July 2018

Corrosion Scale Characteristics and Lead Oxide Dissolution in Chloraminated Water

Daoping Guo
The University of Western Ontario

Supervisor
Herrera, Jose
The University of Western Ontario

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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Abstract

The presence of lead in drinking water is a common issue for utilities where lead pipes are used as service lines in drinking water distribution systems. Dissolved lead concentrations have been linked to the destabilization of stratified lead corrosion scales formed at the inner walls of lead pipe used as drinking water service lines. To develop a framework for lead dissolution control, it is necessary to fully describe the characteristics of the surface layer of the lead corrosion scale in direct contact with drinking water. In the first part of this thesis, a thorough lead corrosion scale characterization is carried using lead pipes collected from four Canadian drinking water systems. The results obtained are contextualized in terms of the preferential presence of lead oxides and aluminosilicates at the surface layer of the corrosion scales. The different phases identified are linked to the corresponding water quality, particularly pH values and dissolved silicate concentrations. In the second part of this work, PbO₂ dissolution processes in the presence of monochloramine were studied. A detailed chemical synthesis protocol, characterization for the PbO₂ solid, analysis of monochloramine decomposition and corresponding lead dissolution profiles have enabled us to identify a surface reaction between PbO₂ and NH₂Cl. Two different reaction regimes for this interaction were revealed. At high PbO₂/NH₂Cl molar ratios, where NH₂Cl is the limiting reagent and the presence of PbO₂ accelerated the decomposition of NH₂Cl. PbO₂ was reduced only by water, resulting in the release of limited amounts of dissolved lead (<10 μg/L). In contrast, at low PbO₂ solid to NH₂Cl molar ratios, monochloramine decomposition rates were similar to those observed for its auto-decomposition. The monochloramine decomposition process triggered the formation of defects in PbO₂, resulting in elevated levels of dissolved lead released to the aqueous phase. The activity of PbO₂ for monochloramine decomposition is determined by its crystal structure, crystallite size, and surface properties in the form of defects. Based on these observations, a proton-containing species in PbO₂ is proposed as the active species for monochloramine decomposition.
Keywords

Lead(IV) oxide, aluminosilicates, UV-Vis spectroscopy, FTIR, pH, $\beta$-PbO$_2$ dissolution, monochloramine, drinking water.
Acknowledgments

I would like to express my greatest gratitude to my supervisor Dr. Jose Herrera for giving me this opportunity to do the research with him and helping me go through my doctoral study. His mentorship teaches me how to think as a scientist and how to perform a scientific research. Without his support, guidance, and patience, I cannot achieve this accomplishment. I also would like to thank Dr. Mita Ray for giving me an opportunity to conduct a project with her, and providing great suggestions for the research. In addition, the grateful thanks will give to Dr. Ajay Ray for granting me use the instrument to measure dissolved inorganic carbon. Thanks my four examiners, Dr. Lars Rehmann, Dr. Ajay Ray, Dr. Martha Dagnew, Dr. Rajesh Seth, and chair of examination board Dr. Aaron Fenster very much for their time and comments on my thesis.

I would like to thank Dr. Clare Robinson and Dr. Jason Gerhard. It is my honor to be a member of RESTORE group. I greatly appreciate the help from the faculty and staff in the Faculty of Engineering at Western University, especially for Ms. Caitlin Corcoran for her great help to facilitate my research and her support for my study life, and Pastor Solano-Flores for teaching me how to measure dissolved inorganic carbon. I also would like to thank my fellow graduate students from the groups of Dr. Herrera and RESTORE for their help, advice, and discussion, especially for Ariel Nunez Garcia and Alexander Stevenson.

My grateful thanks will give to my friends, David Herbert, Irene Herbert, Trent Herbert for their selflessly support and help.

My special grateful thanks will give to my parents, parents-in-law, and my husband, Yu Guo, for their unending love, encouragement, and support.

Lastly, to the Lord, thanks for His great love to me and my families.
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Chapter 1

1 Introduction

1.1 Lead in drinking water

Lead in drinking water is one of the main concerns for water utilities serviced by lead plumbing. Young children and infants are particularly vulnerable to lead exposure. Lead can enter drinking water from the corroded lead pipes that are used as service lines in drinking water distribution system (DWDS). In addition, lead-bearing fixtures and fittings, such as lead solder and brass, also contribute to lead leach into tap water.\(^1\text{-}^5\) Although the use of lead pipes in DWDS was banned in 1975 and lead-bearing solder was prohibited by 1990, pre-1990 existing distribution and plumbing materials are still in place and can be potentially a source of lead in drinking water.\(^6\) The replacement of all lead-bearing plumbing materials is the most effective mean to address lead water issues. This is, however, economically prohibitive and time-consuming. Thus, municipalities with lead contaminated water are required to develop and implement corrosion control plan based on the site-specific characteristics of corrosion scales to reduce the elevated lead concentrations in their drinking water.

The Center for Disease Control and Prevention (CDC) has reported that there is no known safe level of lead in a child’s blood.\(^7\) But elevated blood lead levels have been reported in children due to the consumption of lead contaminated drinking water. Heightened concern is leading to modifications to national and local guidelines for lead action levels.\(^8,^9\) The stricter regulations for lead levels in water may pose a challenge for current corrosion control strategies. It has been acknowledged that the stability of lead corrosion scales is determined by drinking water quality (e.g., pH, alkalinity, temperature, redox potential [ORP], natural organic matter [NOM]), and this also controls dissolved lead concentrations in drinking water. While previous studies\(^3,^{10-18}\) characterized lead corrosion scales collected from the lead pipes, a few of them linked the characterization results with site-specific water quality to understand the influence of water chemistry on its formation and dissolution\(^12,^{19,20}\). Moreover, enhanced understanding of fundamental physicochemical
processes governing lead dissolution under drinking water conditions is essential to develop a generalized tool for the application of a corrosion control plan.

PbO$_2$ is one of common phases present in the surface layer of scales that formed under chlorination conditions. Most studies on the dissolution of PbO$_2$ evaluated the effects of different water quality on this process, but the changes in chemical properties of PbO$_2$ is neglected. With the possibility of changes in water quality induced by updating guidelines, this knowledge is needed to prevent elevated lead releasing and to develop effective corrosion control strategies.

1.2 Research objectives

The objective of this thesis is to understand the relationship between water quality and composition of corrosion scales, and characterize the fundamental processes associated with the dissolution of PbO$_2$ under depleting monochloramine conditions. The specific objectives of this thesis are as follows:

1. Characterize lead corrosion scales using UV/Vis spectroscopy besides other conventional techniques, then identify the dominant phases present in the surface layer of the corrosion scales.

2. Link water quality with the morphology and chemical composition of the lead corrosion scales for a specific region.

3. Elucidate the mechanism regulating the interactions of PbO$_2$ with monochloramine

4. Identify the factors that affect the activity of PbO$_2$ in terms of monochloramine decomposition, and propose the active species present in PbO$_2$ that enhance monochloramine decomposition.

1.3 Original contribution

It is challenging to characterize the surface layer of corrosion scales as it contains complex mixtures and amorphous phases. The current studies reported only qualitative results of lead compounds present in each layer of corrosion scales. In this thesis, UV/Vis
spectroscopy is for the first time used to characterize solid stratified corrosion scales and reveal semi-quantitative results in terms of lead carbonates and oxides. These results are also linked with the corresponding drinking water quality to understand dominant water quality parameter controlling the stability of scales. For the dissolution of PbO\textsubscript{2} under monochloramine conditions, Lin and Valentine\textsuperscript{21, 22} and other groups\textsuperscript{23, 24} have performed comprehensive studies, but either commercial PbO\textsubscript{2} or extremely low solid concentrations were used in their study. These conditions are not representative of the actual PbO\textsubscript{2} phase formed under drinking water conditions. Thus, the work presented in Chapter 4 is the first study to show a surface reaction between PbO\textsubscript{2} and NH\textsubscript{2}Cl, and the potential factors regulating PbO\textsubscript{2} activity in monochloramine decomposition. Further study on this reaction was present in Chapter 5 in which laboratory synthesized PbO\textsubscript{2} was compared with chlorinated PbO\textsubscript{2}, furthering the current state of the art knowledge of this processes by proposing an active species in PbO\textsubscript{2} that enhance monochloramine decomposition.

1.4 Thesis outline

Chapter 1 presents general background for the thesis and the research objectives.

Chapter 2 reviews the studies that performed characterization of lead corrosion scales collected from lead service lines in DWDS and explored the effect of water quality on the stability of PbO\textsubscript{2}. The physicochemical properties of PbO\textsubscript{2} are also discussed in this chapter.

Chapter 3 presents and discusses the characteristic results of lead corrosion scales gathered from four Canadian DWDS and their link with the corresponding drinking water quality.

Chapter 4 and 5 present and discuss the dissolution experimental results of different β-PbO\textsubscript{2} samples under depleting monochloramine conditions (Chapter 4), and further explore this reaction and plausible mechanisms (Chapter 5).

Chapter 6 summarizes the experimental findings and provides recommendations for further work.
References


Chapter 2

2 Literature review

2.1 Current issues associated with lead dissolution in drinking water

Elevated dissolved lead concentrations in drinking water have been reported in the recent past in Canada, United States, United Kingdom, and Germany. Dissolved lead levels have been traced to physicochemical destabilization of lead corrosion scales formed in the inner walls of lead plumbing service lines in drinking water distribution systems (DWDS). The most recent well publicized issue linked to lead in drinking water is the lead-poisoning outbreak in the City of Flint, Michigan. This one however, represents only one of many lead water crises that have occurred around the world. Lead is a cumulative toxicant that affects multiple body systems and triggers serious health issues particularly for infants and young children. No safe blood lead level in children has been identified by Centers for Disease Control and Prevention (CDC). To ensure the safety of drinking water, Health Canada is considering updating the existing guideline for lead, maximum acceptable concentration (MAC), from 10 to 5 μg/L. Based on the report of Health Canada, average concentrations of lead in treated water leaving the water treatment plant are less than 1 μg/L. However, elevated lead concentrations (> 10 μg/L) were observed in water samples that collected in DWDS of municipalities in Saskatchewan, Ontario, and Charlottetown, Prince Edward Island (Table 2.1).

Table 2.1 Concentrations of lead (μg/L) in drinking water distribution systems in Canada (Reproduced from Health Canada, 2013)

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>n</th>
<th>Concentration (μg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Median</td>
<td>Minimum</td>
</tr>
<tr>
<td>2009–2010</td>
<td>Various locations across Canada</td>
<td>65</td>
<td>0.6</td>
<td>&lt;0.5 b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31</td>
<td>&lt;0.5 d</td>
<td>&lt;0.5 d</td>
</tr>
<tr>
<td>2000</td>
<td>Ontario</td>
<td>445</td>
<td>0.32</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2001</td>
<td></td>
<td>447</td>
<td>0.28</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2002</td>
<td></td>
<td>369</td>
<td>0.28</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2003</td>
<td></td>
<td>376</td>
<td>0.23</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2004</td>
<td></td>
<td>390</td>
<td>0.18</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2005</td>
<td></td>
<td>362</td>
<td>0.19</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
It has been found the dissolved lead in tap mainly comes from legacy lead service lines (LSL) that are used in the last part of DWDS serving drinking water to residents. Over time, the lead corrosion scales formed on these LSL, and the destabilization of these corrosion scales contributes to lead contamination in water. Although the use of lead for service lines was banned in 1975 and lead-bearing solider was prohibited by 1990, pre-1990 existing distribution and plumbing materials may be a source of lead in drinking water. Thus, the optimum option to solve lead water issues is to replace all the LSL. However, complete replacement of LSL in a specific community is a lengthy and cost intensive process. Thus, the municipalities with LSL are required to execute a corrosion control plan based on the site-specific characteristics of corrosion scales to reduce the elevated lead concentrations in their drinking water.

### 2.2 Characteristics of lead corrosion scales

#### 2.2.1 Occurrence and composition of lead corrosion scales formed in lead pipes

A clear understanding of the characteristics of lead corrosion scales under different water quality conditions is essential to develop effective long-term corrosion strategies. Due to the presence of oxidants (e.g., dissolved oxygen and disinfectant) in drinking water, metallic lead, Pb (0), is oxidized, forming lead corrosion scales as a passivation layer in the inner
walls of lead pipes. The formation of lead corrosion scales is a complicated process, but it could be simplified as described below. Generally, elemental lead Pb (0) is oxidized to form Pb (II) ions. Then complexation of Pb (II) ions with the anions (e.g., hydroxyl ions, carbonates, phosphates, nitrates, and other species) that are naturally present in drinking water occurs. Amongst various complexes formed, hydroxyl and carbonates complexes are the most common ones under typical drinking water conditions based on theoretical and experimental studies\(^1,9-11\). When the concentrations of Pb (II) hydroxyl and/or carbonates complexes reach their saturation, solid precipitation takes place on the bare lead (0) pipes. The growth of newly formed precipitation is a dynamic process in which solute molecules precipitate out of solution, and dissolve back into solution, finally reaching an equilibrium. If strong oxidant, e.g., free chlorine, is present in drinking water, Pb (IV) species can also form according to Eq. 2.1.

$$\text{Pb}^{2+}_{\text{(aq)}} + \text{OCl}^{-}_{\text{(aq)}} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Cl}^{-}_{\text{(aq)}} + \text{PbO}_2(\text{s}) + 2\text{H}^+_{\text{(aq)}} \quad (2.1)$$

The composition of lead corrosion scales is complex and heavily site-specific due to the diversity of cations and anions naturally present and/or artificially added in drinking water. To understand the composition of lead corrosion scales, several studies\(^1,12-20\) have been performed for the characterization of lead corrosion scales that formed in lead pipes in DWDS in North America and Europe. It has been observed that the stratified lead corrosion scales, in general, consist of lead (II) carbonates, lead oxides, and some non-lead compounds. Hydrocerussite (Pb\(_3\)(CO\(_3\))\(_2\)(OH)\(_2\)) and cerussite (PbCO\(_3\)) are the most common crystalline lead carbonates phases found in the scales in the absence of phosphate.\(^14,18\) Plattnerite (β-PbO\(_2\)) and scrutinyite (α-PbO\(_2\)) are often observed together with other minor lead oxides phases (e.g., minium [Pb\(_3\)O\(_4\)] and litharge [PbO]) in the outermost layer of corrosion scales.\(^12-14,21\)

For non-lead bearing phases, aluminum, iron, and manganese are the most abundant elements observed in the surface layer of corrosion scales.\(^3,14,19,22,23\) While the quantity of these elements could be evaluated accurately, their speciation is not well understood due to the difficulty of characterization and the limited amount of these compounds in the scale. Aluminosilicates are a common phase containing aluminum element present in the surface
layer of corrosion scales, and it is the generic name for various clay minerals. Allophane and imogolite are the two main types of poorly crystalline aluminosilicates. Previous studies\textsuperscript{14, 24} found that allophane is the common phase formed under drinking water conditions. Due to its surface properties, allophane could act as adsorbent for a variety of charged species either anions\textsuperscript{25, 26} (e.g., phosphate, fluoride, citrate, borate, arsenate, and selenite) or metal ions\textsuperscript{27} (e.g. lead, copper, zinc, cobalt, cadmium, magnesium, and calcium). The Al/Si ratio determines the nature of the allophane, and pH is a key parameter that affect its surface properties.\textsuperscript{27-29} As aluminosilicates is an amorphous phase, it will interfere with the characterization of crystalline phases, particularly the ones present in limited amounts. This is the major challenge to understand the speciation of iron and manganese embedded in lead corrosion scales. It is well known that iron and manganese compounds have high affinity to absorb and concentrate arsenic, which may pose arsenic contamination beside lead. Moreover, these non-lead compounds might affect the stability of lead corroded phases under dynamic water quality conditions. Therefore, it is necessary to study the characteristics of non-lead phases to understand their configuration and their impact on stability of lead phases under drinking water conditions.

2.2.2 The effect of water quality on the occurrence and stability of corrosion scales

The formation of lead corrosion scales is heavily dependent on localized water quality which in turn determines the availability and type of disinfectant and the speciation of lead species (solid precipitation, dissolution, etc.). Thus, it is important to understand the interaction between regional water quality and its corrosion scales to inform an effective corrosion control strategy. Kim et al.\textsuperscript{14} performed a comprehensive characterization of the scales formed in LSL of City of London, ON. They have reported that pH and alkalinity are main factors for the abundance of hydrocerussite in the inner layers of scales, while with the presence of free chlorine, PbO\textsubscript{2} and hydrocerussite are dominant phases in the outermost layer of scales. This particular configuration of lead corrosion scales formed is linked with the drinking water treatment history of City of London, ON. In the past, well water with high pH values (~8.0) and alkalinity (250-300 mg CaCO\textsubscript{3}/L) had been used. Under these conditions, hydrocerussite formed in the early stage of passivation. After
switch to surface lake water in the late 1980’s, the water pH values were stabilized around 7 to 8, and alkalinity was decreased to about 60-70 mg CaCO$_3$/L. Under these conditions and in the presence of free chlorine disinfectant, lead (II, IV) oxides (e.g. PbO, Pb$_3$O$_4$, and PbO$_2$) formed via the oxidation of lead (II) carbonates.

It has been reported that the water quality also affects the occurrence mode of solid phases in corrosion scales. A thin and tenacious layer of β-PbO$_2$ and α-PbO$_2$ was observed in the surface layer of scales in the lead pipes collected from City of Cincinnati, Ohio, and underlain by a thin layer of PbO with small amount of hydrocerussite and quartz. The city used surface water to serve the city with chlorinated drinking water at a basic pH (8.3-9.2), moderate alkalinity (50-65 mg CaCO$_3$/L) and 120 mg CaCO$_3$/L hardness. Although similar drinking water quality (e.g., pH, alkalinity and harness) was observed in Madison, WI, Newport, Rhode Island, and other two anonymous cites, the occurrence mode of PbO$_2$ in these scales is quite diverse. Newport samples showed similar characteristic as the Cincinnati scales, whereas patchy superficial deposition of PbO$_2$ was present on the top of cerussite together with other non-lead phases for Madison’s scales. In contrast, when treated ground water with near neutral pH and high alkalinity (285-362 mg CaCO$_3$/L) was used as source water in Oakwood, Ohio, a discrete surface layer of PbO$_2$ over a more-soluble lead (II) compounds (cerussite and PbO) was reported.

The water quality also significantly influences the stability of scales and solid phase transformations. One example is the lead water crisis recently occurred in City of Flint, Michigan. Sudden switch water source from lake water to river water dramatically changed the water quality, further destabilizing lead corrosion scales previously formed in the City’s DWDS. Elevated lead was released into customers’ tap water and poisoned the residents. Another lead water crisis occurred in the Washington D.C. in 2003 when the disinfectant was switched from chlorine to chloramine. A sudden decrease in the redox potential (ORP) regulated by the type of disinfectant has been identified as responsible for elevated lead levels. Later studies has reported that unknown intermediate species generated via monochloramine auto-decomposition could reduce PbO$_2$, resulting in high dissolved lead levels in water. The availability of dissolved inorganic carbon (DIC) and pH values in water could significantly affect the pathway of formation of Pb (II, IV)
compounds from different precursors.\textsuperscript{34-38} Thus, pH adjustment is sometimes used as a corrosion control treatment to suppress the lead release from corrosion scales. However, this treatment is effective only for the systems where corrosion scales are mainly lead carbonates. For corrosion scales rich in PbO\textsubscript{2} phosphates are used as corrosion inhibitors to control lead dissolution\textsuperscript{18, 19, 39}. Lead concentrations at customer’s tap were found to immediately decrease about 50\% after orthophosphate addition (1 mg P/L orthophosphate) due to the formation of insoluble chloropyromorphite (Pb\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}Cl) and/or hydroxypyromorphite (Pb\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}OH). Although orthophosphate is indeed a viable corrosion inhibitor, it only works within a very specific range of pH and DIC.\textsuperscript{1, 9, 40, 41}

### 2.3 The formation of β-PbO\textsubscript{2} under drinking water conditions

As mentioned in the previous sections, plattnerite (β-PbO\textsubscript{2}) is one of the most common lead oxides formed in the surface layer of corrosion scales under aggressive chlorinating (HOCl + OCl\textsuperscript{-}) conditions. Its formation can proceed through the oxidation of either dissolved Pb (II) ions or solid lead (II) compounds. Edwards and Dudi\textsuperscript{32} have reported a color change, from white to reddish brown, when PbO\textsubscript{2} precipitates during the oxidation of dissolved lead by free chlorine at pH of 5.5 and 8.5. In addition, dissolved lead concentrations decreased with the formation of the solid. Thus, they proposed that the observed reddish solid is likely to be PbO\textsubscript{2} that has a low solubility. Similar color changes have been also reported by Lytle and Schock\textsuperscript{36} in Pb\textsuperscript{2+} aqueous solutions with 3 mg/L free chlorine and 10 mg C/L DIC at initial pH of 8. Based on the characterization of solids via XRD, they found that hydorcerussite and/or cerrusite formed initially and over time either disappeared or coexisted with PbO\textsubscript{2}. It should be noted that there was no PbO\textsubscript{2} formed within the first 30 min reaction even in a superchlorinated water solution (about 30 mg Cl\textsubscript{2}/L). Liu et al.\textsuperscript{42} have also reported that formation of PbO\textsubscript{2} did not take place at early stages of chlorination of lead (II) carbonates. Both studies suggest that the formation of PbO\textsubscript{2} from either dissolved lead or lead(II) carbonates is kinetically-controlled process. The formation of this phase is also heavily dependent on water pH.\textsuperscript{36} Consistently, Lytle and collaborators\textsuperscript{43} have proposed the formation of PbO\textsubscript{2} through a pathway of Pb\textsuperscript{2+}(aq) → hydrocerussite → cerussite → PbO\textsubscript{2} based on their experiments using aqueous chlorinated solutions and dissolved Pb(II) ions with 10 mg C/L DIC at pH of 8. Lead (II) carbonates
(hydrocerussite and cerussite)\textsuperscript{34-36, 42} and lead (II) oxides (PbO and Pb\textsubscript{3}O\textsubscript{4})\textsuperscript{34, 44} have also been used as starting materials to perform batch experiments to study the pathways and mechanism for the formation of PbO\textsubscript{2} in chlorinated water. These studies confirm that PbO\textsubscript{2} could form through the chlorination of lead (II) compounds, although the specific pathway for this process is determined by the water quality (e.g., DIC and pH values) as shown in Figure 2.1.

![Figure 2.1](image_url)  

**Figure 2.1** Formation of PbO\textsubscript{2} from Pb(II) phases. Reprinted (adapted) with permission from (Wang et al.\textsuperscript{34}). Copyright (2018) American Chemical Society.
2.4 Structural and physicochemical properties of β-PbO$_2$

Due to the relatively low solubility of PbO$_2$ compared with other lead compounds$^{13, 45}$, its presence in the surface layer of corrosion scales is considered as an effective barrier to prevent lead release.$^{21}$ Besides its low solubility, PbO$_2$ has other pronounced physicochemical properties that may affect its dissolution processes under typical drinking water conditions. However, most studies have focused on the influence of different water quality parameters on the stability of PbO$_2$ rather than exploring its own properties. PbO$_2$ has been widely used as electrodes in lead-acid batteries$^{46, 47}$, and transparent conducting oxides in thin films and glasses$^{48-52}$. Thus, its crystalline structure and electrochemical characteristic have been extensively investigated. In the following two sections, its most notable structural and physicochemical properties are summarized.

2.4.1 Crystalline structure of β-PbO$_2$

β-PbO$_2$ crystalizes in a tetragonal rutile structure as shown in Figure 2.2a. The tetravalent lead ion is in the center of a distorted octahedron surrounded by six oxygen ions. The octahedron has four short Pb-O bonds in a place and two long Pb-O bonds perpendicular to this plane (Figure 2.2b). These octahedra share opposite edges to form a linear chain parallel to the c axis of the unit cell (Fig. 2.2a). Then the resulting chains are connected with each other by sharing corners.$^{37, 50, 53, 54}$

![Figure 2.2](image)

*Figure 2.2 a) Coordination (Mindt$^{50}$) and b) the unit cell of β-PbO$_2$ (Hill$^{54}$)*
PbO$_2$ can be generated in a chemical reaction or an electrochemical reaction. It has been reported that only electrochemically prepared PbO$_2$ electrodes reveals electrochemical activity, whereas chemically prepared PbO$_2$ does not show activity. Several studies$^{54-56}$ have been performed to explore the active phase present in electrolytic PbO$_2$ but not in chemically prepared PbO$_2$. They found that chemically prepared PbO$_2$ contains a highly crystalline phase with better well-defined crystal structure and order than the one prepared using electrochemical methods. In contrast, an amorphous PbO$_2$ phase is commonly observed in electrochemically prepared PbO$_2$. Therefore, the difference in crystal structure has been proposed as a possible factor affecting PbO$_2$ electrochemical activity.

### 2.4.2 Defects in β-PbO$_2$

Besides the effect of crystal structure on the electrochemical activity of PbO$_2$, the non-stoichiometry of PbO$_2$ is also proposed to have an influence. It is well acknowledged that fully stoichiometric PbO$_2$ does not exist due to the presence of defects in its lattice. The high conductivity of PbO$_2$ is attributed to the excess of free electrons generated by these defects$^{57}$, but the nature of defects is still under debate. Oxygen vacancies ($V_0$)$^{38, 58, 59}$, interstitial lead (Pb$_i$)$^{53}$, and adventitious incorporation of hydrogen$^{47, 50, 60}$ in the lattice have all been proposed to account for the unusually high conductivity of PbO$_2$. Rüetschi and Cahan$^{61}$ proposed that some hydroxyl ions replaced oxygen in the PbO$_2$ crystal lattice and provided extra free electrons for electrical conductivity. On the other hand, studies$^{47, 55}$ on PbO$_2$ electrodes have reported that PbO$_2$ is substoichiometric on the cation sublattice rather than in the anion sublattice based on neutron diffraction experiments. Additionally, a substantial amount of disordered hydrogen was observed in electrochemically active PbO$_2$.$^{62}$ A more recent study$^{37}$ has reported a complete oxygen sublattice but lead vacancies ($V_{Pb}$) as dominant defects. Rüetschi$^{47}$ proposed a model in which lead vacancies may serve as hosts for Pb$^{2+}$ ions such that the composition of lead dioxide was expressed as Pb$_{1-x-y}$$^{+4}$Pb$_y$$^{+2}$O$_{2-4x-2}$ OH$_{4x+}$, where x represents the cation vacancy fraction and y represents the fraction of Pb$^{+2}$ ions. Further he rationalized that lead vacancies could undergo electrochemical reduction through solid state transformation during electrochemical discharge process. In contrast, chemically prepared PbO$_2$ is well
crystallized and vacancy-free, so its reduction is concomitant with dissolution, resulting in releasing \( \text{Pb}^{2+} \text{(aq)} \).

The different hydrogen content in electrochemically prepared and chemically prepared \( \text{PbO}_2 \) have been widely studied and proposed as a critical factor determining the activity of \( \text{PbO}_2 \).\textsuperscript{55, 60, 63} Caulder and Simon\textsuperscript{64} observed more hydrogen in electrochemically prepared \( \text{PbO}_2 \) than chemically prepared \( \text{PbO}_2 \), as per their nuclear magnetic resonance (NMR) results. Moreover, two types of hydrogen with different configurations were observed in the NMR results, and one of them did not correspond to hydrogen in water molecules. The magnitude of this non-water hydrogen signal decreased with the increase in crystallinity during charge/discharge cycling. Similarly, Hill\textsuperscript{65} also observed that electrochemical active \( \text{PbO}_2 \) contains protons in two different configurations via solid-state magic-angle-spinning NMR. One of these proton species is related to mobile, isolated, adsorbed hydroxyl groups and/or water molecules that could be removed by outgassing. Another one cannot be removed by outgassing, and is probably associated with water molecules trapped on the internal crystal. Moreover, he observed that the proton species in chemically prepared \( \text{PbO}_2 \) differs from the electrochemically prepared one only by its abundance in the crystal. According to the experimental results on the comparison of electrochemical activity of electrochemically prepared and chemically prepared \( \text{PbO}_2 \), Hill\textsuperscript{66} proposed the incorporation of proton species in \( \text{PbO}_2 \) via a surface hydrolysis mechanism that occurs during crystallization. During crystal growth, some surface hydroxyl groups could be trapped on internal surfaces (e.g., low angle grain boundaries) and/or in micropores. Therefore, Hill\textsuperscript{66} proposed that proton species would reside in disordered/imperfect surface rather than in long-range ordered crystalline surface. His hypothesis is consistent with the experimental observations that the loss in proton species occurred with the better crystal formed during the discharge/charge cycling. In addition, this proposed mechanism explains the non-activity of chemically prepared \( \text{PbO}_2 \) in terms of electrochemical properties.

### 2.5 Monochloramine in drinking water

Historically, chlorination is a common secondary disinfection process. Although free chlorine is an effective disinfectant for pathogenic bacteria, in the presence of natural organic matter it also generates disinfectant by-products (DBPs; e.g., trihalomethanes and
halogenated acetic acids), suspected carcinogens. Compared with free chlorine, NH₂Cl has the same oxidizing capacity on a chlorine atom basis, but it is a weaker disinfectant. Thus, to control the formation of DBPs, chloramine has been used to replace free chlorine by some municipalities as disinfectant in DWDS. One example is Washington D. C. which switched the disinfectant from free chlorine to chloramine in 2003, having an unintended increase in water lead concentrations at the customer’s tap. It was not until Lin and Valentine³³ performed a thorough study that the intermediate species released from auto-decomposition of NH₂Cl were linked to chemical reduction of PbO₂, resulting in dissolved lead released.

Chloramines could be prepared based on two methods. The first method is mixing chlorine with ammoniacal water to obtain a chlorine to ammonia molar ratio below 1 (Cl/N<1), this produces chloramines in the presence of excess ammonia. In the second method, sufficient chlorine is added to fully oxidize ammoniacal water to produce stable products and residual free chlorine. The former process is referred to “chloramination” or “combined residual chloramination”, while the later process is referred to “breakpoint chlorination” in which Cl/N>1.6. Chloramines refer to monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NH₃). Their production is highly dependent on pH and the molar ratio of chlorine to ammonia. Monochloramine is the only chloramine formed when pH values is greater than 8 and Cl/N ratio <1.⁶⁷ From water utilities perspective, monochloramine is the desire species present under typical drinking water conditions.⁶⁸ Thus most extensively studies have been performed on monochloramine. Our work and literature review are focused on the combined chloramine region.

Several studies⁶⁹-⁷¹ have been performed extensively study on the formation of monochloramine. In general, its formation follows Eq.1 in Table 2.2. This reaction is an elementary reaction with a second-order overall kinetics and first order on each reactant. Its specific rate varies with the pH of the solution. The fastest reaction occurs around pH 8.⁷⁰ A decrease in reaction rate is observed with either increase or decrease in pH values from 8. The same order of magnitude rate constants for monochloramine formation have been reported by various investigators.⁷²
Table 2.2 Reactions and associated constants for the auto-decomposition of NH$_2$Cl (Jafvert and Valentine$^1$)

<table>
<thead>
<tr>
<th>reaction stoichiometry</th>
<th>rate expression</th>
<th>rate constant (25 °C)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) HOCl + NH$_3$ → NH$_2$Cl + H$_2$O</td>
<td>$k_{am}$[HOCl][NH$_3$]</td>
<td>$k_{am} = 1.5 \times 10^{10}$ M$^{-1}$ h$^{-1}$</td>
<td>18</td>
</tr>
<tr>
<td>(2) NH$_2$Cl + H$_2$O → HOCl + NH$_3$</td>
<td>$k_{ma}$[NH$_2$Cl]</td>
<td>$k_{ma} = 7.6 \times 10^{-2}$ h$^{-1}$</td>
<td>18</td>
</tr>
<tr>
<td>(3) HOCl + NH$_2$Cl → NHCl$_2$ + H$_2$O</td>
<td>$k_{md}$[HOCl][NH$_2$Cl]</td>
<td>$k_{md} = 1.0 \times 10^6$ M$^{-2}$ h$^{-1}$</td>
<td>4, 17</td>
</tr>
<tr>
<td>(4) NHCl$_2$ + H$_2$O → HOCl + NH$_2$Cl</td>
<td>$k_{dm}$[NHCl$_2$]</td>
<td>$k_{dm} = 2.3 \times 10^{-3}$ h$^{-1}$</td>
<td>17</td>
</tr>
<tr>
<td>(5) NHCl$_2$ + NH$_2$Cl → NHCl + NH$_3$</td>
<td>$k_{mm}$(NH$_2$Cl)$^2$</td>
<td>$k_{mm} = k_{H}[H^+] + k_{H}[HPO_4^2-] + k_{H}[H_3PO_4]$</td>
<td>20, 21</td>
</tr>
<tr>
<td>(6) NHCl$_2$ + NH$_3$ → NHCl + NH$_2$Cl</td>
<td>$k_{dm}$(NHCl$_2$)(NH$_3$)[H$^+$]</td>
<td>$k_{dim} = 2.16 \times 10^6$ M$^{-2}$ h$^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>(7) NHCl$_2$ + H$_2$O → I</td>
<td>$k_{cl}$(NHCl$_2$)[OH$^-$]</td>
<td>$k_{cl} = 4.0 \times 10^6$ M$^{-1}$ h$^{-1}$</td>
<td>20, 28</td>
</tr>
<tr>
<td>(8) I + NHCl$_2$ → HOCl + products$^b$</td>
<td>$k_{dp}$(I)[NHCl$_2$]</td>
<td>$k_{dp} = 1.0 \times 10^8$ M$^{-1}$ h$^{-1}$</td>
<td>9</td>
</tr>
<tr>
<td>(9) I + NH$_2$Cl → products$^b$</td>
<td>$k_{mp}$(I)[NH$_2$Cl]</td>
<td>$k_{mp} = 3.0 \times 10^7$ M$^{-1}$ h$^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>(10) NH$_2$Cl + NHCl$_2$ → products$^b$</td>
<td>$k_{md}$(NH$_2$Cl)[NHCl$_2$]</td>
<td>$k_{md} = 5.0 \times 10^5$ M$^{-1}$ h$^{-1}$</td>
<td>6, 8</td>
</tr>
<tr>
<td>(11) HOCl + NHCl$_2$ → NC$_8$H$_9$ + H$_2$O</td>
<td>$k_{h}$(NHCl$_2$)[HOCl]</td>
<td>$k_{h} = k_{H}[HPO_4^{2-}] + k_{H}[HCO_3^-] + k_{OH}^{-}[OH^-]$</td>
<td>9</td>
</tr>
<tr>
<td>(12) NHCl$_2$ + NC$_8$H$_9$ + 2H$_2$O → 2HOCl + products$^b$</td>
<td>$k_{dp}$(NHCl$_2$)[NC$_8$H$_9$][OH$^-$]</td>
<td>$k_{dp} = 2.0 \times 10^{13}$ M$^{-2}$ h$^{-1}$</td>
<td>6, 9</td>
</tr>
<tr>
<td>(13) NH$_2$Cl + NC$_8$H$_9$ + H$_2$O → HOCl + products$^b$</td>
<td>$k_{mp}$(NH$_2$Cl)[NC$_8$H$_9$][OH$^-$]</td>
<td>$k_{mp} = 5.0 \times 10^5$ M$^{-2}$ h$^{-1}$</td>
<td>d</td>
</tr>
<tr>
<td>(14) NHCl$_2$ + 2HOCl + H$_2$O → NO$_3$ + 5H$^+$ + 4Cl$^-$</td>
<td>$k_{dp}$(NHCl$_2$)[OCl$^-$]</td>
<td>$k_{dp} = 8.3 \times 10^5$ M$^{-1}$ h$^{-1}$</td>
<td>d</td>
</tr>
</tbody>
</table>

$^a k_H = 2.5 \times 10^7$ M$^{-1}$ h$^{-1}$; $k_{HP} = 1.3 \times 10^8$ M$^{-2}$ h$^{-1}$; $k_{H_{2}CO_3} = 7.2 \times 10^2$ M$^{-2}$ h$^{-1}$. In carbonate-buffered systems additional terms include $k_{H}[HCO_3^-] + k_{H}[CO_3^{2-}]$, where $k_{H}[HCO_3^-] = 2.7 \times 10^5$ M$^{-2}$ h$^{-1}$ and $k_{H}[CO_3^{2-}] = 7.2 \times 10^2$ M$^{-2}$ h$^{-1}$ (21). $^b$ Products may include N$_2$, H$_2$O, Cl$^-$, H$^+$, NO$_3$, and unidentified reaction products. For purposes of d[H$^+$] calculation, products were assumed to contain 3H$^+$ for each reaction, consistent with N$_2$ formation. $^c k_{HP} = 5.72 \times 10^7$ M$^{-1}$ h$^{-1}$; $k_{CO_3} = 3.24 \times 10^8$ M$^{-2}$ h$^{-1}$; $k_{OH} = 1.18 \times 10^{13}$ M$^{-2}$ h$^{-1}$. In carbonate-buffered systems an additional term is $k_{CO_3}[CO_3^{2-}]$, where $k_{CO_3} = 2.16 \times 10^{10}$ M$^{-2}$ h$^{-1}$ (3). $^d$ This work.
2.5.1 Auto-decomposition of monochloramine

Monochloramine is relatively persistent in water, but it auto-decomposes through a complex set of reactions (Table 2.2) that result in the oxidation of ammonia and reduction of active chlorine.\textsuperscript{73} Under near neutral pH conditions, auto-decomposition of monochloramine is primarily controlled by the rate of formation of dichloramine which in turn rapidly decomposes.\textsuperscript{73-76} In general, dichloramine forms through two pathways. One is a monochloramine hydrolysis pathway (Eqs. 2 and 3 in Table 2.2). Another one is a monochloramine disproportionation reaction (Eq. 5 in Table 2.2) which is acid catalyzed consisting of two non-elementary\textsuperscript{72} steps:\textsuperscript{77}

\begin{equation}
\text{NH}_2\text{Cl} + \text{H}^+ \text{ or HA} \leftrightarrow \text{NH}_3\text{Cl}^+ (+\text{A}^-) \quad (2.2)
\end{equation}

\begin{equation}
\text{NH}_3\text{Cl}^+ + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3 + \text{H}^+ \quad (2.3)
\end{equation}

Both pathways for dichloramine formation have been studied by several groups.\textsuperscript{67, 71, 77, 78} The hydrolysis of monochloramine and the reverse reaction of monochloramine formation, have been reported to follow a 1\textsuperscript{st}-order kinetics as shown in Table 2.2, generating free chlorine.\textsuperscript{69, 79} Comparing with the instantaneous reaction of free chlorine and monochloramine (Eq. 3 in Table 2.2), the hydrolysis of monochloramine is the rate-limiting step for dichloramine formation. The excess of ammonia present depresses the hydrolysis of monochloramine. Thus, the reaction rate decreases according to Eq. 6 in Table 2.2. The disproportionation of monochloramine (Eq. 5 in Table 2.2) is another pathway for the depletion of monochloramine. Although this reaction is not a fundamental reaction since it can be derived from the monochloramine and dichloramine hydrolytic reactions, it can be used to describe the overall loss in monochloramine and to evaluate some of the fundamental quantities regulating overall reaction rate.\textsuperscript{72} Granstrom\textsuperscript{77} has observed this reaction to be catalyzed by acid and buffer in solution, and reported a 2\textsuperscript{nd}-order kinetic constant, which was four orders of magnitude lower than that obtained for the reaction of free chlorine and monochloramine. Consistently, Leao\textsuperscript{74} also reported the insufficiency of using only a 1\textsuperscript{st}-order reaction for monochloramine hydrolysis to describe the disappearance of monochloramine. With the incorporation of the acid catalyzed
disproportionation of monochloramine (Equation 5 in Table 2.2), the model results improved and could fit the experimental observations. Moreover, Leao\textsuperscript{74} proposed that the rate-limiting step was the breaking Cl-N bond after neutral monochloramine carried a nucleophilic attack on the chlorine atom attached to a positively charged monochloramine (NH\textsubscript{3}Cl\textsuperscript{+}). An intermediate species was proposed to form during this reaction, but the identity of intermediate species was unknown. Valentine and Jafvert\textsuperscript{73, 75, 76} have performed comprehensive studies on the catalytic effect of hydrogen ion and buffer anions (e.g., phosphate, sulfate, and carbonates) on monochloramine disproportionation, and proposed a general acid catalysis pathway for monochloramine disproportionation. The existing model of Leao was adequate for modeling the changes in monochloramine over time, but it overestimated the rate of dichloramine decay. After incorporating both the general acid catalysis and monochloramine hydrolysis pathways in the modified model of Valentine and Jafvert, the simulated profiles of dichloramine decomposition significantly improved.\textsuperscript{75, 76} Based on their model results, both pathways contributed equally under chloramination conditions at near neutral pH values. Hydrogen ion catalysis is expected to be more important than hydrolysis pathway in the presence of a total uncombined ammonia concentration slightly above 5.4 mg N/L at pH values below 9.3. Furthermore, the Valentine and Jafvert’s model was useful in describing monochloramine decay in DWDS with low NOM concentrations (< 3.5 mg C/L).\textsuperscript{80}

Under chloramination conditions (Cl/N<1), dichloramine will decompose through several redox reactions (Eqs. 7-10 in Table 2.2). Leao\textsuperscript{74} proposed a kinetic model that simulates the decomposition of dichloramine under the chloramination conditions. In his model, nitrogen gas was considered as the major oxidation product with other minor nitrogen bearing products (e.g., NO\textsubscript{3} -, NO\textsubscript{2} -, N\textsubscript{2}O) also formed. In addition, the formation of an intermediate species (I) with a short life-time was proposed. Valentine et al.\textsuperscript{81} also observed unidentified products increasing over time during the decomposition of dichloramine. Moreover, they found the formation of these unknown products to be promoted by basic conditions and paralleled by the loss of oxidant in solution. The study performed by Javert and Valentine\textsuperscript{82} on dichloramine decomposition verified the mechanism/model proposed by Leao. While the formation of unidentified species has been observed in both monochloramine and dichloramine decomposition\textsuperscript{83, 84}, dichloramine is essential for the
formation of unidentified species, described by reaction 7 in Table 2.2, which is in turn the rate-limiting step for dichloramine decomposition. However, the exact chemical identity of this intermediate species is still unknown. It has been postulated as nitrite or nitrate\cite{74}, whereas Valentine et al.\cite{81} stated these two ions cannot be the intermediate species based on the spectrophotometric and DPD (N,N-diethyl-p-phenylenediamine) titration results.

Negligible dichloramine and trichloramine concentration will be achieved under typical drinking water conditions with low initial chloramine oxidant concentration (~1.5 mg Cl\textsubscript{2}/L).\cite{85} Under chloramination conditions (Cl/N<1), the overall rate of chloramine oxidant loss is primarily limited by the rate of formation of dichloramine that forms through reactions 1 to 5 in Table 2.2. Then rapid decay of dichloramine occurs through redox reactions (7 to 10) with the resulting formation of the unidentified intermediate species, which enhances the decomposition of chloramine oxidant.

The effects of water quality on the extent of decomposition of NH\textsubscript{2}Cl have also been studied.\cite{33,74,80} Specifically, NH\textsubscript{2}Cl decomposition follows a 2\textsuperscript{nd}-order kinetics in term of monochloramine concentrations. Its decay rate accelerates with the increase in initial monochloramine concentration, carbonates concentration, and temperature, while the decrease in pH value and Cl/N molar ratio could enhance the NH\textsubscript{2}Cl decomposition. The changes in ionic strength (0.1, 0.05, 0.005 M) did not significantly affect the decomposition rate. Moreover, the presence of nitrite\cite{80,86} and bromide\cite{80,87} in drinking water could also accelerate NH\textsubscript{2}Cl decomposition. Natural organic matter (NOM), commonly present in drinking water, could act as a reductant and enhance monochloramine decay.\cite{88,89} Furthermore, metal ions in aqueous solution, such as Fe (II) and Cu (II), have been reported as catalyst to promote the monochloramine decomposition,\cite{90-93} however a link between aqueous Pb\textsuperscript{2+} concentrations and monochloramine decomposition has not been reported.

2.5.2 Current studies on the interactions of PbO\textsubscript{2} and monochloramine

Although monochloramine is a weaker oxidant than free chlorine, theoretically it is able to oxidize metallic lead, Pb(0), or dissolved lead ion (Pb\textsuperscript{2+}) to form PbO\textsubscript{2} based on their standard reduction potential. However, PbO\textsubscript{2} did not form in experiments conducted of
oxidation of Pb(0) or dissolved lead by NH₂Cl under typical drinking water conditions. Edwards and Dudi⁴² have performed the oxidation reaction of dissolved lead in solution with free chlorine and monochloramine. White solid precipitation (lead carbonates) was observed in monochloramine solutions, whereas a reddish brown solid (lead oxides) formed in the presence of free chlorine at pH of 8.5. Similarly, Switzer et al.⁴⁴ reported that only a Pb(II) solid phase (e.g., hydrocerussite) formed on Pb(0) film oxidized by NH₂Cl at pH 8, in contrast, β-PbO₂ was observed in the experiment with free chlorine under the same conditions. They performed electrochemical measurements of standard reduction potential of NH₂Cl and free chlorine at pH of 8, and further confirm NH₂Cl has lower standard reduction potential than that of free chlorine. Rajasekharan et al.⁴⁵ reported that free chlorine is able to oxidize Pb to PbO₂ above pH 1.7, whereas NH₂Cl does so only at pH above 9.5 through measured their redox potential using electrochemical measurements.

A weaker oxidative ability of NH₂Cl compared to that of free chlorine was also reported by Lin and Valentine³³,⁸⁹ through the dissolution of PbO₂ in NH₂Cl solution. Elevated lead concentrations were observed in these experiments compared with the experiments without disinfectant, indicating the reduction of PbO₂ by NH₂Cl. Meanwhile, a linear correlation between dissolved lead concentrations and loss in NH₂Cl was observed in their studies. Thus they proposed that PbO₂ was reduced by the unidentified intermediate species formed during auto-decomposition of NH₂Cl. Interestingly, Xie et al.⁴⁵ observed lower lead concentrations in the presence of NH₂Cl than the one in the absence of disinfectant in a CSTR system. However, elevated lead concentrations were found once the continuous-flow system was sealed and stirred with and flow stopped (batch mode). These different observations were rationalized to the difference in reactor configurations and attributed to the lack of accumulation of the unidentified intermediate species in the flow reactor. Studies also evaluated the effect of water quality on PbO₂ reduction in the presence of NH₂Cl. In the presence of Br⁻, a linear correlation was also observed between the amount of NH₂Cl decomposed and the amount of total Pb(II) released, suggesting Br-catalyzed NH₂Cl decomposition may generate the same intermediate species active towards PbO₂ reduction.⁸⁷ Interestingly, the presence of NOM suppressed the PbO₂ reduction by NH₂Cl, but the mechanism for this inhibition process is still unknown.⁸⁹
2.6 Analytical methods for characterization of lead corrosion scales

2.6.1 X-ray powder diffraction

X-ray powder diffraction (XRD) is one of the most popular techniques used for characterizing the lead corrosion scales and solid lead samples collected from dissolution experiments. The crystalline solid phases reveal clear and sharp peaks in XRD patterns, whereas amorphous phases display ambiguous patterns with broad bands. Therefore, XRD has been widely used to differentiate between crystalline solid phases that illustrate distinctive diffraction patterns. As summarized in section 2.2.1, amorphous aluminosilicates are commonly present in the surface layer of lead corrosion scales, resulting in the difficulties to identify the solid phase. XRD is particularly sensitive to heavy elements in crystalline phases. Thus for lead corrosion scales, XRD results reveal mainly characteristic signals of crystalline lead compounds.\textsuperscript{12, 14, 30, 31} Even for the inner layers of corrosion scales that contain well crystallized species, it may be difficult to interpret the composition based on XRD results since diffraction peaks from different phases could overlap with each other.\textsuperscript{12, 31}

2.6.2 UV/Vis/NIR spectroscopy

UV/Vis/NIR spectroscopy has been widely used to characterize lead-bearing semiconductors, particularly in the field of glasses and conductive thin films. When the energy of optical photons in UV, visible (Vis), or near infrared (NIR) region matches the energy gap in the solid, these photons are adsorbed by the electrons in solids to overcome the energy barrier. This barrier is defined as the optical band gap ($E_g$) which is the energy difference (eV) between occupied states in their valence band and unoccupied states in the conduction band. The exact value can be calculated from the UV/Vis/NIR spectra. Thus, the energy of the light adsorbed provides information on the electronic structure of the solid.

In a previous study\textsuperscript{96} we applied this technique to characterize pure lead compounds. All lead compounds ($\text{PbCO}_3$, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, $\text{PbO}$, $\text{Pb}_3\text{O}_4$, and $\text{PbO}_2$) show adsorption in the UV/Vis range, only $\text{PbO}_2$ reveals the NIR adsorption. The origin of this NIR band is due
to the adsorption of free electrons\textsuperscript{49} that are present as a result of defects in nonstoichiometric PbO\textsubscript{2}\textsuperscript{58,97}. As discussed in section 2.4.2, the nature of defects in PbO\textsubscript{2} is still under debate. Following the methods proposed by Keester and White\textsuperscript{98}, our previous study observed a linear relationship between the solid optical band bag (E\textsubscript{g}) and their corresponding Pb oxidation state, for the case of lead oxides, and then established an empirical equation to calculate the number of Pb\textsuperscript{+2} defects, in the PbO\textsubscript{2} solid based on the calculated band gap. The shifts on optical band gap can also provide insights regarding changes in the crystalline and electronic structure of solids. It is well established that the average domain/crystallite sizes of a semiconductor could be determined by analysis of the optical bandgap energy.\textsuperscript{99-102} Brus\textsuperscript{101,102} has performed comprehensive theoretical and experimental studies on size-dependent development of bulk electronic properties in semiconductor systems (e.g., CdS, GaAs, InSb), and reported that the small crystallite (~15 to 50 Å) has different electronic properties from that of bulk materials. These crystallites can be termed “clusters” as they are too small to have the same bulklike electronic wave functions, although they exhibit similar bulklike crystal structure. Specifically, the optical spectra of these clusters reveal a blue-shift (shorter wavelength). The smaller the clusters, a more pronounced blue-shift is observed.\textsuperscript{102,103}

2.7 Summary

Lead corrosion scales have a complex composition that is highly site-specific. Although several studies have been conducted to characterize the lead corrosion scales, only a few studies focus on the link between site-specific conditions (e.g., water quality) and composition of corrosion scales. Thus, improved knowledge of the mechanism of occurrence, dissolution, and solid phase transformations of lead corrosion scales under different drinking water conditions is required to develop a generalized knowledge toolbox that can be applied to deploy a corrosion control strategy aiming at addressing elevated lead levels. It is known that β-PbO\textsubscript{2} is one of the common phases present in the surface layer of lead corrosion scales that formed in chlorinated water. Its stability under drinking water conditions affects lead concentrations in water. Monochloramine has been used as the substitute of free chlorine for disinfection in DWDS and triggered elevated lead release. However, the mechanistic details for the reaction between PbO\textsubscript{2} and NH\textsubscript{2}Cl are still
unknown. We attempt to fill these knowledge gaps by performing comprehensively characterization of lead corrosion scales with analysis of historical water quality, and dissolution experiments using chlorinated or freshly synthesized PbO$_2$ to simulate the PbO$_2$ formed in field conditions in the presence of monochloramine.
References


Chapter 3

3 Influence of drinking water quality on the formation of corrosion scales on lead-bearing drinking water distribution systems

3.1 Introduction

Elevated lead concentrations have been reported in drinking water services in Canada, the United States, and some cities in Europe.\textsuperscript{1} Lead presence in drinking water is caused by the destabilization of lead corrosion scales formed at the inner surface of lead pipes used as service lines in drinking water distribution systems (DWDS). The composition and stability of these phases are highly site-specific and strongly linked to local water quality. Therefore, if an attempt is made at corrosion control, a critical first step is to understand the interactions between regional water quality and corrosion scale composition. Previous studies\textsuperscript{1-8} have reported characterization of lead corrosion scales from several DWDS in Canada, the U.S., and the U.K. These studies have reported that the corrosion scales, in general, consist of lead(II) carbonates (hydrocerussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$] and cerussite [PbCO$_3$]) and lead oxides (plattnerite [$\beta$-PbO$_2$], scrutinyite [$\alpha$-PbO$_2$], minium [Pb$_3$O$_4$] and litharge [PbO]) if there is no phosphate corrosion inhibitor used in the water.

In addition to lead-bearing phases, other inorganic ions normally present in drinking water also play a role in the formation of corrosion scales. Lead, aluminum, iron, and manganese are the most common elements accumulated on the surface layer of corrosion scales.\textsuperscript{4, 9, 10} To study non-lead elements accumulated in the lead bearing surface scale, most studies\textsuperscript{4, 6, 10, 11} rely on results obtained through elemental analysis after corrosion scale acid digestion, and scanning electron microscopy coupled with energy dispersive X-ray analysis. While this is an excellent first step for a bulk and surface identification and quantification of the elemental composition of the scale, it does not provide information on the chemical environment of each element (oxide, carbonate, etc.) nor their speciation in the solid phase. X-ray diffraction (XRD) could indicate the solid phase speciation, but it is particularly sensitive to heavy elements forming crystalline structures. Thus, for lead corrosion scales that mainly consist of lead compounds, XRD results reveal characteristic signals of
crystalline lead compounds\textsuperscript{2,4,12,13}, but does not provide information on amorphous phases. These limitations make it difficult to fully understand the characteristics of the surface layer of lead-bearing corrosion scales. Techniques such as optical absorption spectroscopy: Ultraviolet/Visible (UV/Vis), is prevalent for characterization and the speciation of solid lead-bearing compounds.\textsuperscript{14} Features in the UV/Vis spectrum are result of valence electronic transitions. Hence UV/Vis spectroscopy has been widely used to study the electronic structure of these solids\textsuperscript{15,16} and their chemical environment\textsuperscript{14}. However, to the best of our knowledge, there is no study of characterization of lead corrosion scales using UV/Vis spectroscopy. Moreover, there are limited studies focused on understanding the role of non-lead compounds in the chemical behavior of lead-bearing corrosion scales. A comprehensive study on the link between site-specific conditions (e.g., water quality) and composition of corrosion scales is yet to be carried. The objective of this study is to explore this possibility through the bulk and surface characterization of lead corrosion scales gathered from four different Canadian Municipalities and to frame to obtained results in terms of drinking water quality.

3.2 Experimental section

3.2.1 Materials and sampling protocol

Lead corrosion scales were collected from lead service pipes exhumated from four Canadian drinking water distributions systems: City of London, ON (one sample used as reference, labeled P3), and other three municipalities: Municipality B (five samples), Municipality C (two samples), and Municipality D (two samples); series B, C and D respectively (Table A.1 in Appendix A). Surface water from the Great Lakes is the drinking water source for the City of London (Lake Huron and Lake Erie) and Municipality B (Lake Ontario), while river water is the source for Municipality C (Ottawa River) and Municipality D (Lawrence River). A depth profile protocol for lead scale harvesting was used, following previously reported sampling protocols.\textsuperscript{4,9} In this protocol, all corrosion layers in direct contact with water are labeled as L1 (outermost layer). The layer underneath L1 is labeled L2. For the samples collected from Municipality D this L2 layer was in direct contact with the metallic lead pipe. For the samples collected from Municipalities B and C a third layer beneath L2 was observed, in this case L3 in direct contact with the metallic
lead pipe. For the sample collected from the City of London a fourth layer was collected (beneath L3). This layer (L4) is in direct contact with the metallic lead pipe.

The details of the characterization for London’s samples have been reported elsewhere. In this study, scale sample P3 from London is used as reference in terms of dominant phases present to test the feasibility of UV/Vis spectroscopy for characterization. Preliminary results for physicochemical characterization of the corrosion scales collected from Municipality B have been reported elsewhere. The corrosion scales obtained from four of these five pipes consisted of two distinctive layers, while the fifth pipe (B5) contained three different corrosion layers. The detailed physical properties of B5 are described in the supporting information. Corrosion scales from Municipalities C and D were collected from two lead pipes (C1 and C2, ~1.2m in length) of Municipality C and two (D1 and D2, ~0.9m in length) from Municipality D, respectively.

3.2.2 Analytical methodology

Lead corrosion scales were analyzed via UV/Vis spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, and XRD. UV/Vis spectra were obtained in the range of 200 to 800 nm in diffuse reflectance mode with 1 nm step size using a UV-3600 Shimadzu instrument equipped with a diffuse reflectance cell (Harrick, Praying Mantis). Infrared spectra were acquired in diffuse reflectance mode at a 4 cm$^{-1}$ resolution and 64 scans per sample using a Harrick Praying Mantis. The UV/Vis and FTIR spectra were transformed to pseudo-absorption spectra using Kubelka-Munk function in the UVProbe® and OPUS® software, respectively. The XRD data were obtained on a Rigaku RPT 300 RC diffractometer using Co K-α ($\lambda=1.78890$ Å) radiation over the range of 10-70° 2θ with a 0.02° step size. Selected pure lead compounds (Sigma-Aldrich, A.C.S reagent grade), plattnerite (β-PbO$_2$), massicot (β-PbO), minium (Pb$_3$O$_4$), hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$), and cerussite (PbCO$_3$), were used as references for solid phase characterization. For elemental analysis, 0.25-0.5 g solid samples were digested using U.S. EPA Method 3051A. The acid digested samples were analyzed using an ICP-OES (Varian, Inc., Vista-Pro Axial). Inorganic carbon (IC) content was measured using a TOC-VCPN analyzer equipped with SSM-5000A (Shimadzu) for solid sample acidification.
Table 3.1 Drinking water quality data for the City of London, Municipality B, Municipality C, and Municipality D

<table>
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</tr>
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<td>pH</td>
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<td>7.55 ± 0.36</td>
<td>7.65 ± 0.12</td>
<td>9.31 ± 0.06</td>
<td>7.59 ± 0.12</td>
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<td>Alkalinity</td>
<td>mg/L</td>
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<td>85.57 ± 1.84</td>
<td>32.97 ± 2.59</td>
<td>85.14 ± 1.86</td>
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<td>Hardness</td>
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<td>102.84 ± 49.41</td>
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<td>116.71 ± 1.50</td>
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<td>TOC</td>
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<td>--</td>
<td>2.23 ± 0.078</td>
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<td>DOC</td>
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<td>2.92 ± 0.13</td>
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<tr>
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<td>0.54 ± 0.05</td>
<td>0.72 ± 0.03</td>
<td>0.12 ± 0.016</td>
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<tr>
<td>Total Chlorine</td>
<td>mg/L</td>
<td>0.94 ± 0.02</td>
<td>1.06 ± 0.02</td>
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<td>Free chlorine</td>
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<td>Calcium</td>
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<td>0.15 ± 0.08</td>
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<td>0.30 ± 0.03</td>
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<td>&lt;DL</td>
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<td>&lt;DL</td>
<td>&lt;0.003</td>
<td>0.0004 ± 0.00028</td>
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<td>2.89 ± 0.82 (silicate)</td>
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<td>--</td>
<td>--</td>
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Note: <DL: the result is below detection limit
--: the value is unavailable
3.2.3 Historical drinking water quality data

Drinking water quality data, water source quality data, and drinking water treatment parameters were collected from official records available to the public. Historical drinking water quality data were provided by the municipalities. Table 3.1 shows the major drinking water quality parameters of the four municipalities in our study. Drinking water treatment process for each municipality is shown in Table A.2. At the time of lead pipe exhumation none of these four municipalities used phosphate as corrosion inhibitor.

3.3 Results and discussion

3.3.1 Physical properties of lead bearing corrosion scales

The detailed physical characteristics of all scale samples are summarized in the Appendix A. Among scale samples, D1 contained the thinnest corrosion scale. All outermost layer (L1) samples contained a layer of rusty brown and porous scales forming a smooth surface layer, except Municipality D’s which showed a sandy texture. For all inner layer (L2) samples (P3-L2, B5-L2, C1-L2, D1-L2), a thick pale brownish orange scale layer was observed, covering the entire inner pipe surface. In terms of the innermost layer (L3), B5-L3 and C1-L3 had a very thin white layer scale strongly attached to the metallic pipe surface. In contrast, a thin dark brown layer was observed for P3-L3, and white patches were found in D1-L3.

3.3.2 X-Ray diffraction characterization

In previous work Kim and Herrera reported the results obtained using XRD on the P3 sample. In brief: the outermost layer, L1, displayed a very noisy XRD pattern in which hydrocerussite was the only identifiable crystalline phase. The presence of PbO$_2$ was proposed in light of Raman results, but could not be confirmed by XRD. Similarly, the XRD patterns obtained for the outermost layer of the samples for Municipalities B and C (B5-L1, result not shown, and C1-L1 in Figure 3.1a) were poorly resolved, though characteristic peaks for hydrocerussite can be discerned. This indicates the presence of amorphous phases together with crystalline hydrocerussite on these samples. Hydrocerussite was identified as the main lead carbonate phase in both the inner layer of
the samples collected from Municipalities B and C (B5-L2 and C1-L2) and their corresponding innermost layer (B5-L3 and C1-L3). A minor contribution from PbO can be also observed. In comparison with the XRD results obtained for surface layer samples P3-L1, B5-L1, and C1-L1, the result obtained for sample D1-L1 (Figure 3.1b), collected from Municipality D, revealed a distinct XRD pattern that suggests hydrocerussite is the main lead carbonate phase, with minor contributions from cerussite and PbO$_2$. Furthermore, this result indicates that the outermost layer sample obtained from Municipality D (D1-L1) contained the least amorphous phases amongst all tested outermost layer samples. For the case of the D1-L2 sample, the XRD indicates hydrocerussite as dominant lead carbonate phase, with some cerussite contribution.
As described above lead bearing compounds are the only phases identified via XRD analysis although non-lead phases are present as well (section 3.3.4). Another limitation of the XRD analysis is the overlap of the characteristic diffraction lines of different phases. Furthermore, unambiguous phase identification is not possible since XRD is unable to resolve amorphous phases. To address these issues complementary techniques were used.

3.3.3 Fourier Transform Infrared spectroscopy characterization

Infrared spectroscopy is able to identify characteristic vibrational transitions in a specific chemical bond of either amorphous or crystalline phases. In this contribution, the scale samples from four municipalities were characterized using FTIR spectroscopy (Figure 3.2). The detailed IR results and chemical bond assignments can be found in Appendix A. Figure A.1 in Appendix A shows the IR spectra of pure lead compounds used as references. The carbonate vibrational band centered around 1450 cm\(^{-1}\) and the Si-O-Si/Al vibrational bands around 1070 and 950 cm\(^{-1}\) are observed for all outermost layer (L1) samples obtained from the four municipalities (Figure A.2a). A band centered in the range from 1585 to 1600 cm\(^{-1}\)
is also observed. This band is attributed to the bicarbonate vibration but in different coordination environments. These suggest that in all cases, the outermost layer sample, in contact with drinking water is rich in hydrated compounds, aluminosilicates and some carbonates. Compared to that observed in the outermost layer samples (L1 series), the intensity of the water band (3450 and 1640 cm\(^{-1}\)) decreases for the case of the inner layers (L2 and L3 series) (Figure 3.2). At the same time, the carbonates bands become more intense compared with those of the outermost layer. It should be noted that all scale samples of outermost layer analyzed in this study (Figure A.2a) displayed infrared absorption bands in the range of 650-500 cm\(^{-1}\), which is the characteristic vibrational region for metal oxides.\(^1\) The low frequency bands are progressively attenuated for the case of the inner layers, to the point to be indiscernible in the spectra of the innermost layers. The complexity of the spectrum in this region makes the identification of specific metal oxide phases extremely complex. However, based on the results obtained by chemical analysis, we could hypothesize that these correspond to lead or iron oxides as they are the most abundant elements accumulated in the scales (section 3.3.4).
Figure 3.2 FTIR spectra obtained on corrosion scale samples collected from the City of a) London, from b) Municipality B, from c) Municipality C, and from d) Municipality D.

The IR results not only indicate similarities between four scale samples for the equivalent layer, but also illustrate some differences (Figure A.2). For instance, the relative intensity of Si-O-Si/Al vibrational bands (1071/950 cm\(^{-1}\)) was weaker in the inner layer of Municipality B (B5-L2) than the band intensity observed in P3-L2 (City of London, Figure A.2b). Meanwhile, the carbonates characteristic peaks (1045 and 680 cm\(^{-1}\)) in B5-L2 are more intense than those observed on the P3-L2 sample. These results suggest that B5-L2 contains more carbonates but less aluminosilicates than the equivalent layer from the sample of the City of London (P3-L2).

Comparison of the IR spectra (Figure A.2) obtained for each layer of pipe sample C1 with equivalent layer of other three samples (P3, B5, and D1) indicate that C1-L1 and P3-L1 as well as B5-L1 closely resemble each other, with one exception: C1-L1 displays a stronger absorption band at 1640 cm\(^{-1}\) (water band) as well as in the range of 750-550 cm\(^{-1}\) with a characteristic peak around 730 cm\(^{-1}\). The assignment of this band will be discussed later in the context of municipal drinking water quality. This characteristic peak was much pronounced in the spectra obtained for the intermediate layer (C1-L2), for this case a shoulder at 703 cm\(^{-1}\) was also observed. In contrast, B5-L2, P3-L2, and D1-L2 only showed a shoulder at 1640 cm\(^{-1}\) associated with water. This suggests that the scale sample C1
contains a larger amount of hydrated compounds compared with those samples of London (P3), Municipalities B (B5) and D (D1). For the case of the innermost layer, the FTIR spectrum of C1-L3 is similar as the spectrum of B5-L3, suggesting the presence of hydrocerussite and cerussite in both cases.

As described previously, the scales of Municipality D have distinctive physical properties. D1 also displayed unique IR spectra (Figure 3.2d) compared with those obtained for the other three municipalities (Figure A.2). Specifically, the sample for the outermost layer (D1-L1) revealed an \(-\text{OH}\) stretching peak at 3538 cm\(^{-1}\) and a Pb-OH vibrational band around 780 cm\(^{-1}\) together with the characteristic peaks of carbonates for hydrocerussite at 1737, 1045, and 692 cm\(^{-1}\). In contrast, the equivalent outermost layer of scales collected from the other municipalities in this study did not show characteristic peaks for hydrocerussite. At the same time, for the D1-L1 sample, intense absorption bands were observed in the metal oxide region (650-400 cm\(^{-1}\)). Specifically, a sharp peak at 480 cm\(^{-1}\) attributed to a Pb-O vibration.

To summarize, it can be proposed that hydrated compounds including aluminosilicates are abundant in the outermost layer scales (L1) gathered from London, Municipality B, and Municipality C, together with some metal oxides and carbonates. Carbonates are dominant phases in D-L1 with some metal oxides and hydrated compounds as well as aluminosilicate. Amongst all scales collected from these four municipalities, Municipality C displays the largest portion of hydrated compounds. For all the scale samples, a decrease in the contribution of hydrated compounds is observed from surface layer to the innermost layer together with increasing amount of carbonates.

### 3.3.4 UV/Vis spectroscopy characterization

While a suite of characterization techniques, e.g., XRD, FTIR, and Raman, have been previously used, to the best of our knowledge, UV/Vis spectroscopy has not been applied to the characterization of corrosion scales. The UV/Vis spectrum of each pure lead compound displays a characteristic band position (Figure A.5). To validate our approach, we first analyzed the sample P3 harvested from the City of London. Figure 3.3a shows the spectra of the layers harvested from sample P3. The spectra show strong absorption bands,
centered at 235 nm and 242-246 nm, characteristic of cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)₂) respectively (Figure A.5a), indicating the presence of lead carbonates in all these four layers. However, L1 and L2 layers exhibited a broad band in the 280 to 350 nm range, characteristic of lead oxides (PbO, Pb₃O₄ and PbO₂, Figure A.5b). For each layer, the intensity of the oxides band compared with that of carbonates band changes, L1 having the highest ratio, followed by L2 and L4, and L3 (Figure 3.4a, circles). This analysis suggests that the layer in contact with water consists mostly of lead oxides while the innermost layer is rich in lead carbonates. Consistently, the inorganic carbon (IC) content of scale samples P3 (Figure 3.4b) shows an increase in concentration from L1 to L3 with a slightly decrease for L4.
Figure 3.3 UV/Vis spectra obtained on corrosion scale samples collected from a) the City of London, from b) Municipality B, from c) Municipality C, and from d) Municipality D.
Additional chemical elements are known to accumulate in the scales, particularly aluminum, iron, and manganese. Our elemental analysis results (Table 3.2) is consistent with this behavior. The accumulated aluminum is likely to be in the form of poorly crystalline aluminosilicate, known as allophane. The UV/Vis spectrum of synthesized allophane (Si/Al molar ratio=0.67) showed a weak absorption band (220-300 nm) centered at 270 nm (Figure A.6). By comparison with the characteristic band region of lead carbonates, there is a slightly overlapping region thus the interpretation of the carbonates band needs to take into consideration the possible contribution of allophane. Iron oxides and hydroxides as well as manganese oxides absorb in both the UV and visible regions (250 to 500 nm). Although the absorption regions of these oxides/hydroxides slightly overlap with those of lead carbonate (250 to 300 nm), a simultaneous strong absorption region (400-600 nm) indicates their presence in oxide form. These compounds, particularly manganese oxides, represent a very small portion (0.02-5.4 wt%) in the chemical composition of the corrosion layers while lead is the most abundant element present (Table 3.2). It is, therefore, reasonable to assume the absorption bands centered at 235 nm and
242-246 nm as prominent lead carbonates band, while the broad band in the range from 280 to 400 nm indicates the presence of, most likely, lead oxides. Thus, the UV/Vis spectroscopy data provides a semi-quantitative depiction of the ratio of oxides to carbonates present in the solids.
Table 3.2 Elemental chemical analysis results for the composition of corrosion scales (weight percentage)\(^1\)

<table>
<thead>
<tr>
<th>London-P3</th>
<th>Al</th>
<th>Fe</th>
<th>Pb</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Cu</th>
<th>Zn</th>
<th>V</th>
<th>B</th>
<th>Ba</th>
<th>Ni</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>IC</th>
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<tbody>
<tr>
<td></td>
<td>2.67</td>
<td>2.46</td>
<td>11.44</td>
<td>0.72</td>
<td>0.31</td>
<td>0.03</td>
<td>0.023</td>
<td>0.007</td>
<td>0.086</td>
<td>N/A</td>
<td>0.003</td>
<td>0.002</td>
<td>0.018</td>
<td>0.0003</td>
<td>0.006</td>
<td>2.10(^3)</td>
</tr>
<tr>
<td>B1-L1</td>
<td>13.38</td>
<td>17.82</td>
<td>2.30</td>
<td>0.04</td>
<td>0.83</td>
<td>0.05</td>
<td>0.023</td>
<td>0.019</td>
<td>0.085</td>
<td>0.069</td>
<td>0.005</td>
<td>0.001</td>
<td>0.081</td>
<td>0.0008</td>
<td>0.022</td>
<td>0.92</td>
</tr>
<tr>
<td>B2-L1</td>
<td>19.59</td>
<td>6.67</td>
<td>4.75</td>
<td>0.03</td>
<td>1.15</td>
<td>0.05</td>
<td>0.017</td>
<td>0.020</td>
<td>0.034</td>
<td>0.070</td>
<td>0.005</td>
<td>0.001</td>
<td>0.083</td>
<td>0.0005</td>
<td>0.006</td>
<td>1.38</td>
</tr>
<tr>
<td>C1-L1</td>
<td>1.42</td>
<td>13.86</td>
<td>42.32</td>
<td>2.18</td>
<td>0.99</td>
<td>0.22</td>
<td>0.030</td>
<td>0.083</td>
<td>0.091</td>
<td>0.217</td>
<td>0.013</td>
<td>0.007</td>
<td>0.060</td>
<td>0.0011</td>
<td>0.011</td>
<td>0.73</td>
</tr>
<tr>
<td>C1-L2</td>
<td>1.56</td>
<td>10.23</td>
<td>37.05</td>
<td>3.53</td>
<td>0.87</td>
<td>0.17</td>
<td>0.032</td>
<td>0.088</td>
<td>0.116</td>
<td>0.103</td>
<td>0.014</td>
<td>0.006</td>
<td>0.036</td>
<td>0.0010</td>
<td>0.011</td>
<td>1.06</td>
</tr>
<tr>
<td>C2-L1</td>
<td>1.39</td>
<td>13.41</td>
<td>25.04</td>
<td>2.88</td>
<td>0.96</td>
<td>0.22</td>
<td>0.039</td>
<td>0.073</td>
<td>0.094</td>
<td>0.099</td>
<td>0.013</td>
<td>0.006</td>
<td>0.024</td>
<td>0.0013</td>
<td>0.009</td>
<td>0.79</td>
</tr>
<tr>
<td>C2-L2</td>
<td>1.41</td>
<td>7.24</td>
<td>16.97</td>
<td>5.44</td>
<td>0.69</td>
<td>0.13</td>
<td>0.030</td>
<td>0.061</td>
<td>0.132</td>
<td>0.090</td>
<td>0.013</td>
<td>0.005</td>
<td>0.024</td>
<td>0.0008</td>
<td>0.009</td>
<td>1.20</td>
</tr>
<tr>
<td>D1-L1</td>
<td>0.18</td>
<td>8.94</td>
<td>9.37</td>
<td>0.37</td>
<td>1.53</td>
<td>0.09</td>
<td>0.100</td>
<td>0.014</td>
<td>0.168</td>
<td>0.070</td>
<td>0.004</td>
<td>0.001</td>
<td>0.070</td>
<td>0.0005</td>
<td>0.006</td>
<td>2.36</td>
</tr>
<tr>
<td>D1-L2</td>
<td>0.06</td>
<td>1.96</td>
<td>9.27</td>
<td>0.10</td>
<td>0.63</td>
<td>0.03</td>
<td>0.024</td>
<td>0.020</td>
<td>0.061</td>
<td>0.066</td>
<td>0.003</td>
<td>0.001</td>
<td>0.020</td>
<td>0.0001</td>
<td>0.004</td>
<td>2.78</td>
</tr>
</tbody>
</table>

Note: \(^1\): As per EPA analysis protocol Method 3051A
\(^2\): IC denotes total inorganic carbon content.
\(^3\): This reflects the average value of results obtained for four layers (P3-L1, P3-L2, P3-L3, and P3-L4).
The results of UV/Vis spectroscopy characterization for Municipality B are shown in Figure 3.3b. At first glance, the UV/Vis spectra of B5 scales resembled those obtained on the samples from the City of London (Figure 3.3a). This is consistent with the similarity observed on FTIR results of P3 and B5 for each equivalent layer (Section 3.3.3). Specifically, the intense UV absorption band near 300 nm (ascribed to lead oxides) was observed in the outermost layer sample (L1, Figure 3.3b), while the same band showed much lower intensity for L2 and L3 samples. Comparing the oxides and carbonates band intensity obtained for the B5 samples (B5-L1, B5-L2, and B5-L3) with those of the P3 scale samples from London (P3-L1, P3-L2, and P3-L3) (Figure 3.4a), similar values and trends are observed: the spectra for the inner layers (B5-L2 and B5-L3) have a larger contribution of lead carbonates than the outermost layer (B5-L1) do, whereas the distribution of oxides phases shows a reverse trend. The same trend was also observed for the other four scale samples (B1-B4, Figures A.7 and A.8).

Figure 3.3c depicts the UV/Vis spectra of two scale samples collected from Municipality C. These two scales displayed comparable spectra for each layer. For C1 and C2 samples, a decrease in the oxides/carbonates band ratio is also observed from the surface layer to the innermost layer with an associated increase in IC content (Figure 3.4 and Table 3.2). Compared with the spectra of B5, C1-L2 and C2-L2 samples might contain more oxides than B5-L2 as these two samples reveal high oxides/carbonates band ratio (Figure 3.4a). This is consistent with the FTIR results obtained on the same samples, where C1-L2 contained a larger amount of hydrated compounds than B5-L2.

The scales in Municipality D had unique physical properties as described previously. The UV analysis indicate that D1-L1 has a stronger carbonates contribution than oxides (Figure 3.3d), suggesting that a larger amount of carbonates is present in its outermost layer. This contrasts with the observations from the UV/Vis analysis of the L1 samples collected from the other three municipalities (P3-L1, B-L1, and C-L1), in which oxides bands were dominant. This is, however, consistent with the FTIR and IC results suggesting that the largest amount of carbonates was found in the surface layer of sample D1, amongst all the outermost layer scale samples analyzed in this work.
In summary, the UV/Vis results for the scales of London, Municipality B, and Municipality C indicate that in these three cases their outermost layer samples contain more oxides than carbonates, whereas L1 layer for Municipality D contains more carbonates than oxides. While all the surface samples revealed the presence of oxides in the surface layer, this information could only be obtained using UV/Vis spectroscopy since neither XRD nor FTIR allows for the unambiguous identification of all these phases. With the depth profile (from L1 to L3) for the same scale sample, an increase in the amount of lead carbonates is observed. This trend is observed for all scale samples as shown in Figure 3.4.

Table 3.3 summarizes the characterization results gathered using all three techniques in this work (XRD, FTIR and UV/Vis spectroscopy). It can be observed that, in general, the outermost layer samples display distinctive patterns of spectra between different municipalities, suggesting site-specific characteristics. In contrast, their innermost layers share more similarities, with lead carbonates as the dominant phases in all cases. This is not unexpected as the innermost layer is most likely the result of corrosion of elemental lead, Pb, oxidized by dissolved oxygen (DO) and/or by disinfectant to form Pb(II) ions. Under typical drinking water conditions, lead carbonates will form firstly when the concentrations of lead and carbonate ions reach saturation, since this process is thermodynamically and not kinetically regulated. Depending on specific water quality, further lead pipe corrosion, solid phase precipitation, corrosion scale dissolution, and transformation could occur leading to different scenarios for the formation of the subsequent corrosion layers. Therefore, to understand the similarities and differences observed in corrosion scale composition between the four regions, particularly for the case of the outermost layer of scale, the water quality data was analyzed.

Table 3.3 Summary of characterization results of lead corrosion scales collected from three municipalities

<table>
<thead>
<tr>
<th></th>
<th>XRD</th>
<th>UV/Vis spectroscopy</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>hydrocerussite</td>
<td>metal oxides</td>
<td>hydrated compounds,</td>
</tr>
<tr>
<td></td>
<td>(very noisy)</td>
<td></td>
<td>aluminosilicates, carbonates, metal oxides</td>
</tr>
<tr>
<td>B5</td>
<td></td>
<td>lead carbonates</td>
<td>hydrated compounds,</td>
</tr>
<tr>
<td>L2</td>
<td>hydrocerussite</td>
<td>lead carbonates</td>
<td>aluminosilicates, carbonates, metal oxides</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table

<table>
<thead>
<tr>
<th></th>
<th>XRD</th>
<th>UV/Vis spectroscopy</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3</td>
<td>hydrocerussite PbO</td>
<td>lead carbonates</td>
<td>hydrocerussite, cerussite</td>
</tr>
<tr>
<td>L1</td>
<td>hydrocerussite (very noisy)</td>
<td>metal oxides, lead carbonates</td>
<td>hydrated compounds, aluminosilicates, carbonates, metal oxides, fluorine bearing solids</td>
</tr>
<tr>
<td>C1</td>
<td>Hydrocerussite</td>
<td>metal oxides, lead carbonates</td>
<td>hydrated compounds, aluminosilicates, carbonates, metal oxides, fluorine bearing solids</td>
</tr>
<tr>
<td>L2</td>
<td>Hydrocerussite PbO</td>
<td>lead carbonates</td>
<td>hydrocerussite, cerussite</td>
</tr>
<tr>
<td>L3</td>
<td>Hydrocerussite PbO</td>
<td>lead carbonates</td>
<td>hydrocerussite, cerussite</td>
</tr>
</tbody>
</table>

### 3.4 The influence of water quality on the composition of corrosion scales

Based on the UV/Vis and FTIR characterization results (Sections 3.3.3 and 3.3.4), the outermost layer of scale samples obtained from the City of London and Municipality B contain similar main phases, i.e. hydrated aluminosilicate, lead carbonates, and lead oxides. Their water quality (the City of London and Municipality B) are also quite comparable (Table 3.1). Additionally, both municipalities use surface water from Great Lakes and similar water treatment processes, except for their secondary disinfection stage (Table A.2). The similarity in their drinking water quality is reflected in the composition of the lead corrosion scale as described above. For both the City of London and Municipality B, relatively high concentrations of aluminum (~0.03-0.07 mg/L) are observed in their drinking water due to the historical usage of alum coagulant in the treatment process. This fact is reflected in the chemical phases, aluminosilicates, identified in both London and Municipality B’s corrosion scales. Moreover, the chemical analysis (Table 3.2) results show relatively high levels of aluminum accumulated in their corrosion scales. Not only hydrated aluminosilicate was observed in London’s and Municipality B’s L1 scale samples, lead carbonates were also present in these samples. It is well known that in the absence of strong oxidant, lead carbonates are thermodynamically stable under neutral pH or slight alkaline water with moderate alkalinity. Thus, the City of London’s and Municipality B’s water with slight alkaline and medium alkalinity poses preferable conditions for the formation of lead carbonates.
conditions for formation of lead carbonates. Although free chlorine, a strong oxidant, was used as disinfectant in the DWDS of London, previous studies\textsuperscript{22, 23} reported that dissolved lead ion would be oxidized by free chlorine to form hydrocerussite or cerussite firstly, then transferred to PbO\textsubscript{2}. Indeed, both lead carbonates and PbO\textsubscript{2} were positively identified in the surface scale of London. Thus, the mechanism of PbO\textsubscript{2} formation from dissolved lead previously proposed is consistent with the observation of coexistence of lead carbonates and PbO\textsubscript{2} in the surface layer of scale. In contrast, chloramines, used as secondary disinfectant by Municipality B, are weak oxidants. Under these water quality conditions lead carbonates are stable, but PbO\textsubscript{2} cannot form.\textsuperscript{24, 25} Thus, lead carbonates are most likely lead-baring phases formed in the surface layer of scales of Municipality B, as the characterization results indicate.

In contrast to the results discussed above for the City of London and Municipality B, the drinking water of Municipality C is soft (\textasciitilde 35 mg/L as CaCO\textsubscript{3}) with a relatively high pH (\textasciitilde 9.3) and the lowest amount of dissolved carbonates (alkalinity\textasciitilde 35 mg/L as CaCO\textsubscript{3}) among the four drinking water systems. The original drinking water quality of Municipality C used to be of low alkalinity (\textasciitilde 25 mg/L as CaCO\textsubscript{3}) with pH values close to neutrality, however to control iron corrosion a slight increase in pH and alkalinity took place. Lead carbonates were identified in C1-L1 via all three techniques used in this study. This indicates that lead carbonates are stable in soft alkaline water. For Municipality C, the relative high concentrations of aluminum (\textasciitilde 0.05 mg/L) and silicate (\textasciitilde 2.4 mg/L) could offer favorable conditions for the formation of Si-rich aluminosilicate. Indeed, the observations obtained by FTIR spectroscopy for samples C1-L1 and C1-L2 revealed a characteristic band centered at 1050 cm\textsuperscript{-1} that corresponds to either Si-rich allophane (Al:Si\textasciitilde 1.0) or silica. The presence of this silica phase might explain the fact that only the spectrum of C1-L2 displays intense water band around 1640 cm\textsuperscript{-1} with the Si-O-Si vibration band around 1070 cm\textsuperscript{-1} in Figure A.2b compared with the spectra obtained for the same layer samples in the other municipalities. The IR spectrum of C1-L1 also displays a strong absorption band in the range of 750-550 cm\textsuperscript{-1} with a characteristic peak around 730 cm\textsuperscript{-1}. This peak is not linked to metal-oxygen vibrations.\textsuperscript{18, 26} But it could be attributed to fluorine bearing solids, e.g. F\textsuperscript{−}, AlF\textsubscript{6}\textsuperscript{3−}, or SiF\textsubscript{6}\textsuperscript{2−} species. Consistently, compared with the other three municipalities, Municipality C has the highest fluoride concentration in its water.
Compared to the other drinking water systems in this study, Municipality C’s water has a relatively high concentration of iron, manganese, and nickel. These metal elements are expected to be present in the surface layer of scales as their compounds have high affinity to each other as well as to aluminosilicates and lead compounds. Consistently the results of elemental analysis for C1-L1 and C2-L1 (Table 3.2) show higher aluminum, iron, manganese, and nickel accumulated on their outermost layers, compared with the L1 samples collected from the other municipalities. Due to the presence of chloramines disinfectant in soft water, it is hypothesized that these metal elements could be in their oxides configurations. This might also explain the UV/Vis results of C1-L1 and C2-L1 that display the highest oxides to carbonate ratios amongst all surface samples collected from four municipalities.

A comparison of the water quality of Municipality D with that of Municipality B and the City of London (Table 3.1) indicates that their treated water has similar pH (~7.6), moderate alkalinity and hardness conditions. Under these conditions lead carbonates are thermodynamically stable, suggesting that lead carbonates are likely to form in D1-L1. Indeed, lead carbonates were observed in D1-L1 although free chlorine was used as disinfectant in Municipality D’s DWDS as for the case of the City of London. PbO\textsubscript{2} was observed in the surface layer of D1 sample due to the presence of free chlorine. Among all municipalities in this study, Municipality D presents the least amount of dissolved aluminum in its water, consistently a chemical analysis of D1-L1 indicates the lowest aluminum concentrations accumulated in its solids. This observation also explains why the XRD pattern obtained for D1-L1 (Figure 3.1b) lacks the characteristic noise associated with the presence of amorphous phase such as aluminosilicates. Relatively high concentrations of copper were reported for the water quality of Municipality D (compared to the other systems in this study). Consistently, the elemental analysis of D1-L1 revealed that this surface layer accumulated the highest amount of copper. The presence of copper-bearing solids could explain the FTIR absorption band obtained for the D1-L1 samples (peak around 610 cm\textsuperscript{-1}, characteristic for Cu-O bonds).\textsuperscript{27}

The results discussed above clearly indicate that the composition of corrosion scales is strongly correlated to drinking water quality, particularly for the surface layer (L1). To
verify the general trend between the water quality and speciation of scales, the results for the analysis of the surface layer samples (L1-series) together with water quality were incorporated in a correlation analysis. For each municipality, the chemical analysis results (Table 3.2) were averaged for the same element. Then a Pearson correlation (ρ) was calculated between averaged water quality data of each municipality (Table 3.1) and its averaged elemental analysis results; reported in Table A.3. As the concentrations of vanadium, chromium, and cadmium in some water are lower than the method’s detection limit, they were not incorporated in this correlation analysis. Based on the correlation results, Al (ρ=0.70), Mn (ρ=0.98), Cu (ρ=0.99), and Ni (ρ=0.85) show strong positive correlation, indicating that the relatively high concentrations of these metals in the surface layer of the corrosion scales is linked to the concentrations of these metals in water. This inference is consistent with the experimental observations discussed above. Specifically, among the four municipalities, Municipality B has the highest aluminum concentration in treated water, followed by Municipality C and the City of London, while Municipality D has the lowest concentration. Consistently, elemental analysis results for aluminum shows that its largest amount is found in B1-L1 and B2-L1 while D1-L1 contains the least amount. For manganese, Municipality B reports concentration of Mn in its treated water below detection limits, while the City of London and Municipality D have comparable concentrations which in turn are one order of magnitude lower than that reported for Municipality C’s water. Consistently the surface layers of scales of Municipality B contain the least amount of manganese amongst the four municipalities, followed by the City of London and Municipality D. Municipality C experiences the most abundant of Mn accumulated in scales. The largest amount of Cu was measured in D1-L1 as the treated water of Municipality D contains the highest concentration of copper, while water of other three municipalities contains one order of magnitude less copper concentration. A similar link was found for Ni accumulated in scales and its concentration in water when compared these data for four municipalities. Arsenic (As), also has strong positive correlation (ρ=0.89) between the aqueous phase and solid phase concentrations. This finding is consistent with previous studies\(^9,^{28}\) reporting As accumulating in corrosion scales.

Surprisingly, Fe and Ca show almost no correlation between its appearance in aqueous phase and its accumulation in solid phase. This suggests that accumulated Fe and Ca in
corrosion scales might not dependent on recent water quality. There is a possibility that their accumulation in solid phase is due to the solid phases interactions, or that took place in the past (such in the case of Municipality C that experienced iron corrosion in the past century).

3.5 Role of the aluminosilicates in the chemical composition of corrosion scales

As discussed above, aluminosilicate was detected in surface layer of all scale samples, although for Municipality D, it is observed in low amounts. It is known that aluminum containing coagulants are one of the main sources of aluminum in drinking water. Previous studies\textsuperscript{29, 30} report that treated water is proportionately high in a divalent monomeric soluble form of aluminates, i.e. $\text{Al(OH)}_{\text{aq}}^{+2}$. At the same time, it is known that the point of zero charge (pH\textsubscript{pzc}) of solid $\text{PbO}_2$ is in the range of 4.8-5.2\textsuperscript{31, 32} and the zeta-potential of hydrocerussite and cerussite is negative under drinking water conditions\textsuperscript{33}, indicating that under typical drinking water conditions, surface of $\text{PbO}_2$ and lead carbonates solids are negatively charged. Thus, positively charged monomeric aluminum hydroxide ions in drinking water could be adsorbed on the negatively charged surface of the solid lead compounds in the corrosion scales via electrostatic interactions. Other positively charged metal complexes could also be adsorbed on surface of lead compounds. At high concentrations, adsorbed ions could form a surface precipitate.

Silica is another important constituent in aluminosilicates. It naturally occurs in the source water as silicic acids (Si(OH)\textsubscript{4}), and could remain in the treated water. Previous reports\textsuperscript{34, 35} indicate that the presence of silica will inhibit the crystallization of aluminum hydroxide, and form poorly crystalline hydroxyaluminosilicates with the aluminum species. It is known that hydroxyaluminosilicates are extremely insoluble, thus coexistence of aluminum and silica in drinking water results in the precipitation of aluminosilicate; however, its formation process and mechanism as well as its composition is still not well understood. Allophane and imogolite are two major types of poorly crystalline aluminosilicate. Based on our characterization results of the lead corrosion scales, allophane is the only form of aluminosilicate observed in the corrosion scales formed in drinking water, imogolite can only formed under acidic conditions (pH<5) at high Al:Si
Based on previous studies, the formation of Si-rich halloysite or feldspathoids allophane is expected under the drinking water conditions of all four systems in our study (the City of London, Municipalities B, C and D), and this should be clearly patent on the surface layer of scale. Consistently the IR spectra of all L1 samples displayed an absorption band in the range of 1150-850 cm$^{-1}$ centered around 1050 cm$^{-1}$, indicating the dominant presence of Si-rich allophane.

It has been previously reported that allophane has distinct surface properties due to its high surface area, the presence of surface functional groups, and defects. Depending on the pH of environment, Si-rich allophane could have either a positive or negative surface charge, thus allophane could act as adsorbent for a variety of charged species. Specifically, phosphate, fluoride, citrate, borate, arsenate, and selenite could form inner-sphere complexes with aluminosilicates. At the same time many metal ions (Pb$>$ Cu$>$ Zn$>$ Co$>=$ Cd$>=$ Mg$>=$ Ca in order of decreasing affinity) could also interact with negatively charged sites, i.e. aluminol and silanol groups on the allophane surface. This decreasing affinity is due to the fact that Pb, Cu, Zn, and Co appear to form inner-sphere surface complexes, whereas Cd, Mg, and Ca are held only by electrostatic forces. This distinct interaction mechanisms by different elements might explain the fact that no obvious correlation between the aqueous Ca and the accumulated Ca in corrosion scales was observed in section 3.4.

The characteristic surface properties of Si-rich allophane are heavily dependent on pH. Thus both pH and surface characteristics of allophane may help in explaining the elemental analysis results obtained for Municipality C, whose corrosion scale seems to accumulate various elements in relatively higher amounts than those observed for the case of the other municipalities. Specifically, elevated iron (Fe), calcium (Ca), magnesium (Mg), boron (B), zinc (Zn), and barium (Ba) were accumulated in the corrosion scales of Municipality C. However, their concentrations in the treated water of Municipality C are similar or even lower than that observed on the other Municipalities in this study. It should be noted that Municipality C has very soft water resulting in the lowest concentration of Ca and Mg amongst the four municipalities. In addition, Municipality C has a relatively high pH value for its treated water (pH$\approx$9.3) compared with those of the other municipalities.
(7.2<pH<8.0). Under these conditions, negative charges should be present on most of the surface of Si-rich allophane. This will enhance the accumulation of these metal cations. In natural waters, boron exists as boric acid with some borate ions depending on the water pH. It is known that boric acid is a weak acid with a pK<sub>a</sub> of 9.15. Su and Suarez<sup>41</sup> have reported that the maximum adsorption of boric acid on allophane could occur at pH near 9. For the case of barium compounds, it is known that their aqueous solubility decreases with the increase in pH.<sup>42</sup> Thus again, the high pH (~9.3) might help in the formation of a Ba-bearing surface precipitate. Not only is direct interaction of allophane surface with these aqueous species possible, the interaction between the metal complexes formed on allophane surface and metal cations via electrostatic force in aqueous phases may be another possibility. To explore the possible links between the accumulation of heavy metals in the corrosion scale, a Pearson correlation calculation was carried on the acid digestion results of the different elements in the corrosion scales. The results obtained are shown in Table A.4. Strong Pearson correlation coefficients were found for several metal-element pairs, i.e. Mn, Mg, Ba, Zn, Ni. It should also notice that for all accumulated elements, arsenic has a strong positive correlation coefficient (ρ=0.70) with aluminum (Table A.4), indicating aluminosilicates could accumulate arsenic. A previous study<sup>40</sup> has reported that dissolved As could be adsorbed by hydroxyl (-OH) groups present in the surface of allophane via ligand exchange. This strong correlation between Al and As was also observed for several corrosion scales collected from the City of London.<sup>4</sup>

Aluminosilicates are not only present in lead corrosion scales either collected in this study or other studies<sup>4, 30</sup>, but it is also commonly observed in corrosion scales collected from iron pipes<sup>43</sup>. Its ubiquitous presence indicates that aluminosilicates are likely to act as absorbents for various species including phosphate (corrosion inhibitor), and control their concentrations in DWDS. Furthermore, the stability of aluminosilicate could play a vital role in safety of drinking water as various heavy metals are preferentially accumulated on it.

### 3.6 Conclusions

The detailed characterization results on the scales indicated that solid lead speciates between carbonate and oxide phases. The water quality plays a key role in the formation
of the specific phase, and this effect is particularly observed for the case of the layers in
direct contact with drinking water. Amorphous solid aluminosilicates were also observed
in all surface layers obtained for the lead corrosion scales tested in this study. Using
drinking water quality information, we inferred that amorphous aluminosilicate was
preferably formed under drinking water conditions of moderate aluminum (~0.001-0.1
mg/L) and silica concentrations (~1.0-1.5 mg/L). Al, Cu, Ni, As, and Mn, accumulated on
the surface of scales, their concentrations on the solid phase are heavily dependent on their
concentrations in drinking water. The local drinking water quality, particularly pH value
and silicate concentration, seemed to have a critical role on the surface properties of the
aluminosilicate, resulting in preferable accumulation for certain elements.
Reference


Chapter 4

4 The interaction between monochloramine and PbO$_2$ under drinking water conditions

4.1 Introduction

The severity of lead contamination in drinking water has been recently brought to the spotlight, such as the case recently reported in the City of Flint, Michigan\textsuperscript{1}. Due to the toxicity of lead, Health Canada is considering updating the existing guideline for lead, maximum acceptable concentration (MAC), from 10 to 5 μg/L\textsuperscript{2}. It has been found the dissolved lead in tap mainly comes from legacy lead service lines (LSL) that are used in the last part of drinking water distribution system (DWDS) serving drinking water to residents. Free chlorine is normally used as disinfectant for drinking water treatment. Due to the presence of disinfectant (a strong oxidant) in drinking water, metallic lead in pipe wall is oxidized, resulting in the formation of lead corrosion scales. Plattnerite (β-PbO$_2$) is one of the common oxides formed in the surface layer of corrosion scales under water chlorination conditions.\textsuperscript{3-6} To control disinfectant by-products (DBPs) formed during chlorination, chloramines have been proposed and used as substitute of chlorine by some municipalities. While the general term “chloramines” may refer to monochloramine (NH$_2$Cl), dichloramine (NHCl$_2$), and trichloramine (NH$_3$), NH$_2$Cl is the main species present under typical drinking water conditions. A switch from free chlorine to monochloramine took place in the drinking water operations of the District of Columbia (U.S.), resulting in elevated dissolved lead concentrations at customers’ tap water in 2003.\textsuperscript{4, 7} It was not until 2008 that Lin and Valentine\textsuperscript{8} reported PbO$_2$ present in the lead plumbing corrosions scale could be reduced by NH$_2$Cl resulting in the release of elevated dissolved lead concentrations, although PbO$_2$ is thermodynamically stable under chloramination conditions. Moreover, they evaluated the effect of water quality on the extent of reduction of PbO$_2$, and reported a linear correlation between loss in NH$_2$Cl and dissolved lead released from PbO$_2$, proposing the presence of an intermediate generated during the auto-decomposition of monochloramine able to reduce PbO$_2$ into soluble Pb$^{+2}$ species. However, the authors were unable to identify these intermediate species.
Xie et al.\textsuperscript{9} also explored the impact of NH\textsubscript{2}Cl on PbO\textsubscript{2} dissolution. They carried out bench scale experiments using both continuous-flow (30min hydraulic residence time) and batch (24h) experiments. While lower lead concentrations were observed in the presence of NH\textsubscript{2}Cl compared with the one in the absence of disinfectant in the flow system at pH 8.5, elevated dissolved lead levels were observed once the continuous-flow system was sealed and stirred with no flow (batch mode) for another 24-hour dissolution. They rationalized these different observations to the different configurations of both systems. Specifically, in the flow system, there would not be accumulation of unidentified intermediate species released during NH\textsubscript{2}Cl auto-decay. It should be noted that commercial PbO\textsubscript{2} was used as starting material in their study to perform dissolution experiments. The studies carried out by Lin and Valentine\textsuperscript{8,10} however, used lab prepared PbO\textsubscript{2} and a low (10 mg/L) solid loading, compared to a more recent study\textsuperscript{9} (1000-100 mg/L).

To the best of our knowledge, current studies on the PbO\textsubscript{2} reduction under drinking water conditions focus on evaluating the effects of different drinking water quality on PbO\textsubscript{2} rather than the effects of different PbO\textsubscript{2} samples on its reduction. Since PbO\textsubscript{2} was considered chemically stable, commercial PbO\textsubscript{2} is widely used as starting materials for the lab experiments. However, PbO\textsubscript{2} is well known for being a non-stoichiometric compound with surprisingly high conductivity. Previous studies have reported that defects in PbO\textsubscript{2} are responsible for its high conductivity. Although the nature of defects is still under debate, oxygen vacancies (V\textsubscript{O})\textsuperscript{11,12} and cation vacancies occupied by Pb(II)\textsuperscript{13,14} in the PbO\textsubscript{2} structure have been proposed to account for the material’s relatively high conductivity. It has been reported that number of defects in PbO\textsubscript{2} will increase during the storing time.\textsuperscript{15} This phenomenon is also known as aging. In other words, a change in electronic structure of PbO\textsubscript{2} is expected over time. This may affect the reactivity of PbO\textsubscript{2} and therefore explain the contradicting results in terms of lead dissolution and monochloramine decomposition reported in the literature. To explore this hypothesis, the dissolution of different PbO\textsubscript{2} samples in water with NH\textsubscript{2}Cl was investigated to evaluate the influence of the structural and/or electronic properties of PbO\textsubscript{2} on lead dissolution and monochloramine decomposition rates.
4.2 Experimental section

**Materials.** Four $\beta$-PbO$_2$ samples (crystalline structure confirmed by XRD in Figure 4.1a and XRD data provided by the manufacturer) subject to different aging treatment were used for the dissolution experiments. In addition, two chlorinated $\beta$-PbO$_2$ samples ($\beta$-PbO$_2$ exposed to a solution of chlorinated water) were prepared and used to perform dissolution experiments. From this point onward PbO$_2$ refers to $\beta$-PbO$_2$. Two commercial PbO$_2$ samples purchased from Sigma-Aldrich were used: one of them was purchased in 2009, and it was exposed to dry air for about 48 months (labeled as 48m-aged-PbO$_2$) before it was used in the dissolution experiments. Another commercial PbO$_2$ was purchased in 2015 and used as received (labeled as unaged-PbO$_2$). Two additional PbO$_2$ samples were obtained after additional aging treatment of the unaged-PbO$_2$ sample: one was aged in dry air for 12 months (labeled as 12m-aged-PbO$_2$), and the other one was prepared using a portion of the 12m-aged-PbO$_2$ and exposing it to humid air for about 3 months (labeled as 12m-3mH$_2$O-PbO$_2$). As mentioned above, two chlorinated PbO$_2$ samples were prepared using commercial PbO$_2$ in a chlorinated solution. Specifically, the 48m-aged-PbO$_2$ was used as starting material to prepare one chlorinated PbO$_2$ sample named as 48m-Cl$_2^0$-PbO$_2$, while the 12m-aged-PbO$_2$ sample was used to prepare another chlorinated PbO$_2$ sample named as 12m-Cl$_2^0$-PbO$_2$. Both chlorinated PbO$_2$ (48m-Cl$_2^0$-PbO$_2$ and 12m-Cl$_2^0$-PbO$_2$) samples were prepared using the following procedure: 0.88 g/L of the starting material was loaded in 300 ml bottles (HDPE, Nalgene) and filled full of stock solution (20 mg C/L DIC, 0.01 M ionic strength, initial pH value 8) with a target initial free chlorine concentration. Duplicate non-sacrificed 48m-Cl$_2^0$-PbO$_2$ samples were generated in two 300 ml reactors with initial 2.5 mg/L free chlorine for 200 days, while duplicate sacrificed 12m-Cl$_2^0$-PbO$_2$ samples were prepared in 300 ml reactors. To generate the 12m-Cl$_2^0$-PbO$_2$ sample, lead oxide was mixed for 10 days with the stock solution (no free chlorine added). After these initial 10 days 1.1 mg/L free chlorine was added. The mixture was kept for 90 days chlorination.

For the dissolution experiments, NaNO$_3$ (Sigma-Aldrich, $\geq$ 99.0%) and NaHCO$_3$ (Sigma-Aldrich, $\geq$ 99.5%) were used to prepare a stock solution with 0.01 M ionic strength (IS) and 20 mg C/L dissolved inorganic carbon (DIC), respectively. NaOCl (Sigma-Aldrich,
reagent grade) and NH$_4$Cl (Sigma-Aldrich, 99.998% trace metals basis) were used as the source of free chlorine and ammonia, respectively. 1 mM NH$_2$Cl was freshly prepared mixing volumes of NaOCl and 20 mM NH$_4$Cl in ultrapure water to achieve a 0.79 Cl/N molar ratio. The preparation of NH$_2$Cl followed the method developed by Vikesland$^{16}$. NaOH (Pellets, Sigma-Aldrich) and HNO$_3$ (EMD Milipore, Omnitrace) were used respectively to prepare diluted NaOH (~0.1 M) and HNO$_3$ (2% or 20% v/v) solutions to adjust the initial pH of the stock solution.

**β-PbO$_2$ batch dissolution experiments.** Four different sets of experiments were performed with the unaged-PbO$_2$, 12m-aged-PbO$_2$, 48m-aged-PbO$_2$, and 12m-3mH$_2$O-PbO$_2$ samples, following previously reported methodology.$^{17}$ In brief, experiments were carried out using 0.88 g/L of PbO$_2$ solid loading in a closed aqueous solution without head space (0.01 M ionic strength [IS], 20 mg dissolved inorganic carbon C/L [DIC], and a target initial NH$_2$Cl concentration [1.5 and 15 mg Cl$_2$/L] at an initial pH value close to 8, unbuffered). Reactors were put in a sealed dark box and continuously mixed using an orbital shaker (Thermo Scientific, MAXQ 2000) at 170 rpm. Sacrificial duplicate samples were collected for both aqueous and solid phases for each experiment. Before analysis a sample solution was filtered using a 0.22 µm polyethersulfone syringe filter (VWR) and a 20 ml syringe (Thermo Scientific). NH$_2$Cl concentration, pH, and dissolved lead ([Pb]) measurements were carried out. The first few drops of the filtrate were discarded when collecting the solution. Solid samples were collected and dried in a vacuum desiccator for about 24 hours and subject to characterization using UV/Vis/NIR spectroscopy.

Two sets of experiments performed using 48m-Cl$_2^0$-PbO$_2$ and 12m-Cl$_2^0$-PbO$_2$ followed a similar experimental protocol except that concentrated NH$_2$Cl was spiked into each reactor after free chlorine depleted completely. Duplicate non-sacrificed 48m-Cl$_2^0$-PbO$_2$ were generated in the presence of initial 2.5 mg/L free chlorine. At 200 days, there was no residual free chlorine, then freshly prepared NH$_2$Cl (~1 mM) was spiked into the duplicate reactors, and well mixed to achieve an initial 1.5 mg/L NH$_2$Cl concentration in the system. This is the starting point of the monochloramine decomposition experiment using the 48m-Cl$_2^0$-PbO$_2$ sample. 25 ml liquid sample was collected from each non-sacrificed reactor at each time data point to monitor the changes in NH$_2$Cl concentration and pH. For the
dissolution experiment using 12m-Cl\textsubscript{2}\textsuperscript{0}-PbO\textsubscript{2}, freshly prepared NH\textsubscript{2}Cl (~1 mM) was spiked into each sacrificial reactor containing 12m-Cl\textsubscript{2}\textsuperscript{0}-PbO\textsubscript{2} solids after 90-day chlorination to reach an initial 1.5 mg/L NH\textsubscript{2}Cl concentration. Duplicate sacrificial samples were collected for both liquid and solid phase for this experiment following the protocol described above. All experiments were conducted at room temperature (21±2 °C).

**Analytical methodology.** The concentrations of free chlorine and monochloramine were determined via an UV/Vis spectrophotometer (Hach, DR5000) following the standard DPD colorimetric method (Method 10069, Hach) and indophenol method (Method 10171, Hach), respectively. The pH values were measured using a pH meter (Hach, H160) with a glass pH probe. 3-points calibration method (pH=4, 7, 10) was used to calibrate pH meter. Dissolved lead concentrations were determined via inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian, Vista-Pro 97 Axial) or inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific, iCAP Q).

Solid samples were analyzed via UV/Visible/Near-Infrared (UV/Vis/NIR) spectroscopy and X-ray powder diffraction (XRD). UV/Vis/NIR spectra were obtained in the range of 200-1600 nm using a UV-3600 Shimadzu equipped with a diffuse reflectance cell (Harrick, Praying Mantis) with 1 nm step size at the highest resolution setting of the instrument. Then the spectra were transformed to pseudo-absorption units using a Kubelka-Munk transform in the UVProbe\textsuperscript{®} software. XRD data were obtained on a Rigaku RPT 300 RC diffractometer using the Co K-\textalpha (\lambda=1.78890 Å) line over the range of 10-70° 2θ with a 0.02° step size.

4.3 Results and discussion

4.3.1 Changes in PbO\textsubscript{2} during aging process

XRD patterns obtained for the 12m-aged-PbO\textsubscript{2}, 48m-aged-PbO\textsubscript{2}, and 48m-Cl\textsubscript{2}\textsuperscript{0}-PbO\textsubscript{2} solids used in this work are shown in Figure 4.1a. The diffraction patterns clearly show that all solids have a plattnerite (\(\beta\)-PbO\textsubscript{2}) crystal structure. More importantly the results indicate that there was no crystalline phase transformation during the different solid aging treatments. Figure 4.1b shows the results obtained for the optical absorption spectra on the
samples with different aging treatment. All spectra show the characteristic absorption band for PbO$_2$ in the near infrared (NIR) region.
Figure 4.1 a) XRD obtained on 48m-aged-, 12m-aged-, and 48m-Cl\textsuperscript{0}-PbO\textsubscript{2} samples, b) UV/Vis/NIR spectra of four PbO\textsubscript{2} samples, and c) dissolved lead concentrations observed in control tests using unaged- and 48m-aged-PbO\textsubscript{2}, respectively.

Optical absorption in solids results from electronic transitions from the valence band to the conduction band when the energy of optical photons in the UV or visible region matches the band gap energy. The optical band gap ($E_g$) is the energy difference (eV) between occupied states in their valence band and unoccupied states in the conduction band, and it can be calculated from the UV/Vis/NIR spectra. The NIR band of PbO\textsubscript{2} is due to photon absorption by free electrons\textsuperscript{18} that are present due to defects in non-stoichiometric PbO\textsubscript{2}\textsuperscript{12, 19}. With an increase in the defects/electrons, the energy of the NIR band will be higher. The optical band gap and NIR band gaps of the samples tested in this work were calculated following previously reported methodology.\textsuperscript{17}

Figure 4.1b shows that the position of the NIR band for the different samples tested upon different aging treatments. Specifically, for the unaged-PbO\textsubscript{2} sample the band shows at 1408 nm, whereas that observed for the 12m-aged-PbO\textsubscript{2} sample sits at 1395 nm, 1352 nm for 12m-3mH\textsubscript{2}O-PbO\textsubscript{2}, and 1295 nm for the 48m-aged-PbO\textsubscript{2} sample. At the same time the optical band edge also presented a blue-shift suggesting that a higher energy band gap develops during the aging process (Table B.1 in Appendix B). Using previously reported methodology and a direct allowed transition formalism\textsuperscript{17}, the optical band gap can be calculated from the visible absorption spectra. The optical band gap values thus obtained
were 1.69 (unaged-PbO$_2$), 1.75 (12m-aged-PbO$_2$), 1.78 (12m-3mH$_2$O-PbO$_2$), and 1.79 eV (48m-aged-PbO$_2$), respectively. These values indicate an increase in the band gap values that can be correlated to the aging time of the samples. This observation is consistent with the optical properties of aged PbO$_2$ films previously reported by Mindt$^{15}$. They reported a blue-shift in the absorption edge (from 1.7 to 1.84 eV) observed when PbO$_2$ was exposed to air for 30 days. They attributed this shift to an increase in electron concentration. They also reported the free electron concentration in PbO$_2$ increased at longer aging times, however free electron mobility decreased$^{15}$. This observation may explain the shifts observed in the NIR band during the aging process since this specific spectral feature is linked to photon absorption by free electrons.$^{18}$ Although the origin and exact identity of the defects that result in the generation of free electrons is under debate, based on the optical absorption data it is clear that 48m-aged-PbO$_2$ sample contained the most defects amongst all four PbO$_2$ samples tested in this study. In other words, although the crystal structure of the PbO$_2$ remained the same, the aging processes severely affects the electronic structure of the PbO$_2$ samples.

To evaluate whether these changes in electronic structure have any consequences on PbO$_2$ dissolution under drinking water conditions, we conducted a set of control dissolution experiments for the unaged- and 48m-aged-PbO$_2$ which represent the least and most aged sample amongst the four aged samples tested in our study. These experiments were carried out using a stock solution (20 mg C/L DIC, 0.01 M IS, and pH 8) without NH$_2$Cl. Their lead release profiles are shown in Figure 4.1c. Compared to the results obtained on the unaged-PbO$_2$ sample, an increase in an order of magnitude was observed for lead dissolution levels in experiment performed using the 48m-aged-PbO$_2$ sample. It should be noted that although both unaged- and 48m-aged-PbO$_2$ initially released a relatively high lead concentration, for the case of unaged-PbO$_2$ its dissolved lead levels decreased rapidly and reached a value of 5 μg/L within 3 days then slightly increased to 6 μg/L at 33 days. In contrast, lead concentrations observed in the experiment conducted using 48m-aged-PbO$_2$ were higher, hovering near 100 μg/L. These observations may be rationalized in terms of a faster exchange observed between Pb$^{2+}$ (aq) in solution and plumbic ions in unaged PbO$_2$(s) compared with that taking place in aged PbO$_2$(s).$^{20}$
4.3.2 Relationship between PbO$_2$ surface quality, NH$_2$Cl decay and aqueous lead release

To understand the effects of changes in electronic structure and surface quality of PbO$_2$ on monochloramine decomposition, four PbO$_2$ samples (48m-aged-PbO$_2$, unaged-PbO$_2$, 12m-aged-PbO$_2$, and 12m-3mH$_2$O-PbO$_2$) were used as starting materials in dissolution experiments in the presence of a nominal 1.5 mg/L concentration of NH$_2$Cl, except for the case of the 48m-aged-PbO$_2$ sample, where an initial concentration of 3.5 mg/L NH$_2$Cl was used instead. Figure 4.2a shows the monochloramine decomposition profiles obtained for these four sets of experiments and the results of two additional control experiments for NH$_2$Cl auto-decomposition experiments in the absence of PbO$_2$. 

![Graph showing monochloramine decomposition profiles and control experiments](image-url)
Figure 4.2 Consumption of NH$_2$Cl over time for a) unaged-PbO$_2$, 48m-aged-, 12m-aged-, and 12m-3mH$_2$O-PbO$_2$, b) chlorinated PbO$_2$, c) dissolved lead concentrations for selected
The decomposition of NH$_2$Cl in the experiment of 48m-aged-PbO$_2$ with an initial monochloramine concentration of 3.5 mg/L showed the same profile as its auto-decomposition in the control test (Figure 4.2a). Both profiles can be fitted using second-order kinetics, resulting in similar observed rate constants (Table 4.1). These results suggest that PbO$_2$ did not directly react with NH$_2$Cl. This observation is consistent with a previous study carried out using 10 mg/L PbO$_2$ solid concentrations and a solid PbO$_2$ to NH$_2$Cl molar ratio ranging from 0.6 to 3. In comparison, in our study we used a 0.88 g/L solid loading and a solid to NH$_2$Cl molar ratio close to 75. This suggests that a relatively high solid concentration had little impact on the auto-decomposition of NH$_2$Cl.

The same solid concentration, 0.88 g/L, was used in the dissolution experiments of unaged-PbO$_2$, 12m-aged-, and 12m-3mH$_2$O-PbO$_2$ samples but using an initial NH$_2$Cl concentration of 1.5 mg/L instead and a solid to NH$_2$Cl molar ratio close to 174. A faster monochloramine decay rate was observed in the experiment conducted using unaged-PbO$_2$ than that of its parallel auto-decomposition control experiment (Figure 4.2a). The same solid to NH$_2$Cl molar ratio, 174, was also used in the experiments of 12m-aged- and 12m-3mH$_2$O-PbO$_2$, however in these two cases the NH$_2$Cl decomposition rates observed were slower than that of unaged-PbO$_2$. This indicates that the PbO$_2$ solid plays a critical role in NH$_2$Cl decay. It should be noted, however, that the second-order kinetics constants of NH$_2$Cl decay in the presence of 12m-aged- and 12m-3mH$_2$O-PbO$_2$ were still one order of magnitude higher than that obtained in the control experiment of NH$_2$Cl auto-decay (Table 4.1). Thus, under the same initial NH$_2$Cl concentration conditions, the NH$_2$Cl decay rates measured in all these experiments follows this order: unaged-PbO$_2$> 12m-aged-PbO$_2$> 12m-3mH$_2$O-PbO$_2$> NH$_2$Cl auto-decay. This indicates a direct reaction between PbO$_2$ and NH$_2$Cl, and a reaction rate that is strongly dependent on the solid pretreat treatment.
Table 4.1 Conditions for experiments presented in Chapter 4. Observed kinetic constants for monochloramine decomposition and aqueous lead concentrations after 30 days for selected experiments.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Solid reactant</th>
<th>Disinfectant type</th>
<th>Stock solution Initial concentration of disinfectant (mg Cl₂/L)</th>
<th>Pb⁺² (mg/L)</th>
<th>Observed 2ⁿᵈ-order kinetic constant* (mM⁻¹·day⁻¹)</th>
<th>[Pb₉₀₀] at 30 days (µg/L)</th>
<th>Reactor size</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1</td>
<td>48m-aged-PbO₂</td>
<td>NH₂Cl</td>
<td>3.57</td>
<td>N/A</td>
<td>0.45</td>
<td>N/A</td>
<td>25 ml</td>
</tr>
<tr>
<td>0-2</td>
<td>N/A</td>
<td>NH₂Cl</td>
<td>3.39</td>
<td>N/A</td>
<td>0.44</td>
<td>N/A</td>
<td>25 ml</td>
</tr>
<tr>
<td>1-1</td>
<td>unaged-PbO₂</td>
<td>NH₂Cl</td>
<td>1.44</td>
<td>N/A</td>
<td>4.00</td>
<td>4.6</td>
<td>300 ml</td>
</tr>
<tr>
<td>1-2</td>
<td>N/A</td>
<td>NH₂Cl</td>
<td>1.44</td>
<td>N/A</td>
<td>0.67</td>
<td>N/A</td>
<td>25 ml</td>
</tr>
<tr>
<td>1-3</td>
<td>unaged-PbO₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>6.2</td>
<td>300 ml</td>
</tr>
<tr>
<td>2-1</td>
<td>12m-aged-PbO₂</td>
<td>NH₂Cl</td>
<td>1.58</td>
<td>N/A</td>
<td>2.61</td>
<td>6.4</td>
<td>300 ml</td>
</tr>
<tr>
<td>2-2</td>
<td>(1 Y old from unaged-PbO₂)</td>
<td>NH₂Cl</td>
<td>1.45</td>
<td>N/A</td>
<td>1.33</td>
<td>12.5</td>
<td>300 ml</td>
</tr>
<tr>
<td>2-3</td>
<td>12m-3mH₂O-PbO₂</td>
<td>NH₂Cl</td>
<td>15.4</td>
<td>N/A</td>
<td>0.26</td>
<td>80</td>
<td>300 ml</td>
</tr>
<tr>
<td>2-4</td>
<td>N/A</td>
<td>NH₂Cl</td>
<td>15.4</td>
<td>N/A</td>
<td>0.26</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>3-1-a</td>
<td>48m-aged-PbO₂</td>
<td>NaOCl</td>
<td>2.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>3-1-b</td>
<td>following E3-1-a</td>
<td>NH₂Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>19.94</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>3-2</td>
<td>N/A</td>
<td>NH₂Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>0.62</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>Experiments</td>
<td>Solid reactant</td>
<td>Disinfectant type</td>
<td>Initial concentration of disinfectant (mg Cl2/L)</td>
<td>Pb(^{2+}) (mg/L)</td>
<td>Observed 2(^{nd})-order kinetic constant* (mM(^{-1})day(^{-1}))</td>
<td>[Pb(_{aq})] at 30 days (μg/L)</td>
<td>Reactor size</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------------------</td>
<td>-------------------</td>
<td>-----------------------------------------------</td>
<td>----------------</td>
<td>-------------------------------------------------</td>
<td>-------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>3-3-a</td>
<td>12m-aged-PbO(_2) (1 Y old from unaged-PbO(_2))</td>
<td>NaOCl</td>
<td>1.1</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>3-3-b</td>
<td>following E3-3-a 12m-Cl(_2)(^0)-PbO(_2)</td>
<td>NH(_2)Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>10.86</td>
<td>3.8</td>
<td>300 ml</td>
</tr>
<tr>
<td>4-1</td>
<td>12m-aged-PbO(_2)</td>
<td>NH(_2)Cl</td>
<td>1.52</td>
<td>~0.1</td>
<td>2.49</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>4-2</td>
<td>N/A</td>
<td>NH(_2)Cl</td>
<td>1.58</td>
<td>~0.1</td>
<td>0.71</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>4-3</td>
<td>N/A</td>
<td>NH(_2)Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>0.97</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>previous study(^{17})</td>
<td>24m-aged-PbO(_2)</td>
<td>NaOCl</td>
<td>2.5</td>
<td>N/A</td>
<td>1.7</td>
<td>300 ml</td>
<td></td>
</tr>
</tbody>
</table>

Note: *observed 2\(^{nd}\)-order kinetic constants are only provided and compared for experiments carried using the same nominal initial NH\(_2\)Cl concentrations.
PbO$_2$ in lead corrosion scales forms under chlorinated water conditions. Our previous study$^{17}$ reported that the electronic structure of PbO$_2$ changes over time when the solid is exposed to free chlorine under typical drinking water conditions. Thus, to evaluate the effect of chlorination on the properties of PbO$_2$ solid, and further on the decomposition of NH$_2$Cl, two chlorinated PbO$_2$ samples, 48m-Cl$_2$$_2^0$-PbO$_2$ and 12m-Cl$_2$$_2^0$-PbO$_2$, were prepared to conduct dissolution experiments under depleting monochloramine conditions. The details on their preparation were described in experimental section. A PbO$_2$ solid to NH$_2$Cl molar ratio of 174 was used in these experiments. The consumption rates of NH$_2$Cl in both experiments were much faster than those observed for the auto-decomposition of NH$_2$Cl (Figure 4.2b). In fact, their calculated second order kinetic constants were an order of magnitude higher than that obtained on the experiment using unaged-PbO$_2$ which showed the fastest reaction rate amongst all previous experiments performed (Table 4.1). It is known that free chlorine could oxidize dissolved Pb$^{+2}$ species released from reduction of PbO$_2$ by water, resulting in the reprecipitation of solid PbO$_2$.$^{6,7,21}$ It is plausible to propose that this newly formed PbO$_2$ solid, generated under chlorinated water conditions, is linked to the high rates of NH$_2$Cl decomposition observed amongst all sets of experiments since this is the only possible structural change triggered by chlorinated water treatment. This result thus suggests that reaction between PbO$_2$ and NH$_2$Cl is a surface reaction and heavily dependent on the surface properties of PbO$_2$. To the best of our knowledge, this is the first study indicating that PbO$_2$ could enhance the decay rate of NH$_2$Cl. Furthermore, comparing these two experiments using 48m-Cl$_2$$_2^0$-PbO$_2$ and 12m-Cl$_2$$_2^0$-PbO$_2$ (Figure 4.2b), their observed NH$_2$Cl decomposition rates were comparable, although 48m-aged- and 12m-aged-PbO$_2$ were used as starting materials to generate the chlorinated solid samples respectively. This also suggests that the surface of PbO$_2$, likely with freshly formed PbO$_2$, plays a dominant role in the decay of NH$_2$Cl rather than the inner core of PbO$_2$. This is also consistent with the results obtained on the aged samples where the higher monochloramine decomposition rates were observed on the unaged-PbO$_2$ sample. Comparing the pH profiles of all experiments discussed above, their pH values did not significantly vary from the initial pH value 8, and the profiles were close to the pH changes observed during NH$_2$Cl auto-decay (Figures B.1a-c in Appendix B).
Figure 4.2c shows the dissolved lead concentrations obtained for the monochloramine decomposition experiments with aged and chlorinated PbO$_2$ solids. The lead profile obtained for the control experiment with unaged-PbO$_2$ in the absence of NH$_2$Cl is also included. At 30 days, the lead concentration observed in the experiment using unaged-PbO$_2$ with NH$_2$Cl was 4.6 μg/L, which was slightly lower than the one obtained in the absence of monochloramine (control test ~6.2 μg/L). This indicates that NH$_2$Cl did not enhance lead dissolution of unaged-PbO$_2$ up to a period of 30 days. While the lead concentrations observed under both conditions were lower than the MAC (10 μg/L), they were still higher than the ones previously reported in the presence of free chlorine instead of monochloramine (1.7 μg/L at 30 days, Table 4.1). We can summarize these results as follows: dissolved lead levels increase in this order: free chlorine< NH$_2$Cl< no disinfectant. This is consistent with the water quality redox potential: free chlorine> NH$_2$Cl> no disinfectant.

For the case of the 12m-aged-PbO$_2$ dissolution experiment in the presence of monochloramine, lead concentrations were slightly higher (~6.4 μg/L) and comparable to those observed for the dissolution of unaged-PbO$_2$ where monochloramine was no present. In comparison with relative low lead levels released from unaged-PbO$_2$ and 12m-aged-PbO$_2$ in the presence of NH$_2$Cl, elevated dissolved lead concentrations were observed in the experiment of 12m-3mH$_2$O-PbO$_2$ carried out under similar conditions (Figure 4.2c). Its lead concentration was about 12.5 μg/L at 30 days of reaction. This indicates that the moisture in air could accelerate the aging process that enhances PbO$_2$ reduction in the presence of NH$_2$Cl resulting in high lead concentrations.

Surprisingly, relatively low concentration of dissolved lead (~3.8 μg/L) were also observed in the experiment using 12m-Cl$_2^0$-PbO$_2$ at 30 days in the presence of monochloramine. It should be noted that both unaged- and 12m-Cl$_2^0$-PbO$_2$ accelerated the decay rate of NH$_2$Cl whereas their lead levels were comparable to those observed in their control experiments carried out in the absence of NH$_2$Cl. This result is quite unexpected since it has been previously proposed that dissolved lead concentrations linearly correlate with the consumption of NH$_2$Cl. Figure 4.2d shows a plot where dissolved lead concentrations were plotted against monochloramine consumption for all experiments depicted above. A
linear relationship with a zero slope was observed instead. This indicates that under our experimental conditions lead dissolution is independent of NH$_2$Cl consumption for experiments of unaged-, chlorinated-, and 12m-aged-PbO$_2$. Instead, the rate of consumption of monochloramine is dependent on the quality of the solid PbO$_2$ sample used in the experiment, suggesting again that the quality of the lead oxide solid surface, plays a crucial role in activity of PbO$_2$ with NH$_2$Cl.

4.3.3 A possible link between monochloramine concentration and PbO$_2$ aqueous lead release

As discussed in the previous section, the higher rates for monochloramine decomposition were observed in the presence of PbO$_2$ containing a fresh surface. A relatively high solid (PbO$_2$) to NH$_2$Cl molar ratio, 174, was used in these experiments, compared with ratios between 0.6 and 3.0 used in previous work by Lin and Valentine.\textsuperscript{8} If our main hypothesis is correct and indeed the decomposition of NH$_2$Cl is a surface mediated phenomenon, a monochloramine decomposition rate dependence on the PbO$_2$ solid to NH$_2$Cl molar ratios is expected. To probe this aspect a new suite of experiments was performed using the same solid concentration (0.88 g/L) as previous experiments but changing the initial NH$_2$Cl concentration to obtain different solid to NH$_2$Cl molar ratios.

Figure 4.3a displays the consumption of NH$_2$Cl profile observed in the experiment conducted using 12m-aged-PbO$_2$ and a 15.4 mg/L initial concentration of NH$_2$Cl (solid to NH$_2$Cl molar ratio of 17). The results observed for a control experiment of NH$_2$Cl auto-decomposition in the absence of solid PbO$_2$ under the same conditions are also shown for comparison. Both experiments yielded the same NH$_2$Cl decay rates, which followed an apparent second-order rate law (Table 4.1). This seems to indicate that there is no direct stoichiometric interaction between PbO$_2$ and NH$_2$Cl. On the contrary, this observation suggests that the reaction between PbO$_2$ and NH$_2$Cl is a surface-controlled process, with the active sites/species in PbO$_2$ acting as the limiting reactant under low solid to NH$_2$Cl molar ratio conditions. This scenario is further explored in Section 4.3.5. In comparison with the auto-decomposition control experiment (no PbO$_2$ solid present) carried out at a lower initial NH$_2$Cl concentrations (1.5 mg/L, Figure 4.2a), the decay rate was faster at the higher initial NH$_2$Cl concentration. This is consistent with previous studies.\textsuperscript{8, 22}
Figure 4.3 a) Decomposition of NH$_2$Cl, b) lead dissolution profiles, and c) relationship between dissolved lead concentrations and NH$_2$Cl consumption for the 12m-aged-PbO$_2$ solid at two different initial NH$_2$Cl concentrations (1.5 and 15 mg/L).
A continuous decrease in pH values over time was also observed in the experiments performed at high initial NH$_2$Cl concentration (PbO$_2$/NH$_2$Cl ratio = 17) over 30 days as shown in Figure B.1d, Appendix B. This is consistent with previously reported observations by Leao (1981)$^{23}$ where a decrease in pH (~0.15 pH units) during monochloramine auto-decomposition was observed for experiments carried using a relatively high initial NH$_2$Cl concentrations (100 mg/L). This decrease in pH value is likely due to hydronium ions released during NH$_2$Cl auto-decay$^{24}$. By contrast, a slightly decrease in pH values was observed initially (rebounding later close to initial pH values) for the experiment carried with 1.5 mg/L NH$_2$Cl (PbO$_2$/NH$_2$Cl ratio = 174) described in section 4.3.2 (Figures B.1a-c).

The results obtained for lead dissolution on this set of experiments are shown in Figure 4.3b. Consistently with previous studies$^{8, 9, 25}$, more dissolved lead was released from the experiment conducted with higher initial NH$_2$Cl concentration (PbO$_2$/NH$_2$Cl ratio = 17). As mentioned in the previous section a linear correlation between loss in NH$_2$Cl and dissolved lead released from PbO$_2$ has been reported by Li and Valentine$^{8}$, however, did not observe for the case of the experiments run at high PbO$_2$/NH$_2$Cl molar ratios (174, Section 4.3.2) in this study. For the case of the experiments carried out at lower PbO$_2$/NH$_2$Cl molar ratios (17), a correlation was indeed observed between the dissolved lead concentrations and the consumed NH$_2$Cl ($\Delta$NH$_2$Cl) as shown in Figure 4.3c. This linear trend, however, was not observed for the whole range of $\Delta$NH$_2$Cl values. Specifically, for the experiment carried on 12m-aged-PbO$_2$ with solid to NH$_2$Cl molar ratio 17, a linear trend was observed up to $\Delta$NH$_2$Cl values close to 5 mg/L, then the dissolved lead levels reached plateau even though another 4 mg/L of NH$_2$Cl was consumed. This observation suggests that the system reached a pseudo steady state where NH$_2$Cl decay may remain constant. Thus, the unknown intermediate species released from monochloramine decomposition could trigger the elevated lead dissolved from 12m-aged-PbO$_2$ in the presence of excessive monochloramine.

The solid samples collected at 30 days were characterized via XRD. The XRD patterns are shown in Figure B.2 in Appendix B. They are very similar to those obtained on the same samples before dissolution, indicating that the residual solid was still $\beta$-PbO$_2$. This suggests
that NH₂Cl is unable to reduce Pb(IV) to Pb(II) through a solid-state transformation process, but it or its decomposition intermediate species could accelerate PbO₂ dissolution and release dissolved lead when the concentration of NH₂Cl is relatively high as the experimental results described above.

4.3.4 The effect of dissolved lead (Pb⁺²) on NH₂Cl decay

Previous studies²⁶-²⁸ have reported that dissolved Fe(II) and Cu(II) could catalyze the auto-decomposition of NH₂Cl. It is thus plausible to propose a scenario where dissolved Pb⁺² ions generated during PbO₂ dissolution could catalyze monochloramine decomposition. To explore this possibility, an experiment was performed where 12m-aged-PbO₂ was exposed to an aqueous solution of NH₂Cl (1.5 mg/L with PbO₂/NH₂Cl ratio = 174) in the presence of dissolved Pb⁺² ions (~0.1 mg/L Pb⁺²) introduced by adding an aqueous solution of Pb(II) ions. Two parallel experiments were carried out as controls: one with only NH₂Cl (no PbO₂ solid nor dissolved Pb⁺²) and another one with NH₂Cl and dissolved Pb⁺², but no PbO₂ solid. The results are shown in Figure 4.4. The results clearly show that the decomposition rates of NH₂Cl were not affected by the presence of dissolved aqueous lead. Similarly, dissolved aqueous lead did not play a role in the decomposition of NH₂Cl in the presence of 12m-aged-PbO₂. A faster monochloramine decomposition rate was indeed observed in the experiment of solid PbO₂ and NH₂Cl than the one without the PbO₂ solid, but as stated above, it is unaffected by the presence of aqueous Pb⁺². This result agrees a hypothesis that the reaction between PbO₂ and NH₂Cl is a surface-controlled process. Although the dissolved lead would adsorb on PbO₂ surface²⁹, this adsorption did not affect the decomposition rate of monochloramine, indirectly suggesting that adsorbed dissolved lead is an inactive site for monochloramine decomposition.
Figure 4.4 NH$_2$Cl decomposition profile obtained on 12m-aged-PbO$_2$ samples and in the presence of dissolved Pb$^{+2}$ ions (no PbO$_2$ solid added). The results of monochloramine auto-decomposition are also presented as reference.

4.3.5 The effect of solid to NH$_2$Cl molar ratios on NH$_2$Cl decomposition

As previously discussed, Figure 4.5 depicts the observed lead dissolution concentrations as a function of monochloramine consumption in all experiments carried out in this Chapter. The data presented can be rationalized in terms of two different reaction regimes. Regime one occurs at high PbO$_2$ solid to NH$_2$Cl molar ratios, where NH$_2$Cl is the limiting reagent, and monochloramine decomposition rates are faster than the auto-decomposition rate, with only limited amounts of lead released from dissolution of PbO$_2$. Regime two takes place at low PbO$_2$ solid to NH$_2$Cl molar ratios, and describes a scenario where the active species for monochloramine decomposition present on the PbO$_2$ solid are limited such that monochloramine decomposition rates are similar to those observed for auto-decomposition. This regime also results in elevated levels of lead released. The presence of these two different regimes explain the contrasting trends observed in our study and the work of Lin and Valentine$^8$ who used a low PbO$_2$ solid to NH$_2$Cl molar ratio.
To explore the possible scenarios for a reaction mechanism within each regime, solid samples before and after dissolution experiments were characterized using UV/Vis/NIR spectroscopy. As discussed in Section 4.3.1 the visible band edge and the NIR band are linked to the electronic structure of PbO₂. Figures B.3a and 3b in Appendix B show the NIR spectra obtained on the unaged- and 12m-Cl²⁰-PbO₂ before and after NH₂Cl decomposition experiments performed at an initial nominal NH₂Cl concentration of 1.5 mg/L (regime 1, high solid to NH₂Cl molar ratio), respectively. In both figures, the NIR spectra obtained on unaged-PbO₂ sample in a dissolution control test (no NH₂Cl present) are also included. For the experiments carried out under regime 2, Figure B.3c shows the NIR spectra obtained on 12m-aged-PbO₂ before and after NH₂Cl decomposition performed at an initial nominal NH₂Cl concentration of 15 mg/L (low PbO₂ solid to NH₂Cl molar ratio). For all these PbO₂ samples, their NIR band positions were plotted versus the time at which the solid samples were collected (Figure 4.6). Regardless of the PbO₂ solid to NH₂Cl molar ratio, all the NIR bands shifted to shorter wavelengths during dissolution either in the presence or absence of NH₂Cl. However, two different trends can be observed. One is obtained on the PbO₂ samples collected in experiments carried out using unaged-
PbO₂ and 12m-Cl₂⁰-PbO₂ with initial 1.5 mg/L NH₂Cl concentration as well as on the control experiment performed with unaged-PbO₂ sample without monochloramine. The second one is observed only for the experiment conducted at low PbO₂ solid to NH₂Cl molar ratios.

Figure 4.6 NIR band position shift observed for unaged-PbO₂, 12m-Cl₂⁰-PbO₂, and 12m-aged-PbO₂ solids in dissolution experiments using 1.5 or 15 mg/L of NH₂Cl over time. The NIR band position of unaged-PbO₂ samples collected in a control experiment (no NH₂Cl) is also included for reference.

In the first set of experiments (Regime 1, high PbO₂ solid to NH₂Cl molar ratio), the NIR band of unaged-PbO₂ in the presence of NH₂Cl shifted to similar positions to that observed in its control test (unaged-PbO₂ without the addition of NH₂Cl). This suggests that water but not monochloramine is the driving force for the blue shift in the NIR band, which in turn indicates that additional free electrons/defects are generated during the dissolution experiments, and likely due to the action of water on the lead oxide solid. Although the presence of NH₂Cl did not trigger a more substantial shift of this band, NH₂Cl was depleted at a faster rate (compared to its auto-decomposition rate, Figures 4.2a and 4.2b). The
obtained lead release profiles (Figure 4.2c) show that soluble lead concentrations were slightly lower in the presence of NH$_2$Cl than in the control test (carried out without NH$_2$Cl). This suggests that NH$_2$Cl did not enhance lead dissolution under the conditions of regime 1. These observations can be rationalized in terms of active sites in the PbO$_2$ solid that accelerate NH$_2$Cl decomposition but do not result in the generation of additional free electrons/defects in solid PbO$_2$ or the release of soluble lead species. Thus, the reaction is unlikely to proceed through the formation of Pb(II) in the solid phase as the extra electrons formed in this case would drive a substantial NIR band shift. We could hypothesize however that a possible mechanism taking place in regime 1 is associated with interstitial species present in the solid PbO$_2$ lattice, which react with NH$_2$Cl. These interstitial species would not contribute to generate electrons/defects in PbO$_2$ or affect its solubility.

The trendline observed for NIR band position obtained on the 12m-aged-PbO$_2$ before and after NH$_2$Cl decomposition experiments performed at an initial nominal NH$_2$Cl concentration of 15 mg/L (low PbO$_2$ solid to NH$_2$Cl molar ratio) shows a much more significant blue shift compared to that of the samples collected under Regime 1 in the presence of initial 1.5 mg/L of monochloramine. As discussed above, the NIR shift observed in the 12m-Cl$_2^0$-PbO$_2$ under Regime 1 is attributed to water action. Clearly, the larger degree of blueshift observed for 12m-aged-PbO$_2$ in regime 2 is due to the presence of NH$_2$Cl excess. Additionally, the most significant shift occurred within 10 days as there was only a slight blue-shift at 30 days compared to that observed after 10 days (Figure 4.6). This band shift is consistent with the lead release profile in Figure 4.3b in which a sharp increase in lead levels occurred during the first 10 days then decreased slightly at 30 days.

Using this information, a reaction mechanism can be proposed under reaction regime 2 (low solid to NH$_2$Cl molar ratio). It is known that β-PbO$_2$ is in a tetragonal rutile structure, in this arrangement Pb(IV) is in the center of a distorted octahedron surrounded by six oxygen ions. The neighboring octahedra form linear chains with sharing opposite edges. The resulting chains are connected to each other by sharing oxygen atoms at the corners. When dissolution occurred, Pb$^{+2}$ would be released starting from edges/kinks of the crystal.
Thus, we could propose that NH$_2$Cl and/or an unknown intermediate species generated during NH$_2$Cl decomposition promotes the formation of electrons/defects by cleaving the imperfect connection between the PbO$_6$ octahedra chains, resulting in generation of oxygen vacancies at the point where PbO$_6$ octahedra chains connect (shared corners of oxygen atoms). Meanwhile coordinatively unsaturated Pb(IV) formed at the edges of crystal could be coordinated by NH$_2$Cl or another Lewis base intermediate species released from NH$_2$Cl decay and form complexes that can be transferred to the aqueous phase, resulting in elevated dissolved lead concentrations. When new solid surface/planes are exposed to the aqueous phase, a relatively fast exchange of Pb$^{2+}$(aq) and PbO$_2$(s) occurs, and finally a steady state reached.

While two possible reaction regimes are proposed, and a potential mechanism is speculated for Regime 2, several questions remain. First: the identity of the active sites or species present on the PbO$_2$ structure that are active for NH$_2$Cl decomposition is still unknown. Moreover, the reaction pathway of NH$_2$Cl decay in the aqueous phase was not addressed. Furthermore, our results indicate that Cl$\text{O}^0$-PbO$_2$, had the highest reactivity toward monochloramine decomposition amongst all PbO$_2$ samples tested on this Chapter. Thus, it is plausible to propose that newly formed PbO$_2$ might have an even higher activity toward monochloramine decomposition than all other PbO$_2$ samples used in this study.

### 4.4 Environmental implications

From this study, a surface reaction was observed between PbO$_2$ and NH$_2$Cl that commonly used as an alternative disinfectant in DWDS. The rate of this reaction heavily depends on the surface properties of PbO$_2$ and the PbO$_2$ solid to NH$_2$Cl molar ratio. Specifically, the age and the number of defects in PbO$_2$ determines the number of active sites/species that accelerate NH$_2$Cl decay. Under high solid to NH$_2$Cl molar ratio conditions, chlorinated PbO$_2$ revealed the highest reactivity amongst all PbO$_2$ used in this study. It is known that PbO$_2$ is a dominant phase formed in the surface layer of lead corrosion scales under chlorination conditions in DWDS. PbO$_2$ formed in lead service lines is most likely to contain an unaged surface since it is not exposed to air. This scenario needs to be considered by municipalities considering a disinfectant switch to monochloramine to avoid elevated lead levels in drinking water.
References


Chapter 5

5 The role of PbO$_2$ structure on monochloramine decomposition

5.1 Introduction

The presence of lead in drinking water is mostly the result of corrosion of lead-bearing plumbing materials used in drinking water distribution systems (DWDS). Historically, free chlorine has been commonly used as disinfectant for drinking water treatment. Under chlorination conditions, PbO$_2$ is formed in the surface layer of corrosion scales.$^{1-4}$ Although free chlorine is an effective disinfectant to kill bacteria and pathogens, it is a strong oxidant and generates disinfectant by-products (DBPs) that are potential carcinogens. Therefore, monochloramine, a weaker oxidant, has been used as substitute of free chlorine by some municipalities. However, elevated lead concentrations have been observed at customer’s tap water when this switch occurred. The sudden decrease in redox potential due to the disinfectant switch is believed to trigger lead leaching. Lin and Valentine$^5$ reported that PbO$_2$ present in the lead plumbing corrosions scale could be reduced by a unknown intermediate species released from NH$_2$Cl decomposition, resulting in the release of elevated dissolved lead concentrations. While other studies$^6, 7$ have been performed to further understand the impact of NH$_2$Cl on PbO$_2$ dissolution, these did not address the effect of monochloramine/PbO$_2$ ratios.

Our previous study$^8$ has reported that the electronic structure of PbO$_2$ changes during the chlorination process. In addition, an aging effect on the stability of PbO$_2$ was observed in the previous Chapter, there we also reported that the surface properties of PbO$_2$ had a big impact on monochloramine decomposition, with the faster decompositions rates observed for the case of newly formed PbO$_2$. As the results discussed in Chapter 3, lead compounds present in field corrosion scales are in crystalline form. In general, two steps, nucleation and crystal growth, occur during the solid crystallization. For PbO$_2$ crystallization, secondary nucleation might be the most plausible mechanism for crystal growth as previous studies$^4, 9, 10$ report that precipitation of lead carbonates precedes PbO$_2$ formation. Under typical drinking water conditions, crystal growth might be a slow process since the
concentration of dissolved lead is very low (compared to other ions present), resulting in very short-range ordered or imperfect crystals. The presence of other ions in drinking water (such as carbonates) could also interfere with PbO\textsubscript{2} crystallization. Lin and Valentine\textsuperscript{7} evaluated the effect of PbO\textsubscript{2} particle size on its dissolution in the presence of a combination of monochloramine, chlorine, and natural organic matter. They reported that more dissolved lead released from reagent grade PbO\textsubscript{2} (~200 nm) than that from synthesized PbO\textsubscript{2} (~20 nm). This unexpected low reactivity observed on the nanoparticles was attributed to extensive particle aggregation. It should be noted that their experiments were conducted at low PbO\textsubscript{2}/NH\textsubscript{2}Cl molar ratios (1.5). There is a lack of information in the open literature on the effect of particle size of PbO\textsubscript{2} on its stability at high PbO\textsubscript{2}/NH\textsubscript{2}Cl molar ratios.

In the previous Chapter, we proposed that the reaction between PbO\textsubscript{2} and NH\textsubscript{2}Cl is a surface-controlled process that can take place under two different regimes. However due to the heterogeneity of the PbO\textsubscript{2} samples tested in the previous Chapter, we were unable to identify the exact identity of the active species in PbO\textsubscript{2} and a mechanism for monochloramine decomposition, although we speculated that it could be linked to interstitial species. In this Chapter we attempt to minimize the heterogeneity of the solid sample and assess the effect of PbO\textsubscript{2} particle/crystallite size and surface functional groups on its activity for monochloramine decomposition. An attempt at establishing a mechanism for the reaction between PbO\textsubscript{2} and NH\textsubscript{2}Cl is also presented.

5.2 Experimental section

**Materials.** NaHCO\textsubscript{3} (Sigma-Aldrich, ≥ 99.5%) was used as source of dissolved inorganic carbon (DIC), while NaNO\textsubscript{3} (Sigma-Aldrich, ≥ 99.0%) was used to prepare a 0.01 M ionic strength (IS) stock solution. NH\textsubscript{4}Cl (Sigma-Aldrich, 99.998% trace metals basis) was used as the source of free ammonia. Following the method developed by Vikesland\textsuperscript{11}, 1 mM NH\textsubscript{2}Cl was freshly prepared mixing volumes of NaOCl (Sigma-Aldrich, reagent grade) and 20 mM NH\textsubscript{4}Cl in ultrapure water to achieve a 0.79 Cl/N molar ratio.

**Synthesis of PbO\textsubscript{2}**. Plattnerite (β-PbO\textsubscript{2}) particles were synthesized from the oxidation of minium (Pb\textsubscript{3}O\textsubscript{4}) following Kang et al.\textsuperscript{12}'s method. Three synthesized PbO\textsubscript{2} samples were
prepared based on his method. To prepare the first sample (labelled as \( \text{n-PbO}_2 \)), 12.5 g \( \text{Pb}_3\text{O}_4 \) was mixed in 300 ml of 1 N HNO\(_3\) solution with a magnetic stir bar at 350 rpm for 1 hour. Then the mixing was stopped, and the stir bar was taken out. The suspension was kept in static mode for 12 hours before filtration. A glass microfiber filter (696, VWR) was used in vacuum filtration set (250ml, Nalgene) to separate the solid particles from the solution. The solid collected was washed using mega-pure water through filtration until the pH of filtrate was close to the pH of the mega-pure water. Then the filter with the washed particles was dried in a vacuum desiccator for 2 days. The second synthesized \( \text{PbO}_2 \) sample (labelled as \( \mu\text{-PbO}_2 \)) was prepared in the exactly same manner as \( \text{n-PbO}_2 \) sample except that the suspension was kept for 11 days instead of 12 hours in static mode. The third \( \text{PbO}_2 \) sample was prepared following the same protocol used to prepare \( \mu\text{-PbO}_2 \), but the solid sample was collected at 30 days of reaction instead of 11 days (labelled as \( \mu\text{-PbO}_2\)-30 days).

**Thermal treated \( \text{PbO}_2 \).** About 1 g of dry synthesized \( \text{PbO}_2 \) solid was loaded into a plug flow reactor (PFR, quartz) for thermal treatment. The scheme of the gas flow system is presented in Figure C.1 in Appendix C. Four different conditions were used to modify the surface of the original \( \text{n-PbO}_2 \). Specifically, \( \text{N}_2(\text{g}) \) (Ultra high purity, Praxair), dry air (Ultra-Zero, Praxair), \( \text{H}_2(\text{g}) \) (5% \( \text{H}_2 \) in \( \text{Ar} \), Praxair), and steam in \( \text{N}_2(\text{g}) \) were used to simulate inert, oxidizing, reducing, and humid conditions respectively, in generating surface modified \( \text{PbO}_2 \). The obtained samples are labeled I-\( \text{n-PbO}_2 \), O-\( \text{n-PbO}_2 \), H-\( \text{n-PbO}_2 \), and W-\( \text{n-PbO}_2 \), respectively. To prepare I-\( \text{n-PbO}_2 \), thermal treatment with \( \text{N}_2(\text{g}) \) were performed at 180 °C for 2 hours at gas flow rate of 40 ml/min. To obtain O-\( \text{n-PbO}_2 \) thermal treatment in dry air was carried out at 180 °C for 2 hours at gas flow rate of 40 ml/min. H-\( \text{n-PbO}_2 \) was obtained in \( \text{H}_2(\text{g}) \) at 180 °C for 3 hours using a flow rate of 52 ml/min. For the case of the W-\( \text{n-PbO}_2 \), mega-pure water was injected at heated port (110°C) via a syringe pump at 0.08 ml/min (liquid flow rate) into a \( \text{N}_2(\text{g}) \) flow (40 ml/min) at 180 °C for 2 hours. All gas lines were kept at 120°C to avoid water condensation.

Two additional samples were prepared, but using the \( \mu\text{-PbO}_2 \) synthesized sample as starting materials. One of these samples, I-\( \mu\text{-PbO}_2 \), was prepared using a flow of 50 ml/min of \( \text{He}(\text{g}) \) and heated at 180 °C for 2 hours. Another sample, H\(_2\)W-\( \mu\text{-PbO}_2 \), was thermally treated in
steam mixed with \( \text{H}_2\text{(g)} \) gas at 180 °C for 2 hours with a 50 ml/min flow rate. Steam was generated following the same protocol described above.

**Characterization of synthesized \( \text{PbO}_2 \).** Solid samples were characterized via X-ray powder diffraction (XRD) and UV/Visible/Near-Infrared (UV/Vis/NIR) spectroscopy. A Rigaku RPT 300 RC diffractometer using Co K-\( \alpha \) (\( \lambda=1.78890 \) Å) radiation was used to obtain XRD profiles over the range of 10-70° 2\( \theta \) using a 0.02° step size. Reflectance UV/Vis/NIR spectra were obtained in the range of 200-1600 nm using a 1 nm step size and the highest resolution setting of the instrument using a diffuse reflectance cell (Harrick, Praying Mantis) attached to a UV-3600 Shimadzu. Then pseudo-absorption spectra were generated using a Kubelka-Munk function in the UVProbe® software. BET \( \text{N}_2 \)-adsorption isotherms were obtained for both synthesized (n-\( \text{PbO}_2 \) and \( \mu \)-\( \text{PbO}_2 \)) samples and commercial \( \text{PbO}_2 \) solid (labeled as aged-\( \text{PbO}_2 \) in Chapter 4).

**\( \beta \)-\( \text{PbO}_2 \) batch dissolution experiments.** Batch dissolution experiments were preformed following the protocol described in the previous Chapter. In brief, either 25ml vails or 300ml bottles were used as reactors with 0.88 g/L solid concentration filled full of stock solution (0.01 M IS, 20 mg C/L DIC, and initial 1.5 mg/L \( \text{NH}_2\text{Cl} \) concentration at an initial pH value close to 8 [unbuffered]). A \( \text{PbO}_2/\text{NH}_2\text{Cl} \) molar ratio of 174 was used in the dissolution experiments to ensure the reaction proceeded under Regime 1 conditions. All reactors were placed inside a box on an orbital shaker rotating at 170 rpm. The box was closed tight to avoid photodecomposition. Sacrificial samples were collected for both aqueous and solid phases samples. The dissolved lead concentrations, \( \text{NH}_2\text{Cl} \) concentrations, and pH values were measured for each sample.

To explore the longevity of reactive species in \( \text{PbO}_2(\text{s}) \), \( \text{NH}_2\text{Cl} \) spike batch dissolution experiments were conducted followed a similar experimental methodology as the one described above. Instead of carrying the experiment under \( \text{NH}_2\text{Cl} \) depleting conditions, 1mM \( \text{NH}_2\text{Cl} \) was spiked into all the rest reactors after every 1-hour reaction interval to obtain a \( \text{NH}_2\text{Cl} \) concentration close to 1.5 mg/L again during each spike. Three or four single samples were collected over the course of the 1-hour interval. Five to six spiking events took place during each experiment. Different \( \text{PbO}_2 \) solid concentrations (0.08, 0.11,
0.4, and 0.88 g/L) were also tested in the spike experiments using different PbO₂ solid to NH₂Cl molar ratios, 16, 22, 79, and 174 respectively.

**Analytical methodology.** NH₂Cl (mg Cl₂/L) and free ammonia concentration (mg N/L) were measured following the indophenol method (Method 10200, Hach) using an UV/Vis spectrophotometer (Hach, DR5000). The same instrument was used to measure free chlorine concentration (mg Cl₂/L) followed the standard DPD colorimetric method (Method 10069, Hach). Inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian, Vista-Pro 97 Axial) or inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific, iCAP Q) was used to measure dissolved lead concentrations. The pH values were measured using a pH meter (Thermo Scientific, Orion Star A111) with a glass pH probe that was calibrated via the three-points calibration method (pH of 4, 7, and 10).

Aliquots of the suspension were taken from batch reactors to determine the values of ξ-potential of the samples using a zeta-potential analyzer (Brookhaven Instrument, ZetaPlus). 3 cycles of measurement were performed for each ξ-potential measurement. 10 measurements were conducted for obtaining the ξ-potential of n-PbO₂ since it has small particles and suspends relatively well. In contrast, μ-PbO₂ sample had larger particles and settled relatively fast during the ξ-potential measurement. Thus 5 measurements were performed for determining its ξ-potential values. Then the average value of these 10 or 5 measurements was reported as the ξ-potential value for n-PbO₂ or μ-PbO₂ with the standard error as the error bar respectively.

### 5.3 Results and discussion

#### 5.3.1 The effect of PbO₂ crystalline structure on its activity for NH₂Cl decomposition

The XRD patterns of three synthesized PbO₂ solids (n-PbO₂, μ-PbO₂, and μ-PbO₂-30 days) are shown in Figure 5.1. The results indicate that both have the crystalline structure of β-PbO₂. When comparing the obtained XRD pattern for n-PbO₂ with that one obtained on a commercial PbO₂ (also shown in Fig. 5.1), it is clear to see that the n-PbO₂ sample shows a larger level of noise and broader peak width suggesting the n-PbO₂ sample particles
contained small crystalline size and likely some amorphous phase. In contrast, the \(\mu\)-PbO\(_2\) diffractogram indicates well crystallized particles, which is expected as this sample crystallized over a period of 11 days compared to the 12hrs used to prepare the n-PbO\(_2\) sample. Comparing the XRD patterns of the two samples: \(\mu\)-PbO\(_2\) and \(\mu\)-PbO\(_2\)-30 days, no detectable difference was observed between them. This indicates that the oxidation reaction of Pb\(_3\)O\(_4\) by 1N HNO\(_3\) has already completed and formed \(\beta\)-PbO\(_2\) with a well crystallized structure after 11 days. From this point onward PbO\(_2\) refers to \(\beta\)-PbO\(_2\). The crystallite sizes of all these samples discussed above were calculated using Scherrer equation using the full width at half maximum values. n-PbO\(_2\) has the smallest crystallite size of 4.57nm amongst all samples, while commercial PbO\(_2\), \(\mu\)-PbO\(_2\), and \(\mu\)-PbO\(_2\)-30 days have a similar crystallite size (around 55 nm).

Figure 5.1 XRD patterns of three synthesized PbO\(_2\) and a commercial PbO\(_2\) (unaged) solid samples.

Figure 5.2 shows the UV/Vis/NIR spectra obtained on the same set of samples. n-PbO\(_2\) and \(\mu\)-PbO\(_2\) samples display a distinct spectrum compared to that obtained on the commercial PbO\(_2\). For the optical band edge/gap, n-PbO\(_2\) sits at the shortest wavelength (the highest energy) amongst all samples, followed by commercial PbO\(_2\), and both \(\mu\)-PbO\(_2\) samples (\(\mu\)-PbO\(_2\)-30 days and \(\mu\)-PbO\(_2\)). As described in the previous chapter, the optical band gap that define the energy required for electronic transitions from the valence band to the
conduction band in solids can be calculated from the UV/Vis/NIR spectra. It is well established that the optical band gaps are related to the average domain size of metal oxides. For a crystalline semi-conductor, a decrease in domain/crystallite size results in a higher optical band gap. Thus, the n-PbO₂ sample with the highest optical band gap (1.97 eV) has the smallest domain size, then followed by commercial PbO₂ (1.69 eV) and both μ-PbO₂ samples (1.56 eV). These values are shown in Table 5.1. Interestingly, both synthesized μ-PbO₂ samples (μ-PbO₂ and μ-PbO₂-30 days) display a larger domain size than that of commercial PbO₂. Consistently, their BET results show that μ-PbO₂ contains a smaller specific surface area than that of commercial PbO₂ (Table 5.1). As described in the previous Chapter, the NIR band of PbO₂ is a result of photon absorption by free electrons that are present due to defects in non-stoichiometric PbO₂. Comparing with the NIR band of all samples characterized, n-PbO₂ sample displays a broad band centered in the range of 1350 to 1400 nm rather than a narrow band centered at a specific wavelength observed for the case of commercial PbO₂. This observation indicates that n-PbO₂ contains imperfect crystals with various defects such that free electrons are in relatively different environments, resulting in a wide range of adsorption. In contrast, commercial PbO₂ and μ-PbO₂ solids contain well-ordered crystal that are close to its stoichiometric value. To evaluate the impact of PbO₂ crystalline structure and/or crystallite size on the decomposition of monochloramine, these samples were tested in dissolution experiments.

![Figure 5.2 UV/Vis/NIR spectra of three synthesized PbO₂ and a commercial PbO₂ (unaged) solid samples.](image)

**Figure 5.2 UV/Vis/NIR spectra of three synthesized PbO₂ and a commercial PbO₂ (unaged) solid samples.**
Table 5.1 Specific surface area and optical band gap values of three synthesized PbO₂ samples.

<table>
<thead>
<tr>
<th></th>
<th>specific surface area (m²/g)</th>
<th>Optical band gap (E₉, eV)</th>
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<tbody>
<tr>
<td>n-PbO₂</td>
<td>21.3</td>
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<tr>
<td>μ-PbO₂</td>
<td>0.31</td>
<td>1.56</td>
</tr>
<tr>
<td>commercial PbO₂</td>
<td>0.52</td>
<td>1.69</td>
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5.3.1.1 Lead release profiles and monochloramine decomposition in the presence of nano-sized n-PbO₂ under depleting monochloramine conditions.

Figure 5.3a shows the NH₂Cl decomposition profiles obtained for an initial 1.5 mg/L of NH₂Cl in the presence of 0.88 g/L of n-PbO₂ (solid to NH₂Cl molar ratio of 174) and in the absence of PbO₂ solid (NH₂Cl auto-decomposition) as control. Surprisingly, NH₂Cl was almost completely depleted within 1 hour in the presence of n-PbO₂, the depletion profile following pseudo 2ⁿᵈ-order kinetics. The NH₂Cl decomposition was so rapid that the residual NH₂Cl in the first sample collected at 2 min of reaction was only 0.8 mg/L (conversion 1-Cₜ/C₀ = 0.44). In contrast, NH₂Cl auto-decomposition was negligible during the first hour (Figure 5.3a). Comparing their 2ⁿᵈ-order kinetic constants, five orders of magnitude difference was observed in these experiments (Table 5.2). At the same time lower lead concentrations (<10 μg/L) were observed in the presence of NH₂Cl than in a control test run in the absence of monochloramine during the first 10 days as shown in Figure 5.3b. These observations are consistent with our previous study (Chapter 4) in which the presence of NH₂Cl inhibited the reduction of PbO₂ under high PbO₂/NH₂Cl molar ratio conditions. In comparison with the activity of commercial and chlorinated PbO₂ for NH₂Cl decomposition presented in the previous chapter, n-PbO₂ displayed the highest activity (Table C1 in Appendix C). This supports our original hypothesis proposed in Chapter 4 that for the surface reaction between PbO₂ and NH₂Cl, a newly formed surface has the highest activity for monochloramine decomposition.
Figure 5.3 a) NH$_2$Cl decomposition profiles, b) lead dissolution profiles, and c) pH profiles obtained on dissolution experiments using solid n-PbO$_2$ and on an aqueous filtrate of aged-n-PbO$_2$ under depleting NH$_2$Cl conditions. The results of two control tests (n-PbO$_2$ dissolution without NH$_2$Cl and NH$_2$Cl auto-decomposition) are also shown.
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<tr>
<th>Experiments</th>
<th>Solid reactant</th>
<th>Stock solution</th>
<th>Disinfectant type</th>
<th>Initial concentration of disinfectant (mg Cl₂/L)</th>
<th>Number of spikes</th>
<th>Observed 2nd-order kinetic constant ((\text{mM}^{-1} \times \text{day}^{-1}))</th>
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<td>n-PbO₂</td>
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<td>N/A</td>
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<td>Observed 2nd-order kinetic constant* (mM⁻¹ x day⁻¹)</td>
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<td>9-4</td>
<td>W-n-PbO₂</td>
<td>NH₂Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>1.35</td>
<td>25ml</td>
<td></td>
</tr>
<tr>
<td>10-1</td>
<td>I-μ-PbO₂</td>
<td>NH₂Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>9.05</td>
<td>25ml</td>
<td></td>
</tr>
<tr>
<td>10-2</td>
<td>N/A</td>
<td>NH₂Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>0.97</td>
<td>25ml</td>
<td></td>
</tr>
<tr>
<td>10-3</td>
<td>H₂W-μ-PbO₂</td>
<td>NH₂Cl</td>
<td>1.5</td>
<td>N/A</td>
<td>7.6</td>
<td>25ml</td>
<td></td>
</tr>
</tbody>
</table>
It should be noted that dissolved lead concentrations in the experiment with monochloramine and n-PbO\textsubscript{2} remained relatively low (<10 μg/L) at 10 days even though NH\textsubscript{2}Cl had depleted within hours. In comparison, relatively high lead concentrations were observed in the early stage of the control experiment of n-PbO\textsubscript{2} in the absence of NH\textsubscript{2}Cl. This relatively high initial dissolved lead levels could be due to the presence of an amorphous and/or labile phase in n-PbO\textsubscript{2}. After 3 days, the lead concentrations in the control experiment decreased rapidly, reaching 9.4 μg/L at 30 days, and then a further decrease to 3.7 μg/L at 60 days. This decrease in lead concentration is most likely due to the crystallization of unstable or small crystallites n-PbO\textsubscript{2} according to Eqs. 5.1 and 5.2:

\[
PbO_2(\text{unstable}) + 2e^- + 2H_2O(l) \leftrightarrow Pb^{2+}(aq) + 4OH^- (aq) \tag{5.1}
\]
\[
Pb^{2+}(aq) + 4OH^- (aq) \leftrightarrow PbO_2(\text{stable}) + 2e^- + 2H_2O(l) \tag{5.2}
\]
\[
PbO_2(s) + H_2O(l) \leftrightarrow Pb^{2+}(aq) + 2OH^- (aq) + 0.5O_2(aq) \tag{5.3}
\]

Consistently, pH values in the control test continuously increased from 7.7 to 7.8 in 1 day and retained at this value until 10 days during which the unstable PbO\textsubscript{2} phase was reduced by water according to Eq. 5.1 dominantly, releasing ionic lead and resulting in the elevated lead aqueous concentrations. At the same time stable crystalline PbO\textsubscript{2} started to form via the electrons transferred through the PbO\textsubscript{2} solid due to its high conductivity (Eq. 5.2). The reduction of PbO\textsubscript{2} by water could also occur according to Eq. 5.3. Consequently, the pH values finally reached to 7.86 at 60 days (Figure 5.3c).

It is interesting to observe the pH value dropped to about 7.6 at 2 min of experiment of n-PbO\textsubscript{2} with NH\textsubscript{2}Cl (Figure 5.3c), while the pH values in NH\textsubscript{2}Cl auto-decay were close to initial pH value 8. It is known that the auto-decomposition rate of NH\textsubscript{2}Cl is faster in the solution with a lower pH value.\textsuperscript{5,20} However, as reported by Lin and Valentine\textsuperscript{5} an increase in an order of magnitude in the value of the second order kinetic constant is expected when pH value decreased from 8 to 7.6. Therefore, the dramatic increase in the value of the
The kinetic constant for monochloramine decomposition in the presence of the n-PbO$_2$ sample cannot be rationalized in terms of pH changes.

To explore a scenario in which soluble active species released during n-PbO$_2$ dissolution are responsible for monochloramine rapid decomposition, 600 mL of filtrate was collected after mixing the stock solution with 0.88 g/L 3-month old n-PbO$_2$ (labelled as aged-n-PbO$_2$) for 30 minutes. Then 1 mM NH$_2$Cl was spiked into a 500 ml batch reactor filled full of filtrate to obtain an initial 1.5 mg/L NH$_2$Cl concentration. The monochloramine decomposition and pH profiles obtained are shown in Figures 5.3a and 5.3c respectively. The aged-n-PbO$_2$ solid left after removing the original filtrate was mixed with fresh stock solution filled and spiked with 1 mM NH$_2$Cl to achieve the initial monochloramine concentration of 1.5 mg/L. The NH$_2$Cl decomposition profile obtained in this case is shown in Figure C.2a in Appendix C and compared with that of freshly prepared n-PbO$_2$.

Several interesting results were observed in these two experiments. Comparing with the swift NH$_2$Cl decomposition rate in the original experiment carried out using n-PbO$_2$, the decomposition of NH$_2$Cl in the filtrate of aged-n-PbO$_2$ solid has a very similar rate of that of its auto-decay (Figures 5.3a). In contrast, the remaining aged-n-PbO$_2$ solid displayed a higher activity for NH$_2$Cl decomposition, even though a lower reaction rate was observed for aged-n-PbO$_2$ compared to that observed for n-PbO$_2$, indicating that the aging process affects the activity of PbO$_2$ for monochloramine decomposition (Figure C.2a in Appendix C).

The most relevant consequence of these results is that the presence of the n-PbO$_2$ solid is responsible for the enhancement on the decay rate of NH$_2$Cl, and the active site/species that are linked to this enhancement are in the solid PbO$_2$ phase and not released from the solid during PbO$_2$ dissolution. Another relevant result is the difference in the pH values observed within the first hour. The pH values hover around 8.0 during the auto-decomposition of monochloramine. When the decomposition of monochloramine is carried out in the presence of n-PbO$_2$, the pH value drops from 8.0 to a value of 7.6 and hovers around this value during first hour. In comparison, when the same experiment is carried out using aged-n-PbO$_2$, the pH values do not significantly drop initially, instead hovering...
around 7.9 (Figure C.2b). This is unexpected since the only difference between n-PbO₂ and aged-n-PbO₂ is the aging treatment. Moreover, it cannot be attributed to the dissolution of a surface carbonate phase formed during samples aging (aged-n-PbO₂) since this would result in an increase of pH values. It is plausible to propose that species in PbO₂ linked to hydronium ions activity affect the pH and hence monochloramine decomposition. However, these species need to be present in a large enough amount to affect water quality, such as in the case of the unaged solid sample. For non-stoichiometric PbO₂, the inclusion of hydrogen into the crystalline PbO₂ structure has been proposed. Specifically, a few studies²¹-²⁴ have proposed that OH⁻ can substitute lattice O⁻² while Pb⁺² can substitute lattice Pb(IV) in PbO₂. Moreover, the loss in hydrogen content in PbO₂ has been linked to decrease in its electrochemical activity.²⁵, ²⁶ Therefore, we could hypothesize that the changes in pH values observed are linked to proton-bearing species in n-PbO₂ which either aged or lose mobility over time. We could speculate even further and attribute the high rates for monochloramine decomposition to the presence of these proton bearing species.

5.3.1.2 Lead release profiles and monochloramine decomposition in the presence of nano-sized n-PbO₂ under monochloramine excess.

During the dissolution of n-PbO₂ in the absence of monochloramine, the quality of the crystal structure substantially improves over time. This can be observed from a close inspection of Figure C.3a. Their crystallite sizes were calculated using Scherrer equation using the full width at half maximum values. The calculated crystallite sizes are plotted in Figure C.3b. In addition, as discussed in the previous section, monochloramine was almost depleted within 1 hour in the presence of n-PbO₂, suggesting the solid phase would remain active for decomposition of additional monochloramine. Thus, to explore the impact of crystal structure on the PbO₂ activity for monochloramine decomposition and the longevity of the active species in PbO₂, a series of NH₂Cl spiking experiments were performed using the n-PbO₂ solid (PbO₂ solid to NH₂Cl molar ratio of 174). In this experiment, sacrificial reactors were prepared. After an initial 1.5 mg/L of NH₂Cl (1ˢᵗ spike) completely depleted in approximately 1 hour, 1 mM of NH₂Cl was spiked into half of the reactors (2ⁿᵈ spike). This is the first part of this experiment, aiming to test the longevity of active species in PbO₂. The change in NH₂Cl concentration after this second monochloramine spike was
monitored using 4 reactors over 1-h reaction interval. Then a third spike of 1mM of NH$_2$Cl was added into the rest reactors, and the change in concentrations was monitored over the course of 1 hour. The other half of the reactors with the contents of the first spike experiments were kept sealed and shook for 30 days. After 30 days a second and third spikes of 1 mM NH$_2$Cl were introduced respectively into these reactors at two sequential 1-h reaction intervals.

Figure 5.4a (left, bottom axis) shows the NH$_2$Cl decomposition profiles obtained on the experiments where the second and third spikes took place after on hour following the first spike. Consistently, the initial 1.5 mg/L NH$_2$Cl spike was depleted within 1 hour at a rapid rate associated with a five orders of magnitude pseudo 2$^{\text{nd}}$-order kinetic constant (Table 5.2). While the NH$_2$Cl decomposition was still relatively fast for the second NH$_2$Cl spike, it was slower than the initial depletion rate and its observed 2$^{\text{nd}}$-order kinetic constant had only four orders of magnitude. For the third NH$_2$Cl spike, after 1 hour of reaction, the residual NH$_2$Cl concentration was about 0.57 mg/L which was higher than the ones observed after one hour of the second NH$_2$Cl spike (0.27 mg/L) and initial NH$_2$Cl depletion (0.03 mg/L, detection limit). This indicates that the active species in n-PbO$_2$ are consumed by NH$_2$Cl. For the second part of experiments (Figure 5.4a right, top axis) where the second spike took place after 30 days, the NH$_2$Cl decomposition rate measured after this second spike still yielded a four orders of magnitude kinetic constant, but it was slower than the rate observed for the decomposition of the second monochloramine spike conducted in the first part of experiments. The only difference between the second spike performed in the first half of the experiments and that of the second half is the PbO$_2$ solid in the second half of reactors being allowed to react with the mother solution 30 days longer. The XRD pattern obtained on the solid collected after 30 days (Figure C.3c) indicates that a higher quality crystal structure formed at 30 days. This suggests that the active species in PbO$_2$ was diminishing during the recrystallization of n-PbO$_2$, and further indicates the PbO$_2$ solid with a better crystal quality had lower activity for NH$_2$Cl decomposition.
Figure 5.4 a) Decomposition of NH$_2$Cl during three successive spikes, the dashed circles represent the initial target 1.5 mg/L NH$_2$Cl concentration, b) lead dissolution profiles, and c) pH profiles obtained on the same experiments.
The dissolved aqueous phase lead released from n-PbO$_2$ during these experiments are shown in Figure 5.4b. An increase in lead levels was observed with the accumulation of NH$_2$Cl in the first half of the experiments (all three monochloramine spikes one hour apart) from 6.7 μg/L at the end of first monochloramine spike to 22 μg/L after the third spike. In contrast, low lead levels (~6 μg/L) were observed after the third spike in the second half of experiments, where the second and third monochloramine spikes were carried out after 30 days. These results could be explained in terms of the recrystallization process taking place during these 30 days (Figure C.3c). Specifically, some small crystallites will dissolve and recrystallize onto larger crystals. This may explain also the relatively high lead concentrations released from n-PbO$_2$ in the first half of experiments, whereas the lead levels remained low in n-PbO$_2$ after 30 days of dissolution and concomitant crystal growth.

The pH values in this experiment were also monitored. The results are shown in Figure 5.4c. For both first and second half of experiments, their pH values hovered at lower values than the initial pH of 8, while slightly higher pH values were observed in the second half of experiments. Coincidently, the NH$_2$Cl decomposition rates in this case were slower than the corresponding values observed in the first part of experiment. At the same time a better crystal quality was observed in the half of experiments. Thus, all these experimental observations indicate that the crystal structure of PbO$_2$ plays a critical role in its stability toward dissolution either in the presence or absence of monochloramine, and that this crystal structure influence its activity for NH$_2$Cl decomposition.

5.3.1.3 Lead release profiles and monochloramine decomposition in the presence of micro-sized μ-PbO$_2$ under depleting monochloramine conditions.

To further explore the influence of crystalline structure of PbO$_2$ and its activity for NH$_2$Cl decomposition, synthesized PbO$_2$ with a well-defined crystal structure (μ-PbO$_2$) was used as starting material to conduct dissolution experiments in the presence of monochloramine using an initial 1.5 mg/L NH$_2$Cl concentration (PbO$_2$/NH$_2$Cl molar ratio of 174). As the μ-PbO$_2$ sample was collected after 11 days of oxidation of Pb$_3$O$_4$ in nitric acid, both its crystalline size and apparent particle size were relatively large as it increased during the long period allowed for crystal growth. To break down agglomerates and evaluate the
effect of apparent particle size on the activity of PbO₂ for NH₂Cl decomposition, a portion of μ-PbO₂ sludge prior to the filtration was stirred at about 500 rpm for 15 min. The resulting μ-PbO₂ solid was labelled as μ-PbO₂_stir. This solid was used to conduct the dissolution experiment under the same conditions as those used in the n-PbO₂ experiment. The monochloramine decomposition profiles obtained on these two solids are shown in Figure 5.5a, the results of a 1.5 mg/L NH₂Cl auto-decomposition control test are also included. Similar NH₂Cl decomposition rates were observed for both μ-PbO₂ and μ-PbO₂_stir, indicating no significant changes in μ-PbO₂ due to stirring or agglomeration. Moreover, their NH₂Cl decomposition rates were much slower than the one observed in the experiment carried out using the n-PbO₂ solid (Figure 5.3a). This may be attributed to two factors: the first factor is the specific surface area. n-PbO₂ (21.3 m²/g) has much larger specific surface area than that of μ-PbO₂ (0.31 m²/g), thus it is expected to observe a faster rate in the experiment with n-PbO₂. Comparing with about 70 times increase in the specific surface area, the kinetic constant, however, increased about 570 times when we compared that of n-PbO₂ (18668 mM⁻¹*day⁻¹) and μ-PbO₂ (32.26 mM⁻¹*day⁻¹). Thus, the higher observed rate is not only due to a difference in surface area but to another factor linked to the quality of the crystalline structure. Hill and Houchin²⁷ reported that the concentration of active species present in PbO₂ necessary for electrochemical activity decreased when the quality of the crystalline structure of PbO₂ improved. Compared to μ-PbO₂, n-PbO₂ has a smaller crystallite size and short-range ordered structure. The decrease in activity for monochloramine decomposition of μ-PbO₂ compared with that of n-PbO₂ confirms our hypothesis that when the PbO₂ solid possess a better crystalline structure it will have a lower activity for NH₂Cl decomposition.
Figure 5.5 a) NH$_2$Cl decomposition profiles, b) lead dissolution profiles, and c) pH values in monochloramine decomposition experiments carried out using μ-PbO$_2$, μ-PbO$_2$-stir, and Cl$_2$*-PbO$_2$ solids with initial 1.5 mg/L NH$_2$Cl concentration.
It should be noted that the kinetic constants values observed in the experiments with μ-PbO₂ and μ-PbO₂_stir were still two orders of magnitude larger than those obtained for NH₂Cl auto-decomposition (Table 5.2). Moreover, their kinetic constants were also one order of magnitude larger than those obtained for the NH₂Cl decomposition experiment using unaged-PbO₂ discussed in the previous Chapter (4 mM⁻¹day⁻¹, Table 4.1). Interestingly, the specific surface area of μ-PbO₂ is about two times lower than that of unaged-PbO₂, however a faster NH₂Cl decay rate was observed for the μ-PbO₂. These results indicate not only that there is not a proportional correlation between PbO₂ surface area and activity for monochloramine decomposition, but that monochloramine decomposition is regulated by the quality of the PbO₂ solids: when the PbO₂ solids have comparable crystallite size the freshness of the surface plays a dominant role in the decomposition of NH₂Cl. This is consistent with the observations depicted on Chapter 4.

Although the synthesized μ-PbO₂ sample has an analogous specific surface area and crystalline structure to those of commercial PbO₂, it may not be comparable with the PbO₂ solids that are commonly observed in the corrosion scales formed under chlorination conditions (Chapter 3 and previous published work⁸). Based on the discussion portrayed in Chapter 4, chlorinated PbO₂ had the highest activity for NH₂Cl decomposition amongst all commercial samples used in dissolution experiments under depleting NH₂Cl conditions. Thus, a chlorinated PbO₂ sample (Cl₂*-PbO₂) was prepared using 22 g/L of commercial PbO₂ as starting materials and forced to react with an initial concentration of 44 mg/L free chlorine under stirring (200 rpm). After 26 days, the chlorinated PbO₂ sludge was pipetted into 300 ml reactors that contained 0.5 mg/L of residual free chlorine concentration filled full of stock solution for further chlorination. After 206 days, chlorine had depleted entirely and then 1 mM of NH₂Cl was spiked into each reactor to generate an initial concentration of 1.5 mg/L NH₂Cl. Duplicated sacrificial samples were collected for each data point. The NH₂Cl decomposition profiles obtained are illustrated in Figure 5.5a, and they resemble those obtained for μ-PbO₂. Moreover, comparable low dissolved lead concentrations (< 10 µg/L) were also observed in all these three experiments (μ-PbO₂, μ-PbO₂_stir, and Cl₂*-PbO₂ in Figure 5.5b). These results suggest that μ-PbO₂ had similar activity and stability in terms of NH₂Cl decomposition as chlorinated PbO₂, and further indicates that a PbO₂ solid which contains a freshly prepared surface could enhance NH₂Cl decomposition.
Figure 5.5c shows the pH profiles of experiments of $\mu$-PbO$_2$, $\mu$-PbO$_2$\_stirr, and chlorinated commercial PbO$_2$ ($\text{Cl}_2^+$-PbO$_2$) under depleting NH$_2$Cl conditions. In contrast with the behavior observed for n-PbO$_2$, no initial pH drop was observed in these experiments. Their pH values slightly decreased within 1 day (~0.1 pH unit) then rebounded after 1 day, finally reaching values between 8.1 to 8.2. This is close to the pH profile of 1.5 mg/L NH$_2$Cl auto-decomposition that also included in Figure 5.5c. Similarly, the changes in pH values of control test (no NH$_2$Cl) of $\mu$-PbO$_2$ follow a similar trend in which no initial pH drop occurred. The initial pH drop was observed only for the n-PbO$_2$ sample, which contains small crystallites and not for the $\mu$-PbO$_2$ samples. This may indicate that proton-containing species are either not present or severely confined in the well crystallized PbO$_2$ sample with large crystallite size while it is semi-confined in the short-range ordered crystal, resulting in a decreased pH value. The mobility of proton-contained species in PbO$_2$ also decreased with the increase in the aging process.

5.3.2 A potential catalytical behavior of solid PbO$_2$ for monochloramine decomposition

Based on the results obtained on the NH$_2$Cl spike dissolution experiments discussed above, n-PbO$_2$ revealed a high activity for NH$_2$Cl decomposition even after 3 successive monochloramine spiking events that cumulatively resulted in a total monochloramine consumption of about 3.6 mg/L of NH$_2$Cl. This behavior seems to indicate that active species in PbO$_2$ could act as a catalyst for NH$_2$Cl decomposition. To explore this potential catalytical behavior and the longevity of the active species in PbO$_2$ that responsible for monochloramine decomposition, NH$_2$Cl spike experiments were performed using n-PbO$_2$ and up to 6 to 7 spiking events. Varied solid concentrations were used to study the effect of solid to NH$_2$Cl molar ratio. Figure 5.6a shows the NH$_2$Cl decomposition profiles obtained on an experiment carried out using 0.88 g/L of n-PbO$_2$ at a PbO$_2$/NH$_2$Cl molar ratio of 174 and 6 spiking events. The same experimental method described in Section 5.3.1.2 was used. Each spiking event was spaced by 1 hour. The initial NH$_2$Cl decomposition profile obtained illustrates the fastest decay rate amongst all rates measured in this experiment, following by the second and third spiking events with a slightly slower decomposition rate. This result is consistent with the experimental observations discussed
in Section 5.3.1.2 (Figure 5.4a). It seems that the NH$_2$Cl decomposition rates did not varied much after 3 spiking events.

![Graph](image)

**Figure 5.6** a) NH$_2$Cl decomposition profiles obtained on an experiment using six consecutive 1.5 mg/L spikes of monochloramine to a suspension of 0.88 g/L of n-PbO$_2$, and b) associated pH profiles.

Similar spikes dissolution experiments were also conducted with lower solid concentrations: 0.4, 0.11, and 0.08 g/L of PbO$_2$ at PbO$_2$/NH$_2$Cl molar ratios of 79, 22, and 16 respectively. Their NH$_2$Cl decomposition profiles are shown in Figure C.4 in Appendix C. For the experiment with 0.4 g/L n-PbO$_2$, each spike was monitored over 1 hour. Similar NH$_2$Cl decomposition rate constants (~230 mM$^{-1}$*day$^{-1}$) were observed after 2 spikes (Figure C.4a insert), and even observed after one day during the decomposition of the eighth monochloramine spike (Figure C.4a). Surprisingly, a similar activity of n-PbO$_2$ for
monochloramine decomposition was also observed after 3 days during the ninth spike (~100 mM⁻¹*day⁻¹), and even after 6 days during the tenth monochloramine spike (~160 mM⁻¹*day⁻¹) as shown in Figure C.4a. Their measured rates were slightly lower than those observed in the first day of the experiment. This indicates that the active species of n-PbO₂ for NH₂Cl decomposition are not consumed in a relatively short time period (a few hours), but they could diminish over a relatively longer period (days). This decrease in activity of n-PbO₂ for NH₂Cl decomposition was also observed in a spike experiment performed over a 30 days period discussed in section 5.3.1.2 (Figure 5.4a). Since n-PbO₂ is composed of small crystallites, during the experiment the crystallites kept growing to form better crystalline structure over time (Figure C.3) but this crystal growth under our experimental conditions takes place over a relatively long period (e.g. days). In other words, no significant changes in crystalline structure are expected to occur during few hours, pointing out, once again, that the acceleration of monochloramine decomposition requires small PbO₂ crystallites that present a newly formed surface. However, this enhancement in monochloramine decomposition rates is negatively impacted by the formation of large well ordered PbO₂ domains. The active species for NH₂Cl decomposition can thus be linked to the accessible sites present in a relatively stable crystalline structure.

When low solid loadings, 0.11 and 0.08 g/L, were used in the NH₂Cl spike dissolution experiments with PbO₂/NH₂Cl molar ratios of 22 and 16 respectively, a decrease in NH₂Cl decomposition rates were observed in these two experiments compared with the ones using high solid loadings. In each experiment, similar NH₂Cl decomposition rates were observed for all spikes that spanned over 2 or 4 hours except for the initial decay that had the fastest decay rate amongst all spiking events (Figures C4.c and C4.e). Thus, to evaluate the effect of PbO₂/NH₂Cl molar ratios on the NH₂Cl decomposition rates, the initial NH₂Cl decomposition profiles of all the experiments carried out using different solid concentrations were plotted in Figure 5.7a. Clearly, faster decay rates were observed in the experiments with higher PbO₂/NH₂Cl molar ratios as expected, since this resulted in an increase in the amount of PbO₂ active species. Their 2nd-order kinetic constants were calculated and plotted against their corresponding solid loading (Figure C.5). An exponential fitting trend is observed, indicating the increase in rates cannot be only
attributed to the total increase in surface area. Thus the lead concentrations measured from these experiments are normalized using initial solid PbO₂ concentration.

Figure 5.7 a) NH₂Cl decomposition profiles obtained on the first spike of 1.5 mg/L monochloramine in consecutive spike experiments using different PbO₂ solid loadings, and b) correlation between lead release normalized per gram of n-PbO₂ solid and the consumed NH₂Cl (ΔNH₂Cl) in these monochloramine spike experiments.
Figure 5.7b displays the normalized lead levels in terms of solid concentrations versus the consumed NH$_2$Cl (∆NH$_2$Cl) for experiments with 0.88, 0.4, and 0.08 g/L of n-PbO$_2$. Two distinct areas hosting the data are clearly observed in the plot. This is in turn consistent with our original hypothesis of two reaction regimes proposed in Chapter 4. One regime takes place under high PbO$_2$/NH$_2$Cl molar ratios conditions, and the NH$_2$Cl decomposition rates could be enhanced with only limited amount of lead released from PbO$_2$ solid. In contrast, elevated lead would be released from PbO$_2$ reduction during NH$_2$Cl auto-decomposition when PbO$_2$/NH$_2$Cl molar ratios are low, this corresponds to the second regime. In this study, the NH$_2$Cl spike dissolution experiments with 0.88 and 0.4 g/L n-PbO$_2$ were performed at high PbO$_2$/NH$_2$Cl molar ratios conditions, whereas the experiment with 0.08 g/L n-PbO$_2$ was carried out at a low PbO$_2$/NH$_2$Cl molar ratio. Comparing these two different regimes in Figure 5.7b, about three times more dissolved lead was released from each gram of n-PbO$_2$ solid under low PbO$_2$/NH$_2$Cl molar ratios compared to dissolved lead levels observed at high PbO$_2$/NH$_2$Cl molar ratios, although identical solid samples were used to perform these experiments.

When the pH profiles obtained in these experiments are evaluated (Figures 5.6b, and C.4b, d, f in Appendix C), an immediate pH drop was observed in the experiments conducted with 0.88 and 0.4 g/L of n-PbO$_2$ at high PbO$_2$/NH$_2$Cl molar ratios, with their pH values stabilizing around 7.6 and 7.75 respectively. In contrast, pH values were observed around 7.9 for the experiments carried out with solid concentrations of 0.11 and 0.08 g/L at low PbO$_2$/NH$_2$Cl molar ratios. These observations are consistent with our hypothesis that proton species in PbO$_2$ could be the active species for NH$_2$Cl decomposition.

### 5.3.3 The nature of the species in PbO$_2$ active for monochloramine decomposition

Based on the previous discussion, the crystal structure and age of the PbO$_2$ sample plays a crucial role in its activity for NH$_2$Cl decomposition. Comparing the activity of n-PbO$_2$ and μ-PbO$_2$ in terms of NH$_2$Cl decomposition, n-PbO$_2$ with small crystallite size revealed much higher activity than that of μ-PbO$_2$. Moreover, a proton-contained species, responsible for the initial pH drop is likely to play a role in decomposition of NH$_2$Cl. The mobility and accessibility of this proton-containing species also decreased as the crystal size becomes
larger. These observations are coincidentally consistent with previous results reported on the electrochemical activity of differently forms of PbO₂. Past studies have established that chemically prepared PbO₂ does not contain electrochemically active species, whereas electrochemically prepared PbO₂ possess sound electrochemical activity (e.g., specific capacity, and charge/discharge cycles). These differences are attributed to the fact that electrochemically active PbO₂ contains more amorphous and disordered components and hydrogen content than chemically prepared PbO₂. Caulder and Simon²⁵,²⁶ have reported that hydrogen present in at least two different chemical environments in active PbO₂, whereas chemically prepared PbO₂ contains hydrogen only on one type. Nuclear magnetic resonance, mass spectroscopy, and thermal decomposition studies for different PbO₂ samples were used to support the hypothesis of loss in proton species in active PbO₂ associated with structural reordering of the PbO₂ crystal lattice. These changes were used to explain the degradation of electrochemical activity. Additional solid-state magic-angle-spinning nuclear magnetic resonance studies on both electrochemically and chemically prepared PbO₂ also indicate that active PbO₂ contains protons species in two different configurations²⁸. One of them is associated with mobile, isolated and adsorbed hydroxyl groups, and water molecules that could be removed by outgassing. The other type cannot be removed via outgassing and might correspond to water molecules and/or hydroxyl groups trapped on the internal crystal structure of the solid surfaces. Hill et al.²⁷ have proposed that these proton species would reside in disordered surface regions in PbO₂ rather than in a well crystallized structure. Thus, it is plausible to propose proton-bearing species in the PbO₂ solid as responsible for NH₂Cl decomposition, through a general acid catalytic pathway. These proton species however need to reside in the solid and do not seem to be transferrable to the aqueous phase, as the results of section 5.3.1.1 indicate. To further study the nature of these active species in PbO₂, both n-PbO₂ and μ-PbO₂ solid samples were treated thermally to induce changes on their surface.

5.3.3.1 Thermally treated nano-sized n-PbO₂ activity for monochloramine decomposition

To study the active species potentially present on the PbO₂ surface, n-PbO₂ was treated under inert, oxidative, reductive, and humid conditions at 180 °C. This temperature was
chosen to avoid a phase transformation of the $\beta$-PbO$_2$ structure. The XRD patterns of the solids before and after treatment (Figure C.6) indicate that phase transformation did not occur after thermal treatments. A slightly higher crystal structure quality developed on these samples, except for the case of the sample treated under hydrogen ($\text{H}_2$-n-PbO$_2$), for which resulted in the formation of a more amorphous phase. The UV/Vis/NIR spectra obtained for these treated n-PbO$_2$ samples illustrate similar NIR bands as the one obtained before thermal treatment (Figure C.7). While changes in their electronic structure are still plausible upon thermal treatment under different environments, these changes are unlikely to be observed in the optical absorption spectra since the NIR band of the original solid is too broad.

Four batch dissolution experiments were performed using these treated n-PbO$_2$ samples as starting material with initial 1.5 mg/L of NH$_2$Cl to achieve a solid to NH$_2$Cl molar ratio of 174. Their NH$_2$Cl consumption profiles are shown in Figure 5.8a, together with a control for the auto-decomposition experiment (initial 1.5 mg/L of NH$_2$Cl) and the monochloramine decomposition profile obtained on the sample before thermal treatment. Surprisingly, all treated n-PbO$_2$ samples display similar activity for NH$_2$Cl decomposition, and their rates are comparable with the NH$_2$Cl auto-decomposition (Table 5.2). This indicates that the active species in n-PbO$_2$ for monochloramine decomposition were eliminated after thermal treatments, regardless of the chemical environment used during thermal treatment. The elimination of active species is consistent with the results reported by Gavarri et al$^{29}$ using neutron quasielastic scattering on PbO$_2$ samples after thermal treatment. They observed proton bearing species departed from PbO$_2$ in the form of water when the sample was heated at 260 °C in dry air at normal pressure. The decrease in electrochemical activity of PbO$_2$ due to heat treatment was also reported by other studies$^{30,31}$. 

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Figure 5.8 a) NH₂Cl decomposition profiles, b) lead dissolution profiles, and c) pH values obtained on monochloramine decomposition experiments using n-PbO₂, I-n-PbO₂, H₂-n-PbO₂, and W-n-PbO₂ with an initial monochloramine concentration of 1.5 mg/L. The data obtained for NH₂Cl auto-decomposition in the absence of PbO₂ is included for reference.
At the same time, relatively high lead concentrations were released from these treated n-PbO2 samples (Figure 5.8b). Dissolved lead levels in the thermally treated samples are two orders of magnitude higher than those observed for the original n-PbO2 sample without thermal treatment (<10 μg/L in Figure 5.3b). This indicates that the elimination of proton species destabilizes the PbO2 structure, perhaps generating more labile sites. Over the course of 10 days of dissolution, subtle differences on the lead releasing profiles were observed among these four thermally treated n-PbO2 samples. Specifically, the samples treated in nitrogen (I-n-PbO2), air (O2-n-PbO2), and steam (W-n-PbO2) showed a maximum in lead release after 1 day of dissolution, which gradually decreased as the time progresses (Figure 5.8b). In contrast, a linear decrease in lead concentrations was observed in the experiment using hydrogen treated n-PbO2 (H2-n-PbO2) sample. These different observations can be attributed to the more ordered crystal structure formed during thermal treatment for the I-n-PbO2, O2-n-PbO2 and W-n-PbO2 compared to that observed for the H2-n-PbO2 sample (Figure C.6).

Figure 5.8c shows the pH profiles obtained on these experiments, compared to that one previously obtained on the n-PbO2 before treatment, together with that observed during NH2Cl auto-decomposition as a control. Three different pH trends are observed amongst these six sets of data. First, as discussed in section 5.3.1.1, an immediate pH drop was observed in the experiment carried out using non-treated n-PbO2. Once the initial 1.5 mg/L NH2Cl completely depleted (within an hour), the pH values slightly increased, reaching a value of 8.2 at 10 days. For the thermally treated n-PbO2 samples, nitrogen (I-n-PbO2), air (O2-n-PbO2), and steam treated n-PbO2 (W-n-PbO2) samples show a similar pH trend, which follows the pH profile of NH2Cl auto-decomposition, but no initial pH drop is observed. This once again indicates that in this case the thermal treatment resulted in the removal or modification of the species in PbO2 responsible for proton release. In contrast, hydrogen treated n-PbO2 sample (H2-n-PbO2) revealed a unique pH trend. Its pH values increased dramatically from 8 to 9.09 during the first day, then decreased gradually to 8.6 after 10 days. This indicates that hydrogen did react with n-PbO2. Specifically, hydrogen possibly reduced the lattice Pb(IV) of n-PbO2 to Pb(II), which is unstable within the solid PbO2 structure and gets released rapidly during dissolution as Eq. 5.1 shows, this in turns resulting in an initial pH increase. Once a critical concentration of aqueous lead ions is
reached, a fast exchange between \( \text{PbO}_2(s) \) and dissolved \( \text{Pb}^{2+}(aq) \) dominates as per Eq. 5.2. This exchange consumes aqueous hydroxyl groups, thus both lead concentration and pH decrease gradually, and crystallization of small crystallites and labile \( \text{PbO}_2 \) takes place.

All treated n-PbO\(_2\) samples displayed similar \( \text{NH}_2\text{Cl} \) decomposition rates, indicating that hydrogen and other reagents do not generate the active species for monochloramine decomposition in n-PbO\(_2\). Since we have proposed the reaction between PbO\(_2\) and \( \text{NH}_2\text{Cl} \) is a surface-controlled process, the \( \xi \)-potential of four treated n-PbO\(_2\) and non-treated n-PbO\(_2\) samples was measured during their dissolution experiments with and without \( \text{NH}_2\text{Cl} \) to explore the changes in surface properties induced by the different thermal treatments. For this purpose, two non-sacrificial 25 ml reactors loaded with 0.88 g/L starting material were prepared following the same protocol used for the dissolution experiments under depleting \( \text{NH}_2\text{Cl} \) conditions. One reactor was used to carry out \( \xi \)-potential measurements, and the second one to carry out pH measurements. For \( \xi \)-potential measurements, the reactor was mixed well, and 1.6 ml of suspension was used.

Figure C.8 displays the \( \xi \)-potential values obtained on the solid samples under depleting \( \text{NH}_2\text{Cl} \) conditions and the values obtained in the absence of \( \text{NH}_2\text{Cl} \) (control test). Their corresponding pH values are also shown. Negative \( \xi \)-potential values in the range of -35 to -40 mV were observed for the untreated n-PbO\(_2\) samples either in the presence (within first 1 hour or 0.04 day) or absence of \( \text{NH}_2\text{Cl} \), as shown in Figure C.8a. This indicates that the presence of 1.5 mg/L \( \text{NH}_2\text{Cl} \) or its decomposition products did not significantly affect the surface charge of this solid sample. Previous studies\textsuperscript{32, 33} indicate that the dominant surface species are likely \( \equiv \text{Pb(IV)O}^- \) and other negatively charged surface complexes with carbonates and nitrates. The \( \xi \)-potential values of the untreated n-PbO\(_2\) samples were stable over the course of 30 days of dissolution, although their pH values increased from 7.6 to 8.2 (Figure C.8b) and some lead was released from n-PbO\(_2\) solids (Figure 5.3b). In contrast, a value close to 0 mV for the initial \( \xi \)-potential values were observed for the thermally treated samples I-n-PbO\(_2\), O\(_2\)-n-PbO\(_2\), and W-n-PbO\(_2\) samples (Figures C.8c, e, and g) both with and without depleting 1.5 mg/L \( \text{NH}_2\text{Cl} \), suggesting no net charge initially was present on their surface. This could be the result of the removal of surface hydroxyl groups or adsorbed water via thermal treatment and/or the adsorption of dissolved lead (Pb\(^{2+}\)) on the
surface, resulting in the formation of positively charged species, $\equiv$Pb(IV)OPb(II)$^{+2}$.$^{32}$ About two to three times more dissolved lead was observed in the experiments with these thermally treated n-PbO$_2$ samples, compared to those observed on untreated n-PbO$_2$ (Figures 5.8b and 5.3b). A decrease in $\xi$-potential values was observed after 1 day of dissolution and reached about -10 to -15 mV at 10 days. Meanwhile, their dissolved lead levels also decreased after 1 day, as discussed above (Figures 5.8b) together with a slight increase in pH values from an initial value of 8 to about 8.2 or 8.3 (Figures C.8d, f, and h).

The development of a negatively charged surface in the treated n-PbO$_2$ samples during dissolution suggests that a regeneration of surface hydroxyl groups might take place or that a new surface of stable PbO$_2$ could form and that hydrolysis of these newly formed surface could occur. However, neither of these two scenarios regenerate the active species responsible for NH$_2$Cl decomposition, indicating that surface hydroxyl groups are not the proton bearing species active species in PbO$_2$ responsible for monochloramine decomposition. Surprisingly, negative $\xi$-potential values, about -15 mV, were observed for hydrogen treated n-PbO$_2$ sample (H$_2$-n-PbO$_2$) initially, suggesting hydrogen treatment somehow preserved the negatively charged surface species, although some loss did take place (untreated n-PbO$_2$: $\xi$-potential value of -35 mV) (Figure C.8i). For the sample treated in hydrogen, a decrease in $\xi$-potential values was observed and reached about -30 mV during dissolution around 1 day, together with a concomitant dramatic increase in the corresponding pH values (about 1 pH unit). This was followed by a slightly increase in $\xi$-potential values and a gradual decrease in pH values after 1 day. This indicates that deprotonated surface species formed or that a newly formed PbO$_2$ surface coordinated with hydroxyl ions in solution in the thermally treated H$_2$-n-PbO$_2$ sample.

All these results can be summarized by proposing that once n-PbO$_2$ sample was treated thermally and regardless of the chemical environment conditions during thermal treatment, the active species present in PbO$_2$ for NH$_2$Cl decomposition substantially decreased. For the W-n-PbO$_2$ sample treated under steam, surface hydrolysis could occur leading to the formation of strongly adsorbed water and/or hydroxyl groups. In addition, regeneration of surface hydroxyl groups or surface hydrolysis for newly formed PbO$_2$ could also occur during the dissolution process. However, none of these resulted in an increase in activity.
for NH₂Cl decomposition. This indicates that adsorbed water and surface hydroxyl groups are not the active species in PbO₂ for NH₂Cl decomposition. The oxygen in air created an oxidative environment to fill the oxygen vacancies (V'O) in PbO₂¹⁹,³⁴ or oxidize any Pb(II) originally present in the lattice structure to Pb(IV), whereas hydrogen likely reduced part of lattice Pb(IV) to form Pb(II). However, neither O₂-n-PbO₂ nor H₂-n-PbO₂ showed an enhanced NH₂Cl decomposition activity. These observations suggest that the active species in n-PbO₂ linked to monochloramine decomposition are thermally unstable and cannot be easily regenerated.

5.3.3.2 Thermal treated micro-sized μ-PbO₂ activity for monochloramine decomposition

In contrast to n-PbO₂, μ-PbO₂ had a well-ordered structure with larger crystallite size and limited activity for NH₂Cl decomposition as discussed in section 5.3.1.3 (Figure 5.5a). Thus n-PbO₂ and μ-PbO₂ could have different physicochemical properties in spite of both having the same atomic arrangement (plattnerite). Morales et al.³⁰ performed thermogravimetric analysis (TGA) of nanostructured PbO₂ and commercial PbO₂ (both similar to n-PbO₂ and μ-PbO₂ respectively), and observed that nanometric PbO₂ exhibited a significant weight loss of water up to temperatures near 300 °C, whereas the commercial PbO₂ did not show such weight loss, remaining quite stable up to 350 °C. The thermal treatment could assist the crystal to heal defects leading to more ordered crystalline structure as observed for the thermally treated n-PbO₂ samples (Figure C.6). Since both loss in active species for monochloramine decomposition and formation of better crystal structure occurred at the same time in the treated n-PbO₂ samples, this could mask the effect of different treatment conditions on adding or removing the active species in PbO₂. The μ-PbO₂ sample with a well-defined crystallinity and larger crystal size is expected to have better thermal stability than that of n-PbO₂ and thus it would aid us to correct for the formation of a better crystal structure. The μ-PbO₂ sample was treated under helium (labelled as I-μ-PbO₂) and hydrogen with steam (labelled as H₂W-μ-PbO₂) to generate inert and humid reductive conditions to further study the properties of active species in PbO₂ for NH₂Cl decomposition.
As anticipated, after thermal treatments, both I-μ-PbO₂ and H₂W-μ-PbO₂ were still in the β configuration of PbO₂, and no other solid phase formed as confirmed by their XRD patterns (Figure C.9). Although these treatments did not change the crystal structure of μ-PbO₂, the NIR band of treated μ-PbO₂ did shift to shorter wavelengths than that of non-treated μ-PbO₂ as shown in Figure C10a. Specifically, the NIR band of untreated μ-PbO₂ centered around 1500 nm, while the band of the treated sample shifted to about 1478 nm for I-μ-PbO₂ sample and even further to about 1450 nm for H₂W-μ-PbO₂ sample. This indicates that more defects or electrons are generated under hydrogen with steam then under inert (helium atmosphere) conditions.

These two treated μ-PbO₂ samples (I-μ-PbO₂ and H₂W-μ-PbO₂) were used as starting materials to perform dissolution experiments using an initial concentration of 1.5 mg/L NH₂Cl at a PbO₂/NH₂Cl molar ratio of 174. Their NH₂Cl decomposition profiles are shown in Figure 5.9a together with those obtained on untreated μ-PbO₂ and a NH₂Cl auto-decomposition experiment run as control. Both I-μ-PbO₂ and H₂W-μ-PbO₂ still revealed some activity on NH₂Cl decomposition, but they were not as active as the non-treated μ-PbO₂ solid. Specifically, the NH₂Cl decomposition rates in the experiments of I-μ-PbO₂ and H₂W-μ-PbO₂ were one order of magnitude higher than that of NH₂Cl auto-decomposition, whereas their rates were slower than the that of non-treated μ-PbO₂ sample (Table 5.2). These results suggest that in the treated μ-PbO₂ samples some active species remain. This result contrasts with those obtained on the treated n-PbO₂ samples for which a complete lost in active species for monochloramine decomposition took place after thermal treatment. This could attribute to the fact that μ-PbO₂ with a well-defined structure and large crystal has a better thermal stability than n-PbO₂ which in turn possess a smaller crystallite size. Thus, some of the active species for monochloramine decomposition remain in the treated μ-PbO₂ lattice. For the NH₂Cl decomposition rates observed among the thermally treated I-μ-PbO₂ and H₂W-μ-PbO₂, I-μ-PbO₂ revealed a slightly faster rate than H₂W-μ-PbO₂. Consistently, less defects were observed in I-μ-PbO₂ than in H₂W-μ-PbO₂, as their UV/Vis/NIR spectra shows (Figure C10a). While the reductive/humid environment boosted the formation of defects/free electrons in μ-PbO₂, this condition might be unable to regenerate the proposed interstitial proton-bearing species responsible for monochloramine decomposition activity. Consistently with the experimental results
observed for W-n-PbO₂ discussed in Section 5.3.3.1, adsorbed water is not the active species in PbO₂ for NH₂Cl decomposition.

Figure 5.9 a) NH₂Cl decomposition profiles, b) lead dissolution profiles, and c) pH values obtained in monochloramine decomposition experiments using μ-PbO₂, I-μ-PbO₂ and H₂W-μ-PbO₂ solids and an initial concentration of 1.5 mg/L NH₂Cl. and NH₂Cl auto-decomposition. The data obtained for NH₂Cl auto-decomposition in the absence of PbO₂ is included for reference.
After 10 days of dissolution of treated $\mu$-PbO$_2$ samples in the presence of monochloramine, the remaining solids were collected and characterized via XRD. The results show similar patterns as their starting material (untreated $\mu$-PbO$_2$) (Figure C.9). Their UV/Vis/NIR spectra obtained after 10 days of dissolution are shown in Figures C.10b and c. The main NIR band for both I-\$\mu$-PbO$_2$ and H$_2$W-$\mu$-PbO$_2$ shifted to shorter wavelength after 10 days of reacting with NH$_2$Cl, consistent with our previous observation (Chapter 4 section 4.3.5) for commercial PbO$_2$ whose physicochemical properties are comparable to that of $\mu$-PbO$_2$. The UV/Vis/NIR spectrum of untreated $\mu$-PbO$_2$ collected at 10 days of dissolution experiment is also shown in Figures C.10b and c. Its band position was comparable to that of I-\$\mu$-PbO$_2$ and H$_2$W-$\mu$-PbO$_2$ samples before dissolution. This may indicate that the remaining untreated $\mu$-PbO$_2$ solid at 10 days still has the activity for NH$_2$Cl decomposition if NH$_2$Cl was spiked into the system. But the NH$_2$Cl spike experiment did not perform for $\mu$-PbO$_2$ sample.

Figure 5.9b shows the lead profiles obtained for this set of experiments, and the results obtained for a control experiment carried out with untreated $\mu$-PbO$_2$ in the absence of NH$_2$Cl. Consistent with the observations for unaged PbO$_2$ discussed on the previous Chapter, the presence of NH$_2$Cl did not enhance lead dissolution of untreated $\mu$-PbO$_2$ sample. The maximum dissolved lead concentration observed was less than 6 $\mu$g/L in the experiment performed using untreated $\mu$-PbO$_2$ in the presence of NH$_2$Cl. Interestingly, neither I-$\mu$-PbO$_2$ nor H$_2$W-$\mu$-PbO$_2$ show higher levels of dissolved lead levels compared to the untreated $\mu$-PbO$_2$ sample. This indicates the thermal treatment in inert or reductive/humid environment at 180 °C did not destabilize the well crystallized $\mu$-PbO$_2$ sample. This contrast with the results observed on the treated n-PbO$_2$ samples where all treatments destabilized the PbO$_2$ lattice and resulting in higher levels of aqueous lead released. The profiles of pH values during dissolution for both treated $\mu$-PbO$_2$ samples follows a similar trend as that of the non-treated $\mu$-PbO$_2$ and NH$_2$Cl auto-decomposition experiments, as shown in Figure 5.9c.

The $\xi$-potential of the non-treated and treated $\mu$-PbO$_2$ (I-$\mu$-PbO$_2$ and H$_2$W-$\mu$-PbO$_2$) were measured in the presence and absence of NH$_2$Cl, following the same protocol as that used for n-PbO$_2$. The results are shown in Figure C.11. For each of the solids, similar $\xi$-potential
values were observed either in the presence or absence of monochloramine. Both solids possess negatively charged surfaces under our experimental conditions. This is consistent with previous studies\textsuperscript{32,35}. Comparing their initial $\zeta$-potential values, the untreated $\mu$-PbO\textsubscript{2} revealed more negative values, -65 mV, than that of the untreated nano-sized n-PbO\textsubscript{2} sample (-35 mV), suggesting a different surface morphology for both samples. This difference is expected since $\mu$-PbO\textsubscript{2} and n-PbO\textsubscript{2} contain distinct crystal quality as observed XRD (Figure 5.1). The $\zeta$-potential values of n-PbO\textsubscript{2} stabilized around -35 mV over the course of 10 days. In contrast, a gradual increase in $\zeta$-potential values from -60 mV was observed for $\mu$-PbO\textsubscript{2} after 1 day, reaching -50 mV at 10 days, indicating that a more positive charged surface species formed during dissolution of $\mu$-PbO\textsubscript{2} compared with its initial state before dissolution. The adsorption of Pb\textsuperscript{+2}(aq) or positively charged products originating from NH\textsubscript{2}Cl decomposition could be dominant process regulating the charge of the untreated $\mu$-PbO\textsubscript{2} surface rather than the adsorption of hydroxyl groups generated as the aqueous pH values increased (from about 8 to 8.15 as shown in Figure C11b).

Similar as for the case of the treated n-PbO\textsubscript{2} samples, an increase in initial $\zeta$-potential values (-20 mV) were observed for both I-$\mu$-PbO\textsubscript{2} and H\textsubscript{2}W-$\mu$-PbO\textsubscript{2} samples compared with their starting material $\mu$-PbO\textsubscript{2} (-65 mV, Figure C.11c and e). This indicates that surface hydroxyl groups and adsorbed water are removed during thermal treatment. Then surface hydrolysis occurred on all treated $\mu$-PbO\textsubscript{2} samples rapidly since their $\zeta$-potential values decreased steeply and reached a relatively large negative value at -50 mV within 1 day. Finally, their $\zeta$-potential values stabilized around -50 mV, which was also the value observed for the untreated $\mu$-PbO\textsubscript{2} sample after 10 days.

After the thermal treatments, the nano-sized n-PbO\textsubscript{2} samples fully lost the active proton species responsible for NH\textsubscript{2}Cl decomposition, while thermally treated micro-sized $\mu$-PbO\textsubscript{2} did remain partial active for monochloramine decomposition. This reflects the relatively low stability of the active species present in n-PbO\textsubscript{2} compared to that of $\mu$-PbO\textsubscript{2}, attributed to its short range ordered crystal structure. But due to the thermal treatment, loss in activity for NH\textsubscript{2}Cl decomposition was observed for both treated n-PbO\textsubscript{2} and $\mu$-PbO\textsubscript{2}. At the same time, the $\zeta$-potential values of both treated n-PbO\textsubscript{2} and $\mu$-PbO\textsubscript{2} samples increased compared with their corresponding starting materials, indicating loss in surface hydroxyl groups. The
interstitial proton, hypothesized in this work as potentially responsible for monochloramine decomposition activity, has been proposed to be located on a common edge between neighboring chains of PbO$_6$ octahedra in the PbO$_2$ lattice, and to aid in stabilizing the connection between neighboring octahedral chains.$^{23}$ Thus we could propose that the loss in these interstitial proton species is associate with O$^{2-}$ ions in the solid lattice and the structural hydroxyl groups in the solid. These groups would react upon thermal treatment according to Eq. 5.4.$^{23,29}$ Once was the proton species eliminated, it is unlikely to be regenerated.

$$\text{OH}^-_{\text{interstitial H bonded}} + \text{OH}^-_{\text{str}} \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^- \quad (5.4)$$

Based on the experimental results discuss above for both non-treated and treated n-PbO$_2$ and μ-PbO$_2$, proton species in PbO$_2$, specifically interstitial protons are proposed as the active species that accelerate NH$_2$Cl decomposition. This proton species is relatively abundant in n-PbO$_2$ as its crystal contains smaller crystallite size, more defects, and a non-stochiometric arrangement compared to that of μ-PbO$_2$. Thus, a faster NH$_2$Cl decomposition rate is observed in the presence of n-PbO$_2$ solid. The decomposition of NH$_2$Cl is known to follow two common pathways.$^{36-38}$ One is NH$_2$Cl hydrolysis, and another one is general acid catalysis. The proton species in PbO$_2$ might act as an acid catalyst that accelerate the decomposition of NH$_2$Cl.

### 5.3.4 Conclusions and environmental implications

The crystal structure of PbO$_2$ plays a crucial role in its stability and activity for NH$_2$Cl decomposition. A proton species in PbO$_2$ is proposed as the active species that accelerate NH$_2$Cl decomposition. High activity was observed for PbO$_2$ solids with small crystalline size. Limited lead concentrations were released from the well crystallized PbO$_2$ samples.

Under chlorinating drinking water conditions, PbO$_2$ forms through the oxidation of either solid lead(II) compounds in the surface layer of the corrosion scales or the oxidation of dissolved ions (Pb$^{2+}$ (aq)) released from lead-bearing corrosion scales. Since plattnerite is a crystalline compound, the crystallization of unstable PbO$_2$ formed from fist stage nucleation needs to take place. The concentration gradient formed, one of the most
important factors for crystallization, will severely impact PbO$_2$ crystal to grow under typical drinking water conditions. Thus, imperfect crystals and short-range ordered PbO$_2$ domains are likely to form on the lead corrosion scales. These are the type of crystal that is more active toward monochloramine decomposition and shows highest level of aqueous lead release. Without a proper corrosion control program in place, once a municipality switches disinfectant from chlorine to monochloramine, elevated lead concentrations will be observed at the customer’s tap.
References


Chapter 6

6 Conclusions and recommendations

6.1 Conclusions

In this thesis, an attempt to establish a link between drinking water quality and composition of lead corrosion scale is described, using scale samples and water quality data collected from four Canadian DWDS. The results obtained are contextualized in terms of the preferential presence of lead oxides and aluminosilicates at the surface layer of the corrosion scales. A heterogenous distribution of the content of oxides and carbonates was observed. This distribution is correlated to the radial distance from the corrosion scales to the water/solid interphase. Statistically analysis suggests that dissolved Al, Mn, Cu, Ni, and As accumulate on the corrosion scales. However, their preferential accumulation is heavily dependent on water quality. Since drinking water quality, particularly pH values and silicate concentration, plays a critical role in the surface properties of aluminosilicate that act as absorbent to various elements.

The dissolution of PbO$_2$ was studied under depleting monochloramine conditions. Different PbO$_2$ samples with different surface properties (through aging), and crystallite sizes were used as starting materials. Aging has an effect on the stability and electronic structure of the PbO$_2$ solids. Elevated dissolved lead concentrations (~100 μg/L) were observed in the dissolution of aged PbO$_2$, whereas only 6 μg/L released from unaged PbO$_2$ at the end of dissolution experiment. In addition, the aged PbO$_2$ solids displayed a larger optical band gap than that of the unaged sample, indicating the presence of more defects in the aged solids. The crystal structure and/or crystallite size also affects the stability of PbO$_2$ under drinking water conditions. Relatively high lead levels were observed initially in the experiment of dissolution of PbO$_2$ with small crystallites compared with that of dissolution of well crystallized PbO$_2$. With recrystallization, this initially elevated lead concentrations decreased dramatically and reached similar levels to those observed in well crystallized PbO$_2$. 
A surface reaction was observed between PbO₂ and NH₂Cl that decomposed at a faster rate, compared to that measured for monochloramine auto-decomposition, in the presence of active PbO₂. The activity of PbO₂ is determined by its crystal structure and/or crystallites size, and surface properties in the form of defects. Two reaction regimes for monochloramine decomposition were revealed based on the PbO₂/NH₂Cl molar ratios. At high PbO₂/NH₂Cl molar ratios, where NH₂Cl is the limiting reagent, PbO₂ with fresh surface and small crystallites reveals the highest activity for monochloramine decomposition amongst all PbO₂ samples tested. At the same time, monochloramine decomposition rates are faster than that of auto-decomposition, with only limited amounts of lead (<10 μg/L) released from dissolution of PbO₂. Under these conditions, the presence of NH₂Cl could depress the reduction of PbO₂ by water. In contrast, with low PbO₂ solid to NH₂Cl molar ratios, monochloramine decomposition rates are similar to those observed for auto-decomposition, resulting in elevated levels of lead released. This is due to the limited availability of active species for NH₂Cl decomposition in PbO₂ under this regime.

UV/Vis/NIR spectroscopy was used to characterize the PbO₂ samples before and after monochloramine decomposition under the two different reaction regimes. When NH₂Cl is the limiting reagent, water is the only driving force for the blue-shift observed in the NIR band, suggesting the formation of defects in PbO₂. But in the presence of excess NH₂Cl, NH₂Cl triggers a more pronounced blue-shift than that observed by water. Thus, more defects are generated in the presence of monochloramine excess, which in turn induces elevated lead release.

Synthesized PbO₂ with small crystallites displayed the highest activity for NH₂Cl decomposition. Compared with commercial and chlorinated PbO₂, synthesized PbO₂ has smaller crystallites and a large specific surface area. While the large specific surface area could contribute to the high activity of synthesized PbO₂, the crystal structure/crystallite size plays a more important role in regulating its activity. A proton-containing species, e.g., interstitial hydrogen, in PbO₂ is proposed as the active species for the decomposition of monochloramine. A catalytic effect of active species was observed in synthesized PbO₂ with small crystallites for which even several NH₂Cl spikes in dissolution experiments performed within a day. With the process of recrystallization, a decreased in activity of this
active species was observed. Thus, its abundance is proposed to decrease with an increase in solid crystallinity.

6.2 Recommendations

Amