*}
\]

In the absence of DIC, a high free chlorine concentration may enhance the formation of PbO₂ from the direct oxidation of PbO, which can be seen by the formation of a possible PbO₂ layer on the surface of PbO at 20 mg Cl₂/L free chlorine (Figure 2.7). This layer may have prevented further chlorine attack of PbO and decreased the dissolution rate of PbO, thus inhibiting the further formation of PbO₂. The presence of DIC may accelerate Pb(II) release from massicot by forming lead(II) carbonate complexes, thus increasing the rate of reaction 3.2, which would allow reaction 3.3 to proceed faster than reaction 3.1. The increased dissolution of PbO at high DIC may prevent the accumulation of PbO₂ on the PbO surface, thus allowing continued PbO dissolution and greater production of PbO₂. In addition, the presence of DIC may help form lead(II) carbonate intermediate solids, which may change the pathways of PbO₂ formation, resulting in a different trend than that observed in the absence of DIC.

**Products of Reaction with Elemental Lead(0) Powder**

PbO₂ could form from lead(0) powder in the presence of free chlorine. Reacting with 20 mg Cl₂/L free chlorine, PbO₂ started to form after 7 days of reaction at pH 8.5 with 20 mg C/L DIC, and it became dominant after 28 days of reaction (Figure 2.8). Small spherical particles
Figure 2.8 X-ray diffraction patterns of solids following reaction of lead(0) powder at pH 8.5 with 20 mg C/L dissolved inorganic carbon and 20 mg Cl₂/L free chlorine after different reaction time together with reference patterns from the ICDD database.

Figure 2.9. Electron micrographs of PbO₂ products from reaction of lead(0) powder at pH 8.5 with 20 mg C/L DIC and 20 mg Cl₂/L free chlorine after (a) 7 days and (b) 28 days of reaction.
Lead(IV) Oxide Formation and Stability in Drinking Water Distribution Systems

were observed after 7 days of reaction, indicating the formation of PbO₂ (Figure 2.9). Plate-like crystals were also found after 7 days of reaction, suggesting that hydrocerussite may be an intermediate solid in the formation of PbO₂ at this condition. After 28 days of reaction, the solids all became small spherical particles, which is consistent with the XRD pattern that PbO₂ was dominant after 28 days of reaction.

The free chlorine concentration affected the extent of PbO₂ formation (Figure 2.10). When no free chlorine was added to the solution, no PbO₂ formed after 28 days of reaction. Hydrocerussite formation was observed, but the dominant solid was still lead(0). With 4 mg Cl₂/L free chlorine, a mixture of scrutinyite and plattnerite formed after 28 days, and these solids coexisted with the lead(0). When the free chlorine concentration was 20 mg Cl₂/L, a mixture of scrutinyite and plattnerite formed after 28 days, and the peaks of lead(0) almost disappeared.

Products of Reaction with Dissolved Lead Chloride

PbO₂ formed from lead chloride at all the conditions tested in the absence of DIC. PbO₂ formed after 28 days of reaction even when the free chlorine concentration was maintained at a value as low as 4 mg Cl₂/L, which indicated that the threshold value of free chlorine

Figure 2.10 X-ray diffraction patterns of solids following reaction of lead(0) powder at pH 8.5 with 20 mg C/L dissolved inorganic carbon with different free chlorine concentrations (in mg/L as Cl₂) after 28 days together with reference patterns from the ICDD database
concentration for PbO₂ formation was less than 4 mg Cl₂/L. The pH affected the phase of PbO₂ formed in the absence of DIC. After 28 days of reaction, a mixture of scrutinyite and plattnerite formed at pH 7.5 and pure plattnerite formed at pH 10 (Figure 2.11). This observation may be due to the different formation pathways of PbO₂ at different pH values. At pH 7.5, no intermediate solid was observed during the formation of PbO₂ (Figure 2.12a), which indicated that the formation was through an aqueous phase oxidation pathway. This pathway includes two steps: first dissolved Pb(II) is oxidized to dissolved Pb(IV), and then PbO₂ nucleates homogenously and precipitates, which is shown as pathway 2B-3A in Figure 2.1. At pH 10 with 4 mg/L free chlorine, an intermediate lead(II) oxide chloride was observed after 1 day of reaction but disappeared after 7 days (Figure 2.12b). This intermediate solid may affect the overall PbO₂ formation process, and the formation of pure plattnerite after 28 days of reaction may be due to the specific trends in solid-solid interfacial free energies.

**Products of Reaction with Lead(II) Carbonates**

The lead(II) carbonates cerussite and hydrocerussite are often found as corrosion products in pipe scales. They were also observed as intermediate solid phases in the formation

![Figure 2.11 X-ray diffraction patterns of solids following reaction of lead chloride solution in the absence of dissolved inorganic carbon with different free chlorine concentrations (in mg/L as Cl₂) after 28 days together with reference patterns from the ICDD database](image)

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Figure 2.12 X-ray diffraction patterns of solids following reaction of lead chloride solution in the absence of dissolved inorganic carbon (a) at pH 7.5 with 20 mg Cl₂/L free chlorine and (b) at pH 10 with 4 mg Cl₂/L free chlorine together with reference patterns from the ICDD database.
of PbO₂ when DIC was present in the system (Lytle and Schock 2005). Cerussite and hydrocerussite may transform into one another if the pH of the solution changes; the general trend is that lower pH favors the formation of cerussite while higher pH leads to hydrocerussite. Cerussite and hydrocerussite may affect the phases of PbO₂ formed and their effect on the formation of PbO₂ was examined in the absence of DIC as a function of pH.

**Reaction with Hydrocerussite**

The pH affected the phase of PbO₂ formed from hydrocerussite (Figure 2.13). At pH 10, no intermediate solids were observed during the process of PbO₂ formation, and pure scrutinyite formed after 28 days of reaction with both 20 mg Cl₂/L free chlorine and 42 mg Cl₂/L free chlorine. This result is consistent with previous studies conducted by Liu and co-workers that found that scrutinyite formed from hydrocerussite (Liu et al. 2008). At pH 7.5 a phase transformation from hydrocerussite to cerussite was observed after 1 day of reaction (Figure B5 in the Appendices), and at this pH PbO₂ could then form from either cerussite or hydrocerussite, which may explain why pure scrutinyite did not form. After 28 days, a mixture of scrutinyite and plattnerite formed, and scrutinyite was more dominant than plattnerite.

![Figure 2.13. X-ray diffraction patterns of solids following reaction of hydrocerussite in the absence of dissolved inorganic carbon with different free chlorine concentrations (in mg/L as Cl₂) after 28 days together with reference patterns from the ICDD database](image-url)
Reaction with Cerussite

A mixture of scrutinyite and platnerite formed from cerussite after 28 days of reaction (Figure 2.14). Except for the condition at pH 7.5 with 42 mg Cl₂/L free chlorine in the absence of DIC, scrutinyite was more dominant than platnerite. A previous study observed that pure platnerite formed from cerussite at pH 6.7 – 7.8 (Lytle and Schock 2005). The formation of a mixture of scrutinyite and platnerite in the present study but not pure platnerite may be due to the partial transformation of cerussite to hydrocerussite. A phase transformation from cerussite to hydrocerussite was observed at pH 10 after 1 day of reaction (Figure 2.15a), and PbO₂ (small roughly spherical particles) formed on the surface of hydrocerussite (hexagonal plate-like crystals). At pH 7.5, although no hydrocerussite was observed with XRD, a hydrocerussite shape-preserved cluster of PbO₂ particles was observed after 7 days of reaction (Figure 2.15b), indicating that at least some transformation from cerussite to hydrocerussite had occurred. Therefore, at the conditions studied, PbO₂ could have formed from both cerussite and hydrocerussite, which makes it difficult to determine the formation products from pure cerussite.

Figure 2.14 X-ray diffraction patterns of solids following reaction of cerussite in the absence of dissolved inorganic carbon with different free chlorine concentrations (in mg/L as Cl₂) after 28 days together with reference patterns from the ICDD database

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Chapter 2: Factors Controlling the Formation of Lead(IV) Oxides

Summary of Lead(IV) Oxide Formation

The extent and identity of PbO$_2$ formed were affected by water chemistry and the precursors. PbO$_2$ is a strong oxidant that only formed in the presence of free chlorine. Starting from lead(0) powder, intermediate lead(II) solid phases were observed in the formation process of PbO$_2$, suggesting that the formation of PbO$_2$ from Pb(0) is a two-step process that involves the oxidation of Pb(0) to Pb(II) followed by the oxidation of Pb(II) to PbO$_2$.

Starting from Pb(II) phases, the formation of PbO$_2$ from different precursors at different conditions is summarized in Figure 2.16. As shown in Figure 2.1, PbO$_2$ could form from Pb(II) phases through several pathways. If PbO$_2$ formed from an aqueous phase oxidation pathway (2B-3A in Figure 2.1), as illustrated in the experiments using dissolve lead chloride as a starting phase at pH 7.5 with no DIC, mixtures of plattnerite and scrutinyite formed after 28 days of reaction. If Pb(II) solids were involved in the process of PbO$_2$ formation, then the mechanisms of PbO$_2$ formation can be more complicated. Pb(II) solids may be directly oxidized to PbO$_2$ through a solid state oxidation pathway (2A in Figure 2.1) or serve as substrates in the heterogeneous nucleation of PbO$_2$ (1A-2B-3B in Figure 2.2). Generally if Pb(II) solids were used as starting phases or were generated as intermediate solids, then mixtures of plattnerite and scrutinyite formed. However, due to the specific trend in solid-solid interfacial free energies, some Pb(II) solids did prefer to form a specific phase of PbO$_2$. For example, lead(II) oxide chloride favored plattnerite; while if hydrocerussite was used as the starting phase and no other intermediate Pb(II) solids formed, then scrutinyite was the only product.

PbO$_2$ solids have frequently been found on lead pipes in drinking water distribution systems using free chlorine as a residual disinfectant. Our findings suggest that PbO$_2$ formed in the presence of free chlorine and that the formation rate of PbO$_2$ increased with increasing free chlorine concentrations with DIC. The threshold value above which the formation of PbO$_2$ is favored is less than 4 mg Cl$_2$/L. In actual distribution systems the free chlorine concentration is typically 0.5 to 1.5 mg Cl$_2$/L, and the formation of PbO$_2$ is still thermodynamically favorable and has been observed on pipes. Although plattnerite is more thermodynamically stable than scrutinyite, mixtures of plattnerite and scrutinyite formed at most conditions, indicating that the systems do not reach equilibrium and that kinetics play an important role in PbO$_2$ formation.

Figure 2.15 Electron micrographs of the solid from cerussite reaction at (a) pH 10, 20 mg Cl$_2$/L free chlorine, and no DIC after 1 day, and (b) pH 7.5, 42 mg Cl$_2$/L free chlorine, and no DIC after 7 days

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**Figure 2.16 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.

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CHAPTER 3
DISSOLVED LEAD CONCENTRATIONS IN SOLUTIONS CONTAINING LEAD(IV) OXIDE

OVERVIEW OF LEAD(IV) OXIDE SOLUBILITY

In the presence of free chlorine to promote the maintenance of lead in the +IV oxidation state, PbO₂ equilibrated in water should achieve stable dissolved lead concentrations. Theoretically the stable dissolved lead concentrations should represent the equilibrium solubility of PbO₂, and if equilibrium can be achieved, then predictions of lead concentrations may be made using equilibrium solubility calculations. However, it was not clear prior to this project whether or not equilibrium could be achieved for aqueous PbO₂ suspensions at near neutral pH.

At the high ORP provided by free chlorine, the dissolution of PbO₂ is affected by two types of reactions. The first is the non-reductive dissolution of PbO₂, which releases Pb(IV) to the solution, and can be expressed by Reactions 1 – 4 in Table 3.1. The total dissolved lead Pb(IV) can be calculated as the sum of all the aqueous Pb(IV) species:

$$\text{[Pb(IV)]}_{\text{diss}} = [\text{Pb}^{4+}] + [\text{PbO}_2^{-}] + [\text{PbO}_4^{4-}]$$  \hspace{1cm} (3.1)

The second process is the reductive dissolution of PbO₂, which may occur even in the presence of free chlorine, that describes equilibrium between PbO₂ and dissolved Pb(II) species (Reaction 5 in Table 3.1). In the system without DIC, the total dissolved Pb(II) can be expressed by:

$$\text{[Pb(II)]}_{\text{diss}} = [\text{Pb}^{2+}] + [\text{PbOH}^+] + [\text{Pb(OH)}_2^+] + [\text{Pb(OH)}_3^-] + [\text{Pb(OH)}_4^{2-}]$$  \hspace{1cm} (3.2)

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<td>-7.60</td>
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Benjamin = (Benjamin 2002)
MINEQL = (Schecher and Mcavoy 1998)
Both pathways would contribute lead release to drinking water. Using the reactions and equilibrium constants in Table 3.1 the calculated dissolved lead concentration as a function of pH is shown in Figure 3.1. Above pH 6 Pb(IV) species become dominant and the dissolved lead concentration increases with increasing pH. It should be noted that the predicted dissolved lead concentrations in equilibrium with PbO₂ are extremely low with concentrations always less than $10^{-9}$ M (0.20 µg/L) over the pH range of 4-11.

The low predicted concentrations are caused by the very low values for the equilibrium constants for the dissolution of either of the two PbO₂ solids (reactions 1-2). Caution should be used when applying these values to the prediction of dissolved lead concentrations in solutions with conditions relevant to drinking water distribution systems. The values reported in the table were calculated from published values of Gibbs free energies of formation ($G^0_{f,\text{sub}}$) for the relevant reactants and products (Pourbaix 1974; Risold et al. 1998); however, these Gibbs free energies were determined from electrochemical potential measurements made at very acidic and very basic conditions (Glasstone 1922) and not from any solubility experiments or experiments conducted at near neutral pH. Further details of the calculation approach are presented in Appendix A. The lack of any direct measurements of PbO₂ solubility at conditions relevant to drinking water distribution was a major motivation for Task 2.

Both of the PbO₂ polymorphs, scrutinyite and plattnerite, have been observed in drinking

![Figure 3.1 Predicted dissolved lead concentration in equilibrium with scrutinyite in the presence of $2.8 \times 10^{-5}$ M HOCl and Cl⁻ based on reactions and equilibrium constants in Table 3.1.](image-url)
water distribution systems. These two polymorphs have different calculated solubility constants, so they may release different amounts of lead over long stagnation time. The primary objectives of Task 2 were to (1) determine lead release from scrutinyite and plattnerite over long stagnation times at different pH values and (2) gain knowledge of the equilibrium solubility of the two PbO$_2$ polymorphs.

MATERIAL AND METHODS

Materials

Two PbO$_2$ polymorphs were used. Scrutinyite was synthesized using the method discussed below. Plattnerite was purchased (Acros) and its purity was confirmed by XRD. Reagent grade PbCl$_2$, NaHCO$_3$, NaOH, NaOCl solution, and concentrated HNO$_3$ were purchased (Fisher Scientific). Ultrapure water (resistivity >18.2 MΩ-cm) was used to prepare solutions.

Synthesis of Scrutinyite

Scrutinyite was synthesized by oxidizing hydrocerussite with a sodium hypochlorite (NaOCl) solution at pH 10 in the absence of DIC. Different hydrocerussite concentrations were tested (0.5 to 5 mM), and preliminary results showed that pure scrutinyite only formed when

![X-ray diffraction patterns](image)

**Figure 3.2 X-ray diffraction patterns of scrutinyite synthesized in this study together with reference patterns from the ICDD database**
starting with 0.5 mM hydrocerussite. Hydrocerussite was prepared using the method described in Chapter 2. The synthesis experiments were conducted in 2-L polypropylene batch reactors at room temperature (21±1 °C). Solid hydrocerussite was first added to the reactor to make a total lead concentration of 0.5 mM. The pH was adjusted to 10.0 ± 0.2 and then an NaOCl solution was added to the reactor to provide a free chlorine concentration of 40 mg/L as Cl₂. The free chlorine concentration was measured and maintained at its initial value by periodic addition of the NaOCl stock solution. The key to forming pure scrutinyite was to maintain the pH in the experiments. If the pH dropped below 8, then hydrocerussite would partially transform to cerussite, which could lead to the formation of plattnerite impurities.

After 1 week of reaction, the solids were separated by centrifugation, washed with 1 mM HNO₃ and then with ultrapure water. The solids were then dialyzed for 48 hours using a regenerated cellulose dialysis membrane, and the dialysis water was changed periodically with fresh ultrapure water. The solids were freeze-dried and the identity of the solids was confirmed using XRD (Figure 3.2). The morphology of the solids was determined using SEM (Figure 3.3).

![Figure 3.3 Electron micrographs showing the morphology of scrutinyite](image)

**Figure 3.3** Electron micrographs showing the morphology of scrutinyite

---

**PbO₂ Dissolution Experiments**

Bench-scale experiments were conducted to determine the lead release from PbO₂ over long stagnation time and to acquire knowledge of the solubility of PbO₂. A set of batch experiments were conducted in 500-mL polypropylene reactors at room temperature (21±1 °C). Factors evaluated included the form of the solid added (i.e. plattnerite vs. scrutinyite), pH, and the presence of DIC (Table 3.2). For experiments in the presence of DIC, a 0.5 M NaHCO₃ stock solution was used to adjust the DIC to 50 mg C/L. The free chlorine concentration was then adjusted to above 2 mg Cl₂/L and maintained subsequently by periodic addition of an
aliquot of a NaOCl stock over the course the 14-21 day experiments. The high free chlorine concentration in the present study should be able to provide a sufficiently high ORP to prevent the reductive dissolution of PbO₂. The pH was adjusted to the target values and maintained by the periodic addition of HNO₃ or NaOH. Finally, plattnerite or scrutinyite was added to the reactors to make the solid concentration 50 mg/L. The reactors were covered with aluminum foil to prevent the photodegradation of free chlorine. To get rid of possible side reactions, no buffers were added to the system. To minimize the uptake of CO₂ from the atmosphere, the solutions were stirred in sealed bottles. For experiments with no DIC, the experiments were conducted in an argon-filled glovebox with the atmosphere in contact with a 0.5 M NaOH solution to absorb any remaining CO₂.

Experiments were conducted for 14 to 21 days. Samples were taken periodically and analyzed for dissolved lead and free chlorine concentrations. The samples for dissolved lead analysis were first filtered through 0.22 µm polyethersulfone (PES) syringe filters, acidified to 2% HNO₃, and preserved prior to analysis. Each experimental condition was run in duplicate.

**Table 3.2**

<table>
<thead>
<tr>
<th>Conditions/#</th>
<th>Experimental conditions studied for the solubility of PbO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Starting solid</td>
<td>plattnerite</td>
</tr>
<tr>
<td>Solid concentration (mg/L)</td>
<td>50</td>
</tr>
<tr>
<td>pH</td>
<td>6, 7.5, 8.5</td>
</tr>
<tr>
<td>DIC (mg C/L)</td>
<td>0, 50</td>
</tr>
<tr>
<td>Free Chlorine (mg Cl₂/L)</td>
<td>&gt; 2 mg Cl₂/L</td>
</tr>
<tr>
<td>Experimental time (days)</td>
<td>21</td>
</tr>
</tbody>
</table>

**Analytical Methods**

Dissolved lead (Pb) concentrations were measured by inductively coupled plasma mass spectroscopy (ICP-MS) on an Agilent 7500ce instrument. The method detection limit for lead was determined to be 0.05 µg/L. The approach followed that of Standard Method 3125. The instrument was calibrated with standards (at least 7) with concentrations from 0.05 to 100 µg/L. For samples with concentrations above the highest standard, dilutions were prepared. Free chlorine concentrations were determined by the standard DPD colorimetric methods (4500-Cl G) (Clesceri et al. 1999). Solution pH was measured with a glass pH electrode and pH meter (Accumet).

**RESULTS AND DISCUSSION**

**Effect of Total Lead Concentration on the Formation of Scrutinyite**

To acquire enough pure scrutinyite for the solubility experiments, a set of experiments were conducted to investigate the effect of total lead concentrations on the formation of
scrutinyite from hydrocerussite precursor at pH 10 in the absence of DIC. Results (Figure 3.4) showed that the identity and purity of the PbO$_2$ that formed strongly depended on the total lead concentration. With 0.5 mM lead as hydrocerussite, 5 days of reaction led to the formation of pure scrutinyite. When the total lead concentration increased to 1 mM, the characteristic peaks of plattnerite at 25$^\circ$ and 32$^\circ$ in addition to those of scrutinyite were observed in the XRD pattern. These peaks were also observed with total lead concentrations higher than 1 mM. Therefore, the critical value for converting hydrocerussite to pure scrutinyite and not to mixtures of scrutinyite and plattnerite is between 0.5 mM to 1 mM of lead at pH 10. From the discussion in Chapter 2, a mixture of scrutinyite and plattnerite formed from an aqueous oxidation pathway. To avoid the impurity of plattnerite and its potential effect on the lead release from scrutinyite, scrutinyite for the solubility test was synthesized using 0.5 mM hydrocerussite as the starting phase.

![Figure 3.4 X-ray diffraction patterns of solids following reaction of hydrocerussite at pH 10 without DIC and with a free chlorine:lead ratio of 1.2:1 together with reference patterns from the ICDD database](image)

Lead Release from Plattnerite

**Effect of pH**

Even in the presence of free chlorine, measurable amounts of lead may be released from PbO$_2$ after long stagnation times at conditions relevant to drinking water. Batch experiments were conducted to determine lead release from plattnerite in the presence of free chlorine at pH 6.0 to 8.5. For experiments at pH 7.5 and 8.5, dissolved lead concentrations increased with...
Figure 3.5 Dissolved lead concentrations with time in plattnerite batch dissolution experiments. Experiments were performed at 50 mg/L plattnerite and 2 mg Cl₂/L free chlorine with (closed symbols) and without (open symbols) 50 mg C/L DIC at pH values of (a) 6.0, (b) 7.5 and (c) 8.5. In all panels dashed lines represent the lead action level of 15 μg/L. “-A” and “-B” represent duplicate experiments.
Lead(IV) Oxide Formation and Stability in Drinking Water Distribution Systems

increasing time, and reached plateaus after 10 days of reaction (Figure 3.5). The total lead concentrations only exceeded the lead action level (0.015 mg/L) after 10 days at pH 8.5 and 4 days at pH 7.5. At pH 6.0, lead concentrations were more variable and did not increase with time. The lead concentrations were much lower at pH 6.0 than at pH 7.5 and 8.5. The fluctuation of the lead concentrations may be partially due to the fluctuation of the system pH since the system was poorly buffered due to the absence of DIC, and it was hard to maintain the pH at the target value.

If the systems were at equilibrium, then the plateau lead concentrations may represent equilibrium between PbO₂ and the solution. The stable lead concentrations achieved in the batch experiments were compared to the equilibrium lead concentrations calculated using the published thermodynamic constants (Figure 3.6). The equilibrium calculation and the measurements in this study do both predict a trend of increasing equilibrium lead concentrations with increasing pH above pH 6. Clearly at all pH values studied, the measured equilibrium lead concentrations were orders of magnitude higher than the predicted values. The large discrepancy between the calculated and measured equilibrium solubility may be attributed to several reasons. First the equilibrium constants used to calculate the solubility were derived from measurements at very acidic and basic conditions, and those measurements were for electrochemical and not solubility experiments. The thermodynamic constants for PbO₂ and Pb(IV) species calculated from published Gibbs from energies of formation may not be applicable to conditions relevant to drinking water distribution.

Figure 3.6 Predicted (solid and dash lines) and measured (triangular points) equilibrium solubility of PbO₂ in the presence of 2 mg Cl₂/L free chlorine and with no DIC.
The second reason may be due to the presence of dissolved Pb(II) species. Although PbO₂ should be very stable in the presence of free chlorine and dissolved Pb(II) species should be negligible, the kinetics of the reduction and re-oxidation reactions may be such that appreciable reduction of PbO₂ by water may still be occurring. The dissolved Pb(II) concentration would then be controlled by the balance of the rates of the following two reactions:

\[
PbO_2(s) + 2H^+ = Pb^{2+} + 0.5O_2(aq) + H_2O \quad (3.3)
\]

\[
HOC_1 + Pb^{2+} + H_2O = PbO_2 + Cl^- + 3H^+ \quad (3.4)
\]

If reaction 3.3 is faster than reaction 3.4, then aqueous Pb(II) species will be released to the solutions even in the presence of free chlorine. The measured dissolved lead concentration will then represent a balance between reactions 3.3 and 3.4, and the intrinsic equilibrium solubility of PbO₂ may not be able to be acquired. A previous study observed that 5 – 10 µg/L dissolved Pb(II) was released from PbO₂ even in the presence of free chlorine, which was in agreement with this statement (Lin and Valentine 2009). The measured dissolved lead concentrations in the present study that were orders of magnitude higher than the predicted values combined with the dissolved Pb(II) detected in the previous study suggest that this second kinetically-based reason may be the primary cause of the discrepancy between the measured and predicted lead concentrations.

**Effect of DIC**

DIC is abundant in drinking water, and its effect on lead release from plattnerite over long stagnation times was determined at pH 6.0 to 8.5 (Figure 3.5). Because carbonate is a good complexing ligand for Pb(II), it may increase Pb(II) release from PbO₂. However, in the present study, DIC had very little effect on lead release at pH 6.0; while at pH 7.5 and 8.5, less lead was actually released in the presence of 50 mg C/L DIC over the 21 days of reaction than in the absence of DIC. The effect of DIC may be obscured by the effect of pH. When DIC was present it served as a pH buffer and the system pH only fluctuated within 0.2 pH units of the target pH values. While in the absence of DIC, the system was unbuffered and the pH fluctuated to a much larger extent, around 0.5 pH units of the target pH values, which could have caused the lead concentrations to be more variable. Overall, the results suggest that DIC has either no effect or a minimal effect on long term lead release from plattnerite in the presence of free chlorine.

**Lead Release from Scrutinyite**

Lead release from scrutinyite (α-PbO₂) was determined at pH 7.5 and 8.5 with no DIC in the presence of free chlorine (Figure 3.7). Dissolved lead concentrations increased with time until reaching plateau values after 10 days of reaction. The lead concentrations were above the lead action level only after 6 days of reaction at both pH 7.5 and 8.5. Similar to the case of plattnerite, the measured dissolved lead concentrations from scrutinyite were orders of magnitude higher than those calculated from published thermodynamic constants (Figure 3.6), suggesting that the lead release was controlled by the kinetics of reactions 3.3 and 3.4 rather than by the intrinsic equilibrium solubility of scrutinyite. Since the measured dissolved lead concentrations were several orders of magnitude higher than predicted using published
thermodynamic data for Pb(IV) species, it is reasonable to assume that nearly all of the measured dissolved lead was present as aqueous Pb(II) species. After 14 days of reaction, more lead was released at pH 8.5 than at pH 7.5.

Lead release from scrutinyite was compared to that from plattnerite (Figure 3.6). At both pH 7.5 and 8.5, dissolved lead concentrations in systems equilibrated with scrutinyite were similar to those in systems equilibrated with plattnerite. Scrutinyite and plattnerite are the two polymorphs of PbO$_2$, and they have similar thermodynamic constants. It was expected that the equilibrium solubility of these two polymorphs would be similar. However, since the dissolved lead concentrations may be controlled by the kinetics of reactions 3.3 and 3.4, these results suggest that scrutinyite and plattnerite may also have similar dissolution kinetics.

**Summary of Lead(IV) Oxide Solubility**

The long term lead release from the two PbO$_2$ polymorphs scrutinyite and plattnerite was determined in batch reactors in the presence of free chlorine. Experiments were initially designed to measure the equilibrium solubility of PbO$_2$ with the assumption that PbO$_2$ is stable in solutions containing free chlorine. However, the measured dissolved lead concentrations were orders of magnitude higher than the predicted values, suggesting that the lead release was not controlled by the equilibrium solubility of PbO$_2$ but rather by the kinetics of the reductive dissolution of PbO$_2$ by water and the re-oxidation of Pb(II) to PbO$_2$. Despite being higher than originally predicted, the stable lead concentrations in the presence of free chlorine were still lower than the action level of 15 µg/L at pH 6 and only exceeded it after long stagnation times at pH 7.5 and 8.5.

Although it is challenging to measure the equilibrium solubility of PbO$_2$ directly from the experiments, our results can provide an indication of the extent of lead release from PbO$_2$ in systems containing free chlorine with very long stagnation times. Most of these stagnation times (4 days or longer) are much larger than those that would normally be encountered for a lead service line. Consequently, for most lead service lines with PbO$_2$ scales, the lead concentrations will be determined by dissolution rates and not by equilibrium solubility. The long-term extent of lead release increased with increasing pH, and plattnerite and scrutinyite released similar amounts of lead. The presence of DIC had a limited effect on the extent of lead release from plattnerite. Since dissolved lead concentrations in drinking water are controlled by the kinetics of PbO$_2$ dissolution rather than the equilibrium solubility of PbO$_2$, it is crucial to determine the dissolution rate of PbO$_2$ at various water chemistry conditions and to elucidate the pathways and mechanisms of PbO$_2$ dissolution. The next chapter presents the results of a systematic study of the dissolution rates of PbO$_2$. 

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Figure 3.7 Dissolved lead concentrations with time in scrutinyite batch dissolution experiments. Experiments were performed at 50 mg/L scrutinyite, 2 mg Cl₂/L free chlorine, no DIC, and pH values of (a) 7.5 and (b) 8.5. In all panels dashed lines represent the lead action level of 15 μg/L. “-A” and “-B” represent duplicate experiments.
CHAPTER 4
DISSOLUTION RATES OF LEAD(IV) OXIDE

OVERVIEW OF RESEARCH ON LEAD(IV) OXIDE DISSOLUTION RATES

Information about the rates and mechanisms of PbO₂ dissolution are important for estimating lead concentrations that may occur in water in contact with pipe scales that contain this corrosion product. Because PbO₂ is often found to coexist with lead(II) corrosion products in drinking water distribution systems (Schock and Giani 2004), it is clear that these systems are not at equilibrium. Consequently, information about rates and not equilibrium solubility is needed. The dissolution rate of PbO₂ is affected by water chemistry parameters including pH and DIC. PbO₂ is such a strong oxidant that it is not stable in pure water. Previous studies indicated that the presence of reductants in drinking water could increase the rate and extent of PbO₂ dissolution. These reductants include natural organic matter (NOM), Fe²⁺, Mn²⁺, I⁻, and Br⁻ (Dryer and Korshin 2007; Lin et al. 2008; Lin and Valentine 2008b; 2010; Shi and Stone 2009a; b). The majority of these studies were not designed to provide quantitative information on dissolution rates, which led to a knowledge gap that the present project sought to fill.

The reductive dissolution of PbO₂ can be described by a mechanism involving coupled chemical reduction and detachment steps. The combined process of reduction and detachment is referred to here as dissolution. In the first step the reductants attach to the surface of PbO₂ and reduce the surface Pb(IV) species to Pb(II) species; in the next step the surface Pb(II) species detach and are released to the solution. Water chemistry parameters can influence the rate of dissolution of PbO₂ by affecting these two steps. Carbonate from DIC can act as a complexing ligand for Pb(II) that may accelerate the detachment step of the overall dissolution process. As noted above, reductants that are naturally present in the water may increase the rate of reduction of Pb(IV) to Pb(II). Free chlorine is a strong oxidant that may either inhibit the reduction of surface Pb(IV) species to Pb(II) species or re-oxidize the Pb(II) species that are released to water. Orthophosphate is often added as a corrosion inhibitor in water treatment, and it may inhibit the dissolution of PbO₂ by either adsorbing and blocking surface sites of PbO₂ or forming a low solubility lead(II) phosphate solid. The primary aims of the task whose results are presented in this chapter were to (1) determine the dissolution rates of PbO₂ as a function of water chemistry, (2) elucidate the mechanisms of the reductive dissolution of PbO₂ at conditions relevant to drinking water, and (3) quantify the inhibitory effects of free chlorine and orthophosphate on the dissolution rate of PbO₂.

MATERIALS AND METHODS

Materials

PbO₂ was purchased (Acros), and XRD patterns confirmed that the PbO₂ was pure plattnerite (Figure 4.1). The PbO₂ solids had primary sizes of around 100 nm (Figure 4.2), and the specific surface area of the PbO₂ was 3.6 m²/g as measured by BET-N₂ adsorption. Reagent grade KH₂PO₄, KI, NaNO₃, NaHCO₃, NaOH, MOPS, NaOCl solution, NH₄Cl, and concentrated HNO₃ were purchased (Fisher Scientific). Ultrapure water (resistivity >18.2 MΩ-cm) was used to prepare solutions.

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Figure 4.1 X-ray diffraction patterns of the PbO₂ used in this study together with the reference pattern from the ICDD database

Figure 4.2 Electron micrographs showing the morphology of pure plattnerite
PbO₂ Dissolution Experiments

Summary of Experimental Conditions

PbO₂ dissolution was examined as a function of water chemistry. The parameters investigated were pH, DIC, the presence of iodide, free chlorine, and orthophosphate. Four sets of experiments were conducted for different purposes in understanding the overall mechanisms of PbO₂ dissolution and the effect of potential inhibitors (Table 4.1). In Set A the dissolution rates of PbO₂ in water were determined in the presence of DIC to provide a baseline. In Set B the dissolution of PbO₂ was investigated in the presence of iodide as a chemical reductant and carbonate as a complexing ligand to probe the pathways and mechanisms of its reductive dissolution. This set integrated the effects of both the reductant and a complexing ligand on the dissolution rate. In Set C the dissolution of PbO₂ was investigated as a function of free chlorine concentration to determine its inhibitory effect and to probe for a critical concentration that might be able to inhibit dissolution. In Set D orthophosphate was added to the solution to evaluate its effect on lead release from PbO₂.

Flow-through Experiment Set-up

Continuously stirred tank reactors (CSTRs) were used to quantify the dissolution rates of PbO₂ at room temperature (21 ± 1 ºC) (Figure 4.3). The volume of each reactor was 84 mL, and PbO₂ was loaded to the reactor to a concentration of 1 g/L. A 0.22 µm mixed cellulose filter membrane was used to seal the reactor and prevent the loss of the solid from the reactor. The influent flow was pumped into the reactor using a peristaltic pump (Cole-Parmer) with a flow rate of 2.8 mL/min, so the hydraulic residence time of the reactor was 30 minutes. The effluent pH was monitored and aqueous samples were periodically collected over 24 hours and preserved for dissolved lead analysis. Selected samples were further filtered using 0.02-µm PES syringe filters and their close agreement with the 0.22-µm filtered samples suggested that the filtrate from the 0.22-µm filters represents dissolved lead and did not include any colloidal lead.

The influents were prepared in 10-L plastic (Tedlar) bags to minimize the exchange of CO₂ between the atmosphere and the solution. Ultrapure water was purged of CO₂ by sparging with N₂ and then pumped into the bags. NaHCO₃ was added to provide the desired concentrations of DIC. 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 PbO₂ dissolution. A 1.0 M NaNO₃ solution was then injected to the bags to set the ionic strength at 0.01 M. The pH was adjusted to the target values by addition of concentrated HNO₃ or freshly prepared 0.5 M NaOH solutions. For Set B iodide was used as a reductant and its concentration was adjusted by addition of an aliquot of 10 mM KI stock solution. For Set C free chlorine was provided by a NaOCl stock solution. For Set D instead of free chlorine, an aliquot of a 200 mg Cl₂/L chloramine stock solution was added to provide a target chloramine concentration of 2 mg Cl₂/L. The stock chloramine solutions were prepared by mixing volumes of 6% (w/w) NaOCl and 2500 mg NH₃/L NH₄Cl solutions in ultrapure water. This mixture provides a 0.79 Cl₂:N molar ratio that can simulate the conditions in drinking water distribution systems and premise plumbing. Under these conditions the dominant form of
chloramine is monochloramine (NH₂Cl). Then the orthophosphate concentration was adjusted to 1 mg P/L by adding a volume of 10 mM KH₂PO₄ stock solution. Solutions with free chlorine or chloramine were shielded from light by aluminum foil to minimize their decomposition.

### Information on Influent Composition

Four sets of experiments were conducted to evaluate the effect of different parameters on the dissolution rate of PbO₂ and to elucidate the pathways and mechanisms of PbO₂ dissolution. The effect of different parameters was examined by varying the influent composition. Four sets of experiments were conducted to evaluate the effect of different parameters on the dissolution rate of PbO₂ and to elucidate the pathways and mechanisms of PbO₂ dissolution. The effect of different parameters was examined by varying the influent composition.

<table>
<thead>
<tr>
<th>Set</th>
<th>Influent Solution</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ultrapure water</td>
<td>pH: 5.7, 6.7, 7.6, 8.5&lt;br&gt;DIC: 50 mg C/L</td>
</tr>
<tr>
<td>B</td>
<td>Reductant (iodide) and complexing ligand solution (DIC)</td>
<td>pH: 5.7, 6.7, 7.6, 8.5&lt;br&gt;DIC: 0, 10, 50, 200 mg C/L&lt;br&gt;Iodide: 0, 1, 2, 5, 10, 20, 100 μM</td>
</tr>
<tr>
<td>C</td>
<td>Free chlorine</td>
<td>pH: 5.7, 6.7, 7.6, 8.5&lt;br&gt;DIC: 50 mg C/L&lt;br&gt;Free chlorine: 0.2, 1 mg Cl₂/L</td>
</tr>
<tr>
<td>D</td>
<td>Orthophosphate</td>
<td>pH: 7.6, 8.5&lt;br&gt;DIC: 0, 50 mg C/L&lt;br&gt;Orthophosphate: 0, 1 mg P/L&lt;br&gt;Chloramine: 2 mg Cl₂/L</td>
</tr>
</tbody>
</table>

#### Figure 4.3 Flow-through reactor for measuring dissolution rates
of experiments with different influents were selected (Table 4.2).

A: Ultrapure water: PbO₂ is a strong oxidant that it is even not stable in water. The reductive dissolution of PbO₂ by water to release Pb(II) is thermodynamically favorable. Experiments were conducted at pH 5.7 to 8.5 in the presence of 50 mg C/L DIC, a concentration that is in the range observed for drinking water. A total of 4 conditions were examined.

<table>
<thead>
<tr>
<th>Conditions studied for PbO₂ dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>Set A &amp; C</td>
</tr>
<tr>
<td>Free chlorine (mg Cl₂/L)</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

| Set B  |  |     |     | 100 |
|--------|  |     |     |     |
| pH     |  5.7 | DIC (mg C/L) | 50 |  |  |  |  |  |  |  | |
|        |  6.7 | DIC (mg C/L) | 50 |  |  |  |  |  |  |  |  |
|        |  7.6 | DIC (mg C/L) | 50 |  |  |  |  |  |  |  |  |
|        |  8.5 | DIC (mg C/L) | 50 |  |  |  |  |  |  |  |  |
|        |  200 |  |  |  |  |  |  |  |  |  |  |

| Set D* |  |     |     |  | 100 |
|--------|  |     |     |  |     |
| pH     |  7.6 | Orthophosphate (mg P/L) | 0 |  |  |  |  |  |  |  |
|        |  8.5 | Orthophosphate (mg P/L) | 0 |  |  |  |  |  |  |  |
| DIC (mg C/L) | 0 | 29 | 33 | 30 | 34 |
|                  | 50 | 31 | 35 | 32 | 36 |

Numbers are experiment identification numbers for each condition. Gray boxes are conditions that were not examined.

*Experiments in Set D were all conducted in the presence of 2 mg Cl₂/L chloramine.
B: Solution with complexing ligand and reductant: The reductive dissolution of PbO$_2$ can be described by a coupled reduction-detachment pathways. The presence of a chemical reductant or a complexing ligand may enhance the overall dissolution of PbO$_2$. Iodide was selected as a model reductant in the present work with a concentration range of 1 – 100 µM. Iodide is present in natural waters and is capable of reducing PbO$_2$ at drinking water conditions to form aqueous iodine species (Fuge and Johnson 1986). Although iodide may not be the most significant reductant in most drinking waters, the observation of its impacts on PbO$_2$ dissolution can provide insights into the overall reductive dissolution of PbO$_2$, which may be induced by other reductants in drinking water that include natural organic matter and Fe(II) and Mn(II). DIC is abundant in drinking water with typical concentrations of 0 – 50 mg C/L. Carbonate is a good complexing ligand for Pb$^{2+}$ that can increase the dissolution rate of PbO$_2$ by forming lead(II)-carbonate complexes. Carbonate was selected as a model complexing ligand with the DIC concentration of 0 – 200 mg C/L. Experiments were conducted at pH 5.7 to 8.5. A total of 17 conditions were examined.

C: Solution with free chlorine: Free chlorine is a strong oxidant and can provide a high ORP that may prevent the reductive dissolution of PbO$_2$. Two free chlorine concentrations were evaluated for their potential inhibitory effect on the dissolution rate of PbO$_2$. Experiments were conducted at pH 5.7 – 8.5 in the presence of 50 mg C/L. A total of 7 conditions were examined.

D: Solution with orthophosphate: Switching the disinfectant from free chlorine to chloramine can decrease the ORP of the system and cause the reductive dissolution of PbO$_2$. Adding orthophosphate is considered as a strategy to mitigate lead release and has been adopted by several water utilities. In this set of experiments the dissolution rate of PbO$_2$ was determined in the presence and absence of 1 mg P/L orthophosphate to evaluate the inhibitory effect of orthophosphate and to determine the mechanisms of the inhibition. To simulate the conditions typically found in drinking water with orthophosphate addition, experiments were performed with 2 mg Cl$_2$/L chloramine in the presence of 50 mg C/L DIC at pH 7.6 and 8.5. A total of 8 conditions were examined.

Dissolution Rate Determination Method

The dissolution rates were determined for the CSTRs by operating the reactors until they reached steady-state behavior. As compared to batch experiments, the flow-through approach avoids the accumulation of reaction products and minimizes the effect of any initial labile phases on the dissolution rates (Samson et al. 2000). Performing a mass balance on the dissolved lead in the reactor, the following relationship can be acquired:

$$V_R \cdot \frac{dC}{dt} = Q \cdot C_{in} - Q \cdot C_{out} + r_{exp} \cdot V_R$$  \hspace{1cm} (4.1)

where:
- $r_{exp}$ = measured net dissolution rate of PbO$_2$ (mol/L·min)
- $V_R$ = volume of the reactor (mL)
- $Q$ = flow rate (mL/min)
- $C_{in}$, $C_{out}$ = influent and effluent lead concentration (M)

The systems approach steady state (i.e. $dC/dt = 0$) after 10 to 20 residence times of operation (Xie et al. 2010). The influent is lead free (i.e. $C_{in} = 0$), and the effluent concentrations at steady state are denoted as $C_{ss}$, which was calculated as the average concentration from at least
8 consecutive samples that did not vary by more than 20% and that spanned at least 8 residence times. Therefore the experimental rate can be determined as:

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

(4.2a)

where:
\[ t_{\text{res}} = \text{the hydraulic residence time (i.e. } V_R/Q \text{)} \text{ (min)} \]

And the rate can be normalized to surface area:

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

(4.2b)

where:
\[ R_{\text{exp}} = \text{measured net dissolution rate of PbO}_2 \text{ normalized to surface area (mol/m}^2 \cdot \text{min)} \]
\[ A = \text{specific surface area of PbO}_2 \text{ (m}^2/\text{g)} \]
\[ [\text{solids}] = \text{concentration of PbO}_2 \text{ solids in the reactor (g/L)} \]

**Pb(II) Adsorption Experiments**

The adsorption of aqueous Pb(II) ions onto the surface of PbO\(_2\) was determined at room temperature \((21 \pm 1 \degree \text{C})\) using 150-mL polypropylene batch reactors. A 10 mg Pb/L lead(II) chloride stock solution was added to achieve a total lead concentration of 200 µg/L (0.96 µM). Then a 0.5 M NaHCO\(_3\) stock solution was added to provide a 50 mg C/L of DIC. The pH was adjusted to 4.5 to 8.5 with HNO\(_3\) or NaOH. Finally, PbO\(_2\) solids were added to provide a solid concentration of 0.1 g/L. The system was well-mixed. After 2 hours, aqueous samples were collected, filtered with 0.22 µm PES syringe filters, acidified to 2% HNO\(_3\), and preserved for dissolved lead analysis. The difference between the total lead added to the reactors and the dissolved lead after 2 hours represents the amount of Pb(II) that had adsorbed to the PbO\(_2\).

**Analytical Methods**

Dissolved lead (Pb) concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500ce instrument. Solids remaining at the end of selected experiments were collected, centrifuged, and characterized by XRD and SEM. A Rigaku Geigerflex D-MAX/A diffractometer with Cu-Ka radiation was used for XRD measurements. Electron microscopy was performed on a JEOL 7001LVF field emission scanning electron microscope. BET-N\(_2\) adsorption was performed on a BET-Autosorb instrument (Quantachrome Instruments). Free chlorine, 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+) (Clesceri et al. 1999). Solution pH was measured with a glass pH electrode and pH meter (Accumet).

**RESULTS AND DISCUSSION**

**Overview**

Four sets of flow-through experiments were conducted to determine the effect of different parameters on the dissolution rate of PbO\(_2\). All experimental conditions studied and the results of
the steady-state dissolved lead concentrations and the dissolution rates are listed in Table 4.3. In DIC-buffered ultrapure water, the dissolution rate of PbO₂ increased with decreasing pH values. The presence of free chlorine inhibited the dissolution of PbO₂, and the dissolution rate decreased with increasing free chlorine concentrations. The presence of orthophosphate inhibited the dissolution of PbO₂ in the presence of DIC and chloramine, which may be due to the adsorption of orthophosphate to the surface of PbO₂ to block the active sites for PbO₂ dissolution.

The presence of the chemical reductant iodide significantly enhanced the dissolution of PbO₂, and the dissolution rate increased with increasing iodide concentrations and decreasing pH. The addition of a small amount of DIC (10 mg C/L) increased the dissolution rate of PbO₂, and further increases in the DIC concentration from 10 to 200 mg C/L had little effect on the dissolution rate of PbO₂. These observations suggested that chemical reduction was usually the rate-controlling step in the dissolution of PbO₂.

**PbO₂ Dissolution at Baseline Conditions – Ultrapure Water (Set A)**

The dissolution rate of PbO₂ in water with 50 mg C/L DIC was determined at pH 5.7 to 8.5. The effluent dissolved lead concentrations used to determine the dissolution rate and the pH are shown as a function of residence times in Figure 4.4. The effluent lead concentrations were more variable during the first 10 – 20 residence times, which may be due to fast initial dissolution of labile phases and more reactive sites. The systems reached steady state by 40 residence times, and the effluent lead concentrations were used to calculate the dissolution rate of PbO₂. Compared to the initial dissolution rate, the steady-state dissolution rate of PbO₂ may be more representative in describing the dissolution of PbO₂ in actual distribution systems since the steady-state dissolution avoids the accumulation of any reaction products and minimizes the effect of the presence of labile phases.

The dissolution rate of PbO₂ increased with decreasing pH values (Figure 4.5). The dissolution rate increased only slightly from pH 8.5 to 6.7, while it increased four times in going from pH 6.7 to 5.7. Results suggested that for a typical drinking water pH range (7.6 and 8.5 in the present study), some Pb(II) would be released to drinking water from the dissolution of PbO₂, but the dissolution rate is expected to be low. However, if the system is acidic, then the dissolution rate of PbO₂ would increase significantly. Although pH 5.7 is outside of the range anticipated for drinking water distribution systems, it might be present in dead zones of distribution networks or regions of low flow where biofilms grow or nitrification occurs (Zhang et al. 2009). Investigation at this pH was also helpful in establishing the overall trend with pH.

The effect of pH may be caused by several reasons. First, the reductive dissolution of PbO₂ by water is thermodynamically favorable and pH may affect the electrochemical driving force for PbO₂ reduction. The reductive dissolution of PbO₂ by water can be described by Reaction 4.3:

\[
PbO_2(s) + 2H^+ = Pb^{2+} + 0.5O_2(aq) + H_2O \tag{4.3}
\]

Decreasing the pH would increase the electrochemical driving force (\(\Delta E_H\)) for Reaction 4.3. Based on the Nernst equation and published \(E^{\circ}_H\) values for the relevant half reactions (Reactions 1 and 2 in Table 4.4), \(\Delta E_H\) will increase by 0.059V for a 1 pH unit decrease. Increasing the \(\Delta E_H\)
### Table 4.3
Conditions and results of plattnerite dissolution experiments

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(continued)
### Table 4.3 (Continued)

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<th>DIC (mg C/L)</th>
<th>Iodide (µM)</th>
<th>Free chlorine (mg Cl₂/L)</th>
<th>Chloramines (mg Cl₂/L)</th>
<th>Orthophosphate (mg P/L)</th>
<th>Measured pH&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Steady state effluent lead (nM)</th>
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<td>18</td>
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</table>

<sup>a</sup> The letters A-B indicate duplicate experiments.

<sup>b</sup> 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.

<sup>c</sup> 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.
would increase the electrochemical driving force for PbO₂ reduction, thus increasing the dissolution rate of PbO₂.

Table 4.4  
Thermodynamics of PbO₂ dissolution

<table>
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<th>Reaction</th>
<th>E₉ H° (V)</th>
<th>No</th>
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<td>PbO₂ reduction:</td>
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<tr>
<td>Water oxidation:</td>
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<td>Iodide oxidation:</td>
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<tr>
<td>Free chlorine reduction:</td>
<td>1.48</td>
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</table>

E₉ H° was calculated using the thermodynamic data from (Stumm and Morgan 1996).
Figure 4.5 The dissolution rate of plattnerite in the 50 mg C/L DIC-buffered water at pH 5.7 to 8.5 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.

Figure 4.6 Adsorption of 0.96 µM Pb(II) onto 0.1 g/L PbO₂(0) in the presence of 50 mg C/L dissolved inorganic carbon (DIC) as a function of pH.
A second reason may be related to the adsorption of Pb$^{2+}$ ions onto the surface of PbO$_2$. Pb$^{2+}$ could adsorb to the PbO$_2$ surface at neutral or slightly basic environments (Figure 4.6), which may passivate the PbO$_2$ surface by blocking the active sites for the dissolution of PbO$_2$. At acidic conditions Pb$^{2+}$ does not adsorb as completely to the PbO$_2$ surface such that more surface sites would be unoccupied and available for reductive dissolution of PbO$_2$.

Effect of Chemical Reductant and Complexing Ligand on PbO$_2$ Dissolution (Set B)

Effect of Iodide and pH

The reductive dissolution of PbO$_2$ by iodide can be described by the half reactions involving PbO$_2$ reduction and iodide oxidation (Reactions 1 and 3 in Table 4.4). The overall redox reaction between PbO$_2$ and iodide can be expressed as:

$$\text{PbO}_2 + 2\text{I}^- + 4\text{H}^+ = \text{Pb}^{2+} + \text{I}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} (4.4)

The presence of 10 µM iodide increased the dissolution rate of PbO$_2$ at all pH values studied (Figure 4.7). The presence of a reductant can significantly affect the stability of PbO$_2$. The dissolution rate increased with decreasing pH, and the apparent reaction order with respect

![Figure 4.7 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.](image)
to H⁺ concentrations was 0.61 over the range of pH 5.7 to 8.5 in the present study. This observation was comparable to that of a previous study that measured the dissolution rate of PbO₂ by iodide and found that the reaction order with respect to H⁺ was 0.66 for pH 6.0 – 8.0 (Lin et al. 2008).

The effect of pH may be caused by its effects on the electrochemical driving force for PbO₂ reduction by iodide and by its impact on iodide adsorption onto the PbO₂ surface. Increasing the difference in the electrochemical potentials for PbO₂ reduction and iodide oxidation (ΔE_H) would increase the electrochemical driving force for PbO₂ reduction, and increase the dissolution rate. Based on the Nernst equation and published E_H° values for the relevant half reactions (Reactions 1 and 3 in Table 4.4), the ΔE_H of Reaction 4.4 will increase by 0.118V for a 1 pH unit decrease. In addition, more iodide would be expected to be adsorbed onto the surface of PbO₂ at lower pH since this behavior is typically observed for anion adsorption. The greater extent of PbO₂ surface coverage by iodide at lower pH may result in faster dissolution of PbO₂ at lower pH.

**Effect of Iodide Concentration**

The effect of different iodide concentrations on the dissolution rate of PbO₂ was evaluated at pH 7.6 and 8.5 in the presence of 50 mg C/L DIC. Increasing iodide concentrations generally increased the dissolution rate of PbO₂. A threshold value above which the dissolution

![Figure 4.8](image-url)
of PbO₂ was accelerated was observed for experiments both at pH 7.6 and 8.5 (Figure 4.8). At pH 7.6, the PbO₂ dissolution rate with 1 µM iodide was comparable to that in the absence of DIC; increasing the iodide concentrations to 2 µM doubled the dissolution rate, and the dissolution rate further increased with increasing iodide concentrations. The threshold iodide concentration that enhanced the dissolution of PbO₂ at pH 7.6 was between 1 and 2 µM. At pH 8.5, the presence of 5 µM iodide did not increase the dissolution rate of PbO₂. PbO₂ started to dissolve faster with 10 µM iodide, indicating that the threshold value was between 5 and 10 µM at pH 8.5. The higher threshold value at pH 8.5 than at pH 7.6 was qualitatively consistent with equilibrium calculations based on Reaction 4.4 that suggest that higher iodide concentrations are required at higher pH to result in comparable PbO₂ dissolution extents as at lower pH.

Trends of the steady-state PbO₂ dissolution rate may be different than those acquired from the initial dissolution of PbO₂ in batch experiments. Due to the presence of labile phases and highly reactive sites, the initial dissolution of PbO₂ may be more variable and much faster than the steady-state dissolution determined over longer time periods. Using the flow-through reactors, the dissolution products were continuously flushed out of the reactor. This approach allowed us to measure the long term steady-state dissolution of PbO₂, which was more representative of real distribution systems and was not affected by any labile phases. Indeed, the effluent lead concentrations over the first several residence times were more variable than the steady-state concentrations. For iodide concentrations above 5 µM the initial dissolution rates were also higher than the ultimate stable steady-state dissolution rate achieved, which suggests the dissolution of some labile phases during the initial period of the CSTR experiments (Figure

![X-ray diffraction patterns](image)

Figure 4.9 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 together with reference patterns from the ICDD database. Some cerussite formation is apparent when the iodide concentration was 100 µM.
C3 in the Appendices).

Faster initial dissolution of PbO₂ with high iodide concentrations may release sufficient Pb(II) to form Pb(II)-precipitates. For example, when starting with 100 µM iodide at pH 7.6, the initial lead release was fast and the system became supersaturated with respect to the Pb(II)-carbonate cerussite (PbCO₃). The XRD patterns for the solids after the experiment show the formation of cerussite (Figure 4.9). Cerussite formation was also confirmed from the SEM observation. Long-bar shaped crystals were only observed at the condition with 100 µM iodide, suggesting the formation of cerussite at this condition but not for lower iodide concentrations (Figure 4.10). The formation of the secondary lead(II) precipitates can provide a sink for Pb(II) species, and they may also change the available surface area of PbO₂. Therefore for this highest iodide concentration studied, the steady-state effluent lead concentrations do not represent the dissolution rate of PbO₂, but rather they indicate the balance between PbO₂ dissolution and cerussite formation. Consequently for the iodide concentrations above 20 µM, the dissolution rates cannot be acquired from Equation 4.2.

![Figure 4.10 Electron micrographs of solids: (a) before reaction, and after 24 hours of reaction in the CSTR with 50 mg C/L DIC and (b) 10 µM iodide at pH 7.6, and (c) 100 µM iodide at pH 7.6.](image)
**Effect of Dissolved Inorganic Carbon**

DIC is abundant in drinking water and carbonate is a good complexing ligand for Pb\(^{2+}\). For example, at pH 7.6 with 50 mg C/L DIC, 93% of the dissolved lead is composed of Pb(II)-carbonate complexes that include PbCO\(_3\)(aq), Pb(CO\(_3\))\(^{2-}\), and PbHCO\(_3\)\(^+\). The effect of different DIC concentrations on the dissolution rate of PbO\(_2\) was determined with 5 or 10 μM iodide at pH 7.6 and 8.5. Experiments in the absence of DIC were conducted at pH 7.6 with 5 and 10 μM iodide using 1 mM MOPS as a buffer. The inclusion of the buffer was critical to being able to provide a stable pH for comparison with the carbonated system when no DIC was available to buffer the pH. Organic buffers can accelerate the dissolution of PbO\(_2\) due to their chemical reduction of PbO\(_2\). When compared with other organic buffers (MES or HEPES), MOPS was a mild reductant and only slightly enhanced the dissolution of PbO\(_2\) (Figures C1 and C2 in the Appendices). Even after accounting for the enhancement of MOPS on the dissolution of PbO\(_2\), the presence of 50 mg C/L DIC still significantly accelerated PbO\(_2\) dissolution (Figure 4.11). With either 5 or 10 μM iodide, the dissolution rates of PbO\(_2\) with 50 mg C/L DIC were nearly twice as high as those without DIC. Carbonate from DIC can serve as a complexing ligand and react with Pb\(^{2+}\) ions to form Pb(II)-carbonate complexes to enhance the dissolution of PbO\(_2\).

![Figure 4.11 Dissolution rate of plattnerite at pH 7.6 in the absence and presence of 50 mg C/L DIC with different iodide concentrations 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.](image)
Although the presence of DIC increased the dissolution rate of PbO$_2$, varying the DIC concentrations from 10 to 200 mg C/L had little effect on the dissolution rate of PbO$_2$ at both pH 7.6 and 8.5 with 10 μM iodide (Figure 4.12). The reductive dissolution of PbO$_2$ can be described as a coupled process of chemical reduction and detachment, and the presence of carbonate may affect the detachment of Pb(II) from PbO$_2$ surface. Our results suggest that once some DIC was present in the system, the detachment step would not be rate-limiting in determining the overall dissolution of PbO$_2$ by iodide and that chemical reduction may play the most important role in controlling the dissolution rates.

**Comparison of Iodide with Different Reductants**

The PbO$_2$ dissolution rates acquired in the present study using flow-through reactors were compared to those determined in batch reactors with other reductants found in drinking water (Table 4.5). The presence of chemical reductants was proved to enhance the dissolution of PbO$_2$ in all of the studies, but to different extents. In the present study, the dissolution rate of PbO$_2$ was $4.7 \cdot 10^{-9}$ mol·m$^{-2}$·min$^{-1}$ at pH 7.6 in the presence of 10 mg C/L DIC and 10 μM iodide, which was comparable to the rate determined in a phosphate-buffered system in a previous study. Lin and Valentine studied the initial dissolution of PbO$_2$ by iodide using batch experiments. Based on the general rate expression they provided, the dissolution rate of PbO$_2$ at pH 7.0 with 10 μM
iodide was $2.1 \times 10^{-9}$ mol·m$^{-2}$·min$^{-1}$ (Lin et al. 2008). NOM is widely present in drinking water and was found to be able to reduce PbO$_2$ (Dryer and Korshin 2007; Lin and Valentine 2008b). A previous study investigated the effect of NOM on the dissolution rate of PbO$_2$ at pH 7.0 with 20 mg/L NOM and acquired a dissolution rate of $4.0 \times 10^{-9}$ mol·m$^{-2}$·min$^{-1}$ (Lin and Valentine 2008b), which was comparable to the rate determined from iodide in the present work. If metal cations, like Fe$^{2+}$ and Mn$^{2+}$ were present in drinking water, then they may accelerate the dissolution of PbO$_2$ more significantly than do iodide or NOM (Shi and Stone 2009a).

Generally, if the concentrations of the reductants discussed earlier are similar, then the order of PbO$_2$ dissolution rates can be summarized as NOM < I$^-$ < Mn$^{2+}$, Fe$^{2+}$. A more relevant case is to consider the dissolution rate with the relative abundance of the different reductants. In actual distribution systems, the Mn$^{2+}$ concentrations may be as high as 0.2 mg/L (4 µM) (Cerrato et al. 2006), the NOM concentration could be several mg C/L (Volk et al. 2002), and the typical iodide concentration is below 20 $\mu$g/L (0.16 µM) (National Academy of Sciences 1980), which is below the threshold value that could accelerate the dissolution of PbO$_2$. Therefore iodide may play a less important role than NOM or Mn$^{2+}$ and Fe$^{2+}$ in enhancing lead release from PbO$_2$ dissolution in typical distribution systems. Nevertheless, iodide was useful as a model reductant for elucidating the general mechanisms and pathways of the reductive dissolution of PbO$_2$.

### Table 4.5
Summary of the dissolution rate of PbO$_2$ by different reductants.

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<th>Reductant</th>
<th>Experimental Condition</th>
<th>Dissolution Rate (mol·m$^{-2}$·min$^{-1}$)$^a$</th>
<th>Ref</th>
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<tbody>
<tr>
<td>NOM</td>
<td>pH 7.0 DIC $10^{-4}$ 10 mg/L DOC</td>
<td>36 Batch 4.8·10$^{-9}$</td>
<td>(Dryer and Korshin 2007)</td>
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<tr>
<td>NOM</td>
<td>pH 7.0 DIC $10^{-3}$ 20 mg/L$^b$</td>
<td>4 Batch 4.0·10$^{-9}$</td>
<td>(Lin and Valentine 2008b)</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>pH 7.8 DIC 0 40 µM</td>
<td>4.8 Batch 1.3·10$^{-6}$</td>
<td>(Shi and Stone 2009a)</td>
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<tr>
<td>Mn$^{2+}$</td>
<td>pH 7.8 DIC 0 20 µM</td>
<td>4.8 Batch 3.2·10$^{-6}$</td>
<td>(Shi and Stone 2009a)</td>
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<tr>
<td>I$^-$</td>
<td>pH 7.0 DIC 0 500 µM</td>
<td>8.0 Batch 1.5·10$^{-6}$</td>
<td>(Lin et al. 2008)</td>
</tr>
<tr>
<td>I$^-$</td>
<td>pH 7.0 DIC 0 10 µM</td>
<td>$10^3$ Batch 2.1·10$^{-9c}$</td>
<td>Present study</td>
</tr>
<tr>
<td>I$^-$</td>
<td>pH 7.6 DIC 8.3·10$^{-4}$ 10 µM</td>
<td>$10^3$ Flow 4.7·10$^{-9}$</td>
<td>Present study</td>
</tr>
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</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 the reference (Lin et al. 2008) applied to experimental conditions similar to those of the present study.
Pathways of the Reductive Dissolution of PbO₂

The reductive dissolution of a metal oxide, like Fe(III) or Mn(III, IV), can be described by several steps, including the adsorption of the reductant to the surface of the metal oxide, electron transfer between the metal oxide and the reductant, and detachment of the reduced metal ions from the metal oxide surface (Hering and Stumm 1990; Stone and Morgan 1984). The reductive dissolution of PbO₂ will follow these general steps, and the following reactions can be used to describe the reactions of PbO₂ with iodide (Figure 4.13):

(a) adsorption of iodide to the surface of PbO₂ to form a precursor surface complex:

\[ > Pb(IV)OH + I^- + H^+ \xrightleftharpoons{k飨}{k逆} > Pb(IV)I + H_2O \]  
\[ (4.5) \]

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

\[ > Pb(IV)I \xrightarrow{k_1} > Pb(III)I \xrightarrow{\text{fast}} > Pb(II)OH \]  
\[ (4.6) \]

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

\[ > Pb(II)OH \xrightarrow{k_2} > Pb(IV)OH + Pb^{2+} \]  
\[ (4.7) \]

Steps a and b are affected by the iodide concentrations and step c would be accelerated by the presence of a Pb(II)-complexing ligand. In the presence of DIC, changing the DIC concentrations from 10 to 200 mg C/L had little effect on the dissolution rate of PbO₂, suggesting that step c was fast. Increasing the iodide concentrations accelerated the dissolution of PbO₂, indicating that steps a and b were rate-limiting. Since iodide is involved in both steps a and b, they will be collectively referred to as “steps related to chemical reduction.” If the chemical reduction steps are rate-limiting, then at a given pH the reductive dissolution of PbO₂ follows Langmuir-Hinshelwood kinetics, and the dissolution rate can be expressed by:

Figure 4.13 Pathways of the reductive dissolution of PbO₂ by iodide
where \( k \) (\( \mu M^{-1} \)) and \( k' \) (mol\cdot m^{-2}\cdot min^{-1}) are rate constants at a given pH. When the iodide concentration is low, the dissolution rate of PbO_2 is first order with respect to iodide concentrations. As the iodide concentration increases, the dissolution rate would reach a plateau. This type of behavior was observed at pH 7.6 (Figure 4.8).

Employing least squares optimization of the experimental data to Equation 4.8, at pH 7.6 the optimal value of \( k' \) was \( 99 \cdot 10^{-10} \) mol\cdot m^{-2}\cdot min^{-1} and of \( k \) was \( 8.1 \cdot 10^{-2} \) \( \mu M^{-1} \); at pH 8.5 the optimal values of \( k' \) and \( k \) were \( 96 \cdot 10^{-10} \) mol\cdot m^{-2}\cdot min^{-1} and \( 1.0 \cdot 10^{-2} \) \( \mu M^{-1} \). The model can generally fit the data quite well as shown in Figure 4.14 which shows the comparison of the model dissolution rate with the experimental dissolution rate. It is anticipated that the mechanism and model proposed in the present work may also be applicable to interpreting the reactions of PbO_2 with other reductants in distribution systems.

**Effect of Free Chlorine on PbO_2 Dissolution (Set C)**

Free chlorine is often used as a disinfectant in drinking water distribution systems. PbO_2 is thermodynamically stable in systems containing free chlorine since free chlorine provides a high ORP. The effect of free chlorine on the dissolution rate of PbO_2 was examined over a pH
range from 5.7 to 8.5 with 50 mg C/L and 1 mg Cl₂/L free chlorine. The presence of 1 mg Cl₂/L free chlorine significantly inhibited the dissolution of PbO₂ (Figure 4.15). For pH 6.7 to 8.5, the presence of free chlorine decreased the dissolution rate of PbO₂ by more than an order of magnitude.

Since the presence of 1 mg Cl₂/L free chlorine effectively inhibited the dissolution of PbO₂, the possibility of a critical free chlorine concentration that can prevent the reductive dissolution of PbO₂ was investigated. A lower free chlorine concentration of 0.2 mg Cl₂/L was selected, and the dissolution rate of PbO₂ was determined at pH 7.6 and 8.5 with 50 mg C/L DIC. Although PbO₂ dissolved a little bit faster with 0.2 mg Cl₂/L free chlorine than with 1 mg Cl₂/L free chlorine, the dissolution rates with 0.2 mg Cl₂/L free chlorine were still an order of magnitude lower than those without free chlorine (Figure 4.16). These results demonstrated that even the presence of 0.2 mg Cl₂/L free chlorine dramatically inhibited the dissolution of PbO₂ and maintained low dissolved lead concentrations. The threshold value of free chlorine concentration that inhibited the dissolution of PbO₂ was below 0.2 mg Cl₂/L.

The inhibitory effect of free chlorine on the dissolution rate of PbO₂ may be due to several reasons. Free chlorine may provide a high enough ORP so that the reductive dissolution of PbO₂ was not thermodynamically favorable. But it is more likely that free chlorine affected the kinetics of a rate-limiting step in the overall PbO₂ dissolution process. Free chlorine may re-oxidize the dissolved Pb(II) species released from PbO₂ (Reactions 4.9 and 4.10), thus mitigating the lead release to water.
Effect of Orthophosphate on PbO₂ Dissolution (Set D)

The effect of orthophosphate on the dissolution rate of PbO₂ was investigated at pH 7.6 and 8.5 in the absence and presence of 50 mg C/L DIC with 2 mg Cl₂/L chloramine. The addition of 1 mg P/L orthophosphate inhibited the dissolution of PbO₂ at pH 7.6, but the orthophosphate had little effect on the dissolution rate of PbO₂ at pH 8.5 (Figure 4.17). For the experiments at pH 8.5 in the absence of DIC, the dissolution rate of PbO₂ was actually higher in the presence of orthophosphate. This observation may be due to the pH difference between the conditions with and without orthophosphate. No buffer was used at pH 8.5 in the absence of DIC and therefore the pH fluctuated more widely and was not always maintained at the target pH value. The average pH was 8.69 to 8.85 in the absence of orthophosphate, and it was 8.07 to 8.44 in the presence of orthophosphate. Consequently, the dissolution rate acquired at this condition may actually be caused by the pH but not by the orthophosphate.
Figure 4.17 Effect of orthophosphate concentration on the dissolution rate of plattnerite with 0 and 50 mg C/L DIC at pH 7.6 and 8.5 using flow-through reactors with 1 g/L plattnerite and a residence time of 30 min. The legend shows the orthophosphate concentrations in mg P/L. Error bars represent one standard deviation from duplicate experiments.

Figure 4.18. Conceptual model of the potential pathways of PbO₂ dissolution in the presence of orthophosphate.
Orthophosphate may inhibit the dissolution of PbO₂ through several mechanisms (Figure 4.18). The lead(II)-phosphate solid hydroxylpyromorphite (Pb₅(PO₄)₃OH) has a very low solubility. When the dissolved lead released from PbO₂ dissolution exceeds the equilibrium solubility of hydroxylpyromorphite, hydroxylpyromorphite may precipitate and control the lead concentration. Precipitation of hydroxylpyromorphite on the PbO₂ surface may also block reactive sites on the surface of PbO₂ and prevent its reductive dissolution. Hydroxylpyromorphite precipitates were observed at pH 7.6 with 1 mg P/L orthophosphate in the absence of DIC (Figure 4.19c). The dissolution rate at this condition was lower than that in the absence of orthophosphate, suggesting that precipitation of hydroxylpyromorphite inhibited the dissolution of PbO₂.

![Figure 4.19](image)

*Figure 4.19. Electron micrographs of (a) plattnerite before reaction, (b) pure hydroxylpyromorphite, (c) solids after reaction of plattnerite at pH 7.5, 0 mg C/L DIC, 1 mg P/L phosphate, and 2 mg Cl₂/L monochloramine, and (d) solids after reaction of plattnerite at pH 8.5, 50 mg C/L DIC, 1 mg P/L orthophosphate, and 2 mg Cl₂/L

A second possible mechanism of orthophosphate inhibition of PbO₂ dissolution involves the adsorption of phosphate to the surface of PbO₂. Adsorbed phosphate may block the reactive sites for PbO₂ reduction or detachment, thus passivating the PbO₂ surface and mitigating lead release. In the presence of DIC, the predicted equilibrium solubility of hydroxylpyromorphite is higher than that without DIC due to the formation of soluble Pb(II)-carbonate complexes. At the
conditions with 1 mg P/L and 50 mg C/L DIC at pH 7.6 and 8.5, the steady-state effluent lead concentrations did not reach the equilibrium solubility of hydroxylpyromorphite (Figure 4.20). SEM observations also indicated that no secondary lead(II) solid phases formed following the reaction of PbO$_2$ with orthophosphate in the presence of DIC (Figure 4.19d), which is consistent with the lead concentrations being undersaturated with respect to hydroxylpyromorphite. Therefore the inhibitory effect of orthophosphate is probably due to adsorption and not precipitation when DIC is present. Orthophosphate adsorption should follow the general trend of anion adsorption with less extensive adsorption with increasing pH. Consequently, a larger extent of the PbO$_2$ surface would be covered by orthophosphate at pH 7.6 than at pH 8.5, which is in agreement with the observation that orthophosphate had a larger inhibitory effect on the dissolution of PbO$_2$ at pH 7.6 than at pH 8.5.

Overall, there are two mechanisms through which orthophosphate can inhibit the release of lead to solution during the reductive dissolution of PbO$_2$. In the absence of DIC the formation of the lead(II) phosphate hydroxylpyromorphite limited lead release to solution. With DIC present, the inhibition of lead release to solution was probably caused by the adsorption of orthophosphate to the PbO$_2$ surface to block sites of reduction or dissolution.

![Figure 4.20](image_url)

**Figure 4.20** Steady-state concentrations for plattnerite dissolution in the presence of 1 mg P/L orthophosphate and predicted lead concentration in equilibrium with hydroxylpyromorphite.
Summary of PbO₂ Dissolution Rates

The dissolution rate of PbO₂ was strongly dependent on water chemistry. For the conditions studied, the pH was an important factor with dissolution rates always increasing with decreasing pH. The presence of free chlorine or orthophosphate inhibited the dissolution of PbO₂, and free chlorine was more effective than orthophosphate at maintaining low dissolved lead concentrations in the reactor effluents. Free chlorine concentrations as low as 0.2 mg Cl₂/L decreased the dissolution rate of PbO₂ by more than an order of magnitude at conditions relevant to drinking water; the presence of 1 mg P/L orthophosphate decreased the dissolution rate to a lesser degree. The presence of iodide (i.e. a chemical reductant) and DIC (i.e. a complexing ligand) accelerated lead release from PbO₂, and iodide was more important in controlling the overall dissolution because of the significance of chemical reduction as the rate-controlling step in the overall PbO₂ dissolution process for most conditions.

The reductive dissolution of PbO₂ can be described by several sequential steps: (1) the adsorption of the reductant to the surface of PbO₂; (2) electron transfer between the surface Pb(IV) species and the reductant, resulting in the reduction of the surface Pb(IV) to surface Pb(II); and (3) detachment of the surface Pb(II) from the PbO₂ surface. The effects of the different water chemistry factors on PbO₂ dissolution rates can be interpreted with respect to their different impacts on the pathways of PbO₂ dissolution. At a given pH, the presence of iodide can accelerate steps (1) and (2), and the presence of DIC can accelerate step (3). Collectively the iodide and DIC result in an enhancement of PbO₂ dissolution. The presence of free chlorine can inhibit the dissolution of PbO₂ by re-oxidizing the Pb(II) ions released from step (3) to form PbO₂ solids. The presence of orthophosphate may inhibit the PbO₂ dissolution by either forming an insoluble Pb(II)-phosphate precipitate from the Pb(II) ions released from step (3) or adsorbing to the surface of PbO₂ to block reactive sites, which may then prevent the surface from the attack of the chemical reductants or complexing ligands in steps (1), (2), or (3). Varying the pH may affect the extent of the iodide and orthophosphate adsorption to the PbO₂ surface, thus affecting the overall dissolution rate of PbO₂.
CHAPTER 5
SUMMARY AND CONCLUSIONS

SUMMARY OF PROJECT

The project involved three integrated tasks that focused on the formation and dissolution of the important lead corrosion product PbO₂. PbO₂ formation was systematically examined in Task 1. Batch experiments were performed to determine the extent of formation and identity of PbO₂ (plattnerite versus scrutinyite) as a function of important water chemistry parameters. The results of this task were presented in Chapter 2. The chapter included the results of characterization of the solid phases and interpretation of the PbO₂ formation pathways. In Task 2, PbO₂ dissolution was examined over long equilibration times in batch reactors. Lead release from the two PbO₂ polymorphs, scrutinyite and plattnerite, was determined in the presence of free chlorine. The results of this task were presented in Chapter 3. In Task 3, continuously stirred tank reactors were used to investigate the dissolution rate of PbO₂ as a function of the water chemistry parameters pH, DIC, iodide, free chlorine, and orthophosphate. The results of this task were presented in Chapter 4. These results included dissolved phase analysis, characterization of the solid phases, and description of the dissolution pathways and mechanisms using a reaction-based framework.

FORMATION OF LEAD(IV) OXIDE

The extent of formation and identity of the PbO₂ formed strongly depended on the water chemistry and the lead-containing precursor. PbO₂ only formed in the presence of free chlorine. The threshold free chlorine concentration above which PbO₂ could form was below 4 mg Cl₂/L. While PbO₂ formed in the presence and absence of DIC, the presence of DIC accelerated PbO₂ formation. The pH and DIC affected the PbO₂ formation pathways by forming different intermediate lead(II) solid phases, thus affecting the extent and phase of the PbO₂ formed.

Starting from elemental lead(0) powder, intermediate lead(II) solid phases were observed, confirming that the formation of PbO₂ from Pb(0) is a two-step process that involves the oxidation of Pb(0) to Pb(II) followed by the oxidation of Pb(II) to PbO₂. Starting from the lead(II) precursors, PbO₂ formed through several pathways, including an aqueous phase oxidation pathway and solid phase mediated pathways. Mixtures of plattnerite and scrutinyite formed from the aqueous phase oxidation pathway. When Pb(II) solids were involved in the process of PbO₂ formation, mixtures of plattnerite and scrutinyite formed at most experimental conditions. However, due to the specific trend in solid-solid interfacial free energies, some Pb(II) solids result in the preferential formation of a specific phase of PbO₂. Lead(II) oxide chloride favored plattnerite. When no intermediate solids formed, hydrocerussite led to the formation of scrutinyite.

SOLUBILITY OF LEAD(IV) OXIDE

The solubility of PbO₂ was investigated in batch reactors that maintained a free chlorine residual to provide a high ORP. Over long stagnation times, dissolved lead concentrations were orders of magnitude higher than the values calculated from equilibrium constants derived from
published thermodynamic data. It is very likely that the dissolved lead measured was aqueous Pb(II) rather than aqueous Pb(IV), and therefore the solubility of PbO$_2$ equilibrated with only aqueous Pb(IV) species cannot be determined experimentally. The results suggested that even in the presence of free chlorine, the dissolved lead release from PbO$_2$ still represents a balance of two kinetic processes: reductive dissolution of PbO$_2$ by water and re-oxidation of aqueous Pb(II) species by free chlorine.

Although the measured concentrations did not match the extremely low predicted concentrations, the final stable dissolved lead concentrations were still very low when free chlorine concentrations were maintained; dissolved lead concentrations never exceeded the action level at pH 6.0 even after several weeks of equilibration, and at pH 7.5 and 8.5 the lead concentrations only exceeded the action level after four days or longer. Increasing the pH increased the dissolved lead concentrations over long stagnation times. Relative to pH, DIC had less impact on lead release from PbO$_2$ in the presence of free chlorine. The two PbO$_2$ polymorphs, scrutinyite and plattnerite, released similar amounts of dissolved lead over long stagnation times.

**DISSOLUTION RATE OF LEAD(IV) OXIDE**

The dissolution rate of PbO$_2$ was influenced by all five water chemistry parameters tested. The pH consistently played a role in affecting dissolution rates with higher rates almost always observed with decreasing pH. The pH may affect the distribution of the PbO$_2$ surface species and the pathways of the PbO$_2$ dissolution.

Free chlorine or orthophosphate decreased the dissolution rate of PbO$_2$, and free chlorine was more effective than orthophosphate at inhibiting PbO$_2$ dissolution. The presence of free chlorine concentrations even as low as 0.2 mg Cl$_2$/L decreased the dissolution rate by more than an order of magnitude. Free chlorine may inhibit the dissolution of PbO$_2$ by re-oxidizing the Pb(II) species back to PbO$_2$. The presence of 1 mg P/L orthophosphate slightly inhibited the dissolution of PbO$_2$ at pH 7.5. There are two mechanisms through which orthophosphate may inhibit the release of lead to solution during the reductive dissolution of PbO$_2$. In the absence of DIC the formation of the lead(II) phosphate hydroxylpyromorphite limited lead release to solution. With DIC present, the inhibition of lead release to solution was probably caused by the adsorption of orthophosphate to the PbO$_2$ surface to block sites of reduction or dissolution.

The presence of iodide and DIC accelerated the dissolution of PbO$_2$. The reductive dissolution of PbO$_2$ can be described by several sequential steps: (1) the adsorption of the reductant to the surface of PbO$_2$; (2) electron transfer between the surface Pb(IV) species and the reductant, resulting in the reduction of the surface Pb(IV) to surface Pb(II); and (3) detachment of Pb(II) from the PbO$_2$ surface. Iodide accelerated the steps related to the chemical reduction, and increasing the iodide concentration increased the dissolution rate of PbO$_2$. The presence of DIC accelerated the detachment of Pb(II) from PbO$_2$ surface by forming soluble Pb(II)-carbonate complexes, thus enhancing PbO$_2$ dissolution, but further increases in DIC from 10 to 200 mg C/L had little impact on the dissolution rate of PbO$_2$ in the systems containing iodide. Chemical reduction was more important than detachment in controlling the overall dissolution of PbO$_2$. Although iodide may not be a significant reductant in many distribution systems, the overall mechanism of reductive dissolution of PbO$_2$ determined with iodide may be applicable to PbO$_2$ dissolution as influenced by natural organic matter and other reductants.
CHAPTER 6
RECOMMENDATIONS TO UTILITIES

DETERMINING WHETHER OR NOT LEAD(IV) OXIDES ARE PRESENT

Lead(IV) oxides (PbO₂) can be an important component of corrosion products on pipe scales for utilities that have lead service lines in their distribution systems and that currently use or have used free chlorine as the secondary disinfectant. PbO₂ can only form in systems with free chlorine present; however, because of the low solubility of this phase and the complexity of pipe scales, PbO₂ may persist well after a switch from free chlorine to chloramine. The rate of PbO₂ formation and consequently the likely extent of PbO₂ formation on lead service lines as well are strongly affected by the water chemistry of the distribution system. Utilities should assume that PbO₂ is present on lead service lines if free chlorine is used; however, it is possible that not all systems using free chlorine will have PbO₂ present despite its predicted formation. When samples of lead service lines become available (e.g., during replacements as part of water main repair), characterization of the composition of the pipe scales can be performed to confirm the presence of PbO₂. Such identification is best accomplished using X-ray diffraction. The susceptibility of PbO₂ to reductive dissolution and its likely enrichment at the surface of the pipe scale can make it a major contributor to lead release to water even when it is only present as a minor constituent of a pipe scale.

The presence of PbO₂ is a more important finding than the exact identity of the form of PbO₂ (plattnerite versus scrutinyite) that is present. Both plattnerite and scrutinyite can form on lead pipes in the presence of free chlorine, and the specific solid that is formed is affected by both the water chemistry and the precursor lead(II) phase from which it forms. The coexistence of scrutinyite and plattnerite and previous observations of their co-occurrence with Pb(II) solids indicates that the systems have not reached equilibrium and that rates play an important role in PbO₂ formation. Despite predictions that plattnerite should have a lower solubility than scrutinyite, similar dissolved lead concentrations were achieved in aqueous solutions equilibrated with the two solids.

MAINTAINING LOW DISSOLVED LEAD CONCENTRATIONS IN DISTRIBUTION SYSTEMS THAT CONTAIN LEAD(IV) OXIDES

Lead(IV) oxides are only stable in solutions with a high oxidation-reduction potential maintained by a free chlorine residual. In the absence of free chlorine, PbO₂ dissolves through a reductive dissolution process. For systems without free chlorine or for which free chlorine has been depleted, dissolved lead concentrations will be controlled by the rate of the dissolution reaction and not by equilibrium solubility. Even in the presence of free chlorine, while stable low dissolved lead concentrations can be achieved, it is likely that those stable concentrations are controlled by a balance of reductive dissolution and re-oxidation reactions and not by true equilibrium. As a general rule equilibrium solubility calculations are not useful for predicting dissolved lead concentrations in waters in contact with PbO₂. Because rates play such an important role in affecting lead concentrations, the flow regime (e.g., flowing water versus stagnation) must also be considered when estimating lead concentrations in water that is in contact with PbO₂ as a corrosion product.
The dissolution rate of PbO₂ is a very strong function of the water chemistry, and orders of magnitude differences can occur in the rates depending on the composition. Even in the absence of free chlorine, water compositions with moderate to high pH, low DIC, and the absence of any chemical reductants (e.g., natural organic matter) can have such slow dissolution of PbO₂ that low lead concentrations are maintained over reasonable stagnation times. Similarly for such systems, PbO₂ could persist as a component of pipe scales for long periods of time (years or longer) even after a switch from free chlorine to another disinfectant. Consequently, utilities should still be cautious in altering water compositions in ways that could affect PbO₂ stability even after secondary disinfection is switched from chlorination.

Utilities should be aware of conditions that could accelerate the dissolution of PbO₂ and the release of lead from this potential reservoir of unstable lead in scales on lead service lines. This is particularly important for water distribution systems that have recently switched from using free chlorine to chloramine as the secondary disinfectant and for regions of distribution systems with high water ages such that the residual chlorine may have been completely consumed. Dissolution rates of PbO₂ will increase in response to process changes that lower the pH of the water in the distribution system. The most significant parameter affecting PbO₂ dissolution rates is the concentration and identity of species that can act as chemical reductants to accelerate PbO₂ dissolution. These species include natural organic matter, dissolved iron(II) and manganese(II), and iodide. Measurements of these properties of the finished water can provide information regarding the potential for lead release from PbO₂ present on lead service lines. Carbonate can also act to accelerate PbO₂ dissolution, but since this effect is only eliminated at very low DIC concentrations that would correspond to low alkalinites, the benefits of pH buffering from the alkalinity will likely outweigh any benefits that might be achieved by lowering the DIC of the finished water.

The impacts of water chemistry on the dissolution rate of PbO₂ can also be used to promote conditions with the slowest dissolution rates and consequently the best abilities to maintain low lead concentrations in distribution systems. Not surprisingly, free chlorine is an excellent inhibitor of the reductive dissolution of PbO₂. Even very low concentrations of residual free chlorine (0.2 mg/L as Cl₂) can substantially inhibit dissolution. Orthophosphate can also be effective at limiting the release of lead to water in systems that contain PbO₂. The benefits of orthophosphate addition may be limited to pH values near neutral. The inhibition of PbO₂ dissolution by orthophosphate does not necessarily require the precipitation of lead(II) phosphate solids.
# APPENDIX A
EQUILIBRIUM CONSTANTS AND REACTIONS

## Table A.1
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>$H_2O = H^+ + OH^-$</td>
<td>-14.00</td>
<td>MINEQL</td>
</tr>
<tr>
<td>2</td>
<td>$CO_2(g) + H_2O = H_2CO_3^*$</td>
<td>-1.46</td>
<td>MINEQL</td>
</tr>
<tr>
<td>3</td>
<td>$H_2CO_3^* = 2H^+ + CO_3^{2-}$</td>
<td>-16.68</td>
<td>MINEQL</td>
</tr>
<tr>
<td>4</td>
<td>$HCO_3^- = H^+ + CO_3^{2-}$</td>
<td>-10.33</td>
<td>MINEQL</td>
</tr>
<tr>
<td>5</td>
<td>$H_3PO_4 = 3H^+ + PO_4^{3-}$</td>
<td>-21.70</td>
<td>MINEQL</td>
</tr>
<tr>
<td>6</td>
<td>$H_2PO_4^- = 2H^+ + PO_4^{3-}$</td>
<td>-19.56</td>
<td>MINEQL</td>
</tr>
<tr>
<td>7</td>
<td>$HPO_4^{2-} = H^+ + PO_4^{3-}$</td>
<td>-12.35</td>
<td>MINEQL</td>
</tr>
<tr>
<td>8</td>
<td>$Pb^{2+} + H_2O = PbOH^+ + H^+$</td>
<td>-7.71</td>
<td>Benjamin</td>
</tr>
<tr>
<td>9</td>
<td>$Pb^{2+} + 2H_2O = Pb(OH)_2^0 + 2H^+$</td>
<td>-17.12</td>
<td>Benjamin</td>
</tr>
<tr>
<td>10</td>
<td>$Pb^{2+} + 3H_2O = Pb(OH)_3^* + 3H^+$</td>
<td>-28.06</td>
<td>Benjamin</td>
</tr>
<tr>
<td>11</td>
<td>$Pb^{2+} + 4H_2O = Pb(OH)_4^{2-} + 4H^+$</td>
<td>-39.70</td>
<td>Benjamin</td>
</tr>
<tr>
<td>12</td>
<td>$Pb^{2+} + CO_3^{2-} = PbCO_3^0$</td>
<td>6.48</td>
<td>MINEQL</td>
</tr>
<tr>
<td>13</td>
<td>$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$</td>
<td>9.94</td>
<td>MINEQL</td>
</tr>
<tr>
<td>14</td>
<td>$Pb^{2+} + CO_3^- + H^+ = PbHCO_3^+$</td>
<td>13.20</td>
<td>MINEQL</td>
</tr>
<tr>
<td>15</td>
<td>$2Pb^{2+} + 3H_2O = Pb_2(OH)_3^+ + 3H^+$</td>
<td>-6.40</td>
<td>MINEQL</td>
</tr>
<tr>
<td>16</td>
<td>$3Pb^{2+} + 4H_2O = Pb_4(OH)_4^{2+} + 4H^+$</td>
<td>-23.89</td>
<td>MINEQL</td>
</tr>
<tr>
<td>17</td>
<td>$4Pb^{2+} + 4H_2O = Pb_4(OH)_4^{4+} + 4H^+$</td>
<td>-19.99</td>
<td>MINEQL</td>
</tr>
<tr>
<td>18</td>
<td>$HOCl + 2e^- + H^+ = Cl^- + H_2O$</td>
<td>50.20</td>
<td>Benjamin</td>
</tr>
<tr>
<td>19</td>
<td>$Pb^{4+} + 2e^- = Pb^{2+}$</td>
<td>28.64</td>
<td>Benjamin</td>
</tr>
<tr>
<td>20</td>
<td>$O_2(aq) + 4H^+ + 4e^- = 2H_2O$</td>
<td>86.00</td>
<td>Benjamin</td>
</tr>
<tr>
<td>21</td>
<td>$2H^+ + 2e^- = H_2(aq)$</td>
<td>3.10</td>
<td>Benjamin</td>
</tr>
<tr>
<td>22</td>
<td>$Pb^{4+} + 3H_2O = PbO_3^{2-} + 6H^+$</td>
<td>-23.06</td>
<td>Calculated$^a$</td>
</tr>
<tr>
<td>23</td>
<td>$Pb^{4+} + 4H_2O = PbO_4^{4+} + 8H^+$</td>
<td>-63.80</td>
<td>Calculated$^a$</td>
</tr>
</tbody>
</table>

$^a$ values were calculated using the thermodynamic data in Table A.3.
Benjamin = (Benjamin 2002)
MINEQL = (Schecher and Mcavoy 1998)
Table A.2.
Solubility products of select lead solids

<table>
<thead>
<tr>
<th>#</th>
<th>Solid</th>
<th>Reaction</th>
<th>Log K</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>Massicot PbO(s) + 2H⁺</td>
<td>Pb²⁺ + H₂O</td>
<td>12.91</td>
<td>MINEQL</td>
</tr>
<tr>
<td>25</td>
<td>Litharge PbO(s) + 2H⁺</td>
<td>Pb²⁺ + H₂O</td>
<td>12.72</td>
<td>MINEQL</td>
</tr>
<tr>
<td>26</td>
<td>Pb(OH)₂(s) Pb(OH)₂(s) + 2H⁺</td>
<td>Pb²⁺ + 2H₂O</td>
<td>8.15</td>
<td>MINEQL</td>
</tr>
<tr>
<td>27</td>
<td>Cerussite PbCO₃(s) Pb²⁺ + CO₃²⁻</td>
<td>-13.13</td>
<td>Benjamin</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Hydrocerussite Pb₅(CO₃)₂(OH)₂(s) + 2H⁺</td>
<td>3Pb²⁺ + 2CO₃⁻ + 2H₂O</td>
<td>-18.77</td>
<td>MINEQL</td>
</tr>
<tr>
<td>29</td>
<td>Pb₃(PO₄)₂(s) Pb₃(PO₄)₂(s)</td>
<td>3Pb²⁺ + 2PO₄³⁻</td>
<td>-44.50</td>
<td>Benjamin</td>
</tr>
<tr>
<td>30</td>
<td>PbHPO₄(s) PbHPO₄(s)</td>
<td>Pb²⁺ + PO₄³⁻ + H⁺</td>
<td>-37.80</td>
<td>MINEQL</td>
</tr>
<tr>
<td>31</td>
<td>Hydroxyl-pyromorphite Pb₅(PO₄)₃OH(s) + H⁺</td>
<td>5Pb²⁺ + 3PO₄⁻ + H₂O</td>
<td>-62.79</td>
<td>MINEQL</td>
</tr>
<tr>
<td>32</td>
<td>Plattnerite Pb(IV)O₂(0) + 4H⁺</td>
<td>Pb⁴⁺ + 2H₂O</td>
<td>-8.91</td>
<td>Calculated¹</td>
</tr>
<tr>
<td>33</td>
<td>Scrutinyte Pb(IV)O₂(0) + 4H⁺</td>
<td>Pb⁴⁺ + 2H₂O</td>
<td>-8.26</td>
<td>Calculated</td>
</tr>
</tbody>
</table>

¹values were calculated using the thermodynamic data in Table A.3.
Benjamin = (Benjamin 2002)
MINEQL = (Schecher and Mcavoy 1998)
Appendix A: Equilibrium Constants and Reactions

Table A.3
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>Pb3O4(s)</td>
<td>-601,200</td>
<td>Benjamin</td>
</tr>
<tr>
<td>Pb2O3(s)</td>
<td>-411,769</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>α-PbO2(s)</td>
<td>-218,987</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>β-PbO2(s)</td>
<td>-222,674</td>
<td>Risold</td>
</tr>
<tr>
<td>Pb2+</td>
<td>-24,309</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>HPbO2-</td>
<td>-338,898</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>Pb4+</td>
<td>302,498</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>PbO3$^{2-}$</td>
<td>-277,562</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>PbO4$^{4-}$</td>
<td>-282,084</td>
<td>Pourbaix</td>
</tr>
<tr>
<td>H+</td>
<td>0.00</td>
<td>Benjamin</td>
</tr>
<tr>
<td>OH^-</td>
<td>-157,300</td>
<td>Benjamin</td>
</tr>
<tr>
<td>H2O</td>
<td>-237,180</td>
<td>Benjamin</td>
</tr>
</tbody>
</table>

Benjamin = (Benjamin 2002)
Pourbaix = (Pourbaix 1974)
Risold = (Risold et al. 1998)

The equilibrium constant for Reaction 22 was calculated by first determining the Gibbs free energy of the reaction by the summation of the molar Gibbs free energies of formation ($G^0_{f,i}$) for each component ($i$), Equations A.1 and A.2. The Gibbs free energies of formation are listed in Table A.3:

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

(A.1)

where $\Delta G_r = \text{Gibbs free energy of reaction (r)}, \text{ joules (J/mol)}$

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

$N_i = \text{stoichiometric coefficient}$

$$
\Delta G_{r,20} = \mu_{PbO_2}^- + 6 \cdot \mu_{H^+} - \mu_{Pb^{2+}} - 3 \cdot \mu_{H_2O} = -131,481 \text{ J}
$$

(A.2)

The equilibrium constant can then be calculated by Equation A.3:

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\[ \log K_{eq} = -\frac{\Delta G_r}{2.303RT} \]  

(A.3)

where \( R \) = equilibrium gas constant, joules per mole per Kelvin (J/mol·K)

\( T \) = temperature, Kelvin (K)

\[ \log(K_{eq}) = -\frac{131,481}{2.303RT} = -23.04 \]  

(A.4)

The equilibrium constant for Reaction 23 was calculated by the summation of the chemical potentials in an analogous manner to Reaction 22.

The Gibbs free energy of reaction for Reaction 32 and 33 were determined by the summation of free energies of formation (Table A.3), Equation A.1. The equilibrium constant was then determined by Equation A.3.
Figure B.1 X-ray diffraction patterns of solids following reaction of massicot at pH 10 in the absence of DIC with 20 mg Cl\textsubscript{2}/L free chlorine. (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 B.2 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 together with reference patterns from the ICDD database.
Figure B.3 X-ray diffraction patterns of solids following reaction of massicott at pH 10 in the presence of 20 mg C/L DIC with 20 mg Cl₂/L free chlorine together with reference patterns from the ICDD database.
Figure B.4 X-ray diffraction patterns of solids following reaction of massicot at pH 7.5 in the presence of 20 mg C/L DIC with 20 mg Cl₂/L free chlorine together with reference patterns from the ICDD database.
Figure B.5 X-ray diffraction patterns of solids following reaction of hydrocerussite at pH 7.5 in the absence DIC with 20 mg Cl₂/L free chlorine together with reference patterns from the ICDD database.
Figure B.6 X-ray diffraction patterns of solids following reaction of hydrocerussite at pH 10 in the absence DIC with 20 mg Cl\textsubscript{2}/L free chlorine together with reference patterns from the ICDD database.
Figure B.7 X-ray diffraction patterns of solids following reaction of cerussite at pH 7.5 in the absence DIC with 20 mg Cl₂/L free chlorine together with reference patterns from the ICDD database.
Figure B.8 X-ray diffraction patterns of solids following reaction of cerussite at pH 10 in the absence DIC with 20 mg Cl₂/L free chlorine together with reference patterns from the ICDD database.
APPENDIX C
SUPPORTING INFORMATION ON LEAD(IV) OXIDE DISSOLUTION RATES

EFFECT OF ORGANIC BUFFER ON PLATTNERTITE 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. A previous study suggested that organic buffers, like 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), and 2-(N-morpholino)ethanesulfonic acid (MES), could significantly enhance the dissolution of PbO₂, probably by acting as reductants for PbO₂ (Xie et al. 2010). 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 ºC) 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. 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 reactors (CSTRs). Experiments were conducted at pH 7.6 with 50 mg C/L DIC and 10 mM NaNO₃ 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 C.1). 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 to 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 C.2). 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 because 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.
Figure C.1 Dissolved lead concentration from batch reactors over time at pH 7.6 with 50 mg C/L DIC and different concentrations of MOPS.
Figure C.2 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 squares and triangles) were conducted for each condition.
Figure C.3 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 squares and triangles) were conducted for each condition.
REFERENCES

American Society of Civil Engineers (2005) Report Card for America's Infrastructure.
AWWA (2005) Managing change and unintended consequences: Lead and Copper Rule corrosion control treatment, American Water Works Association, Denver, CO.


U.S. Environmental Protection Agency (2007b) Summary of Research Relevant to the D.C. Lead Issue, Washington, D.C.


ABBREVIATIONS

\( A \) specific surface area

AWWA American Water Works Association

BDL below detection limit

BET Brunauer Emmett and Teller adsorption isotherm

\( ^\circ C \) degrees Celsius

\( C(t) \) concentration as a function of time

\( C_{\text{eff}} \) effluent concentration

\( C_{eq} \) predicted equilibrium concentration

\( C_{\text{inf}} \) influent concentration

\( \text{cm}^2 \) square centimeters

\( C_{ss} \) steady-state concentration

\( C_{\text{STR}} \) Continuously-stirred tank reactor

\( C_T \) total dissolved inorganic carbon concentration

DIC dissolved inorganic carbon

\( E_a \) activation energy

EDX energy dispersive X-ray analysis

\( f(\Delta G) \) generic expression of function of Gibbs free energy effect on rate

\( \text{ft/s} \) feet per second

FTIR Fourier transform infrared spectroscopy

\( \text{g/L} \) grams per liter

\( G_f^{\circ_i} \) Gibbs free energy of formation of species \( i \)

\( \Delta G \) Gibbs free energy of reaction

IAP ion activity product

ICDD International Centre for Diffraction Data

ICP-MS inductively coupled plasma mass spectrometry

\( k \) dissolution rate constant

\( k_0 \) intrinsic dissolution rate constant

\( K_{sp} \) solubility product

\( \text{L} \) liters

LCR Lead and Copper Rule

\( \text{M} \) moles per liter

\( \text{m/s} \) meters per second

\( \text{m}^2/\text{g} \) square meters per gram

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<table>
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<tr>
<th>Symbol</th>
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<td>mg Cl₂/L</td>
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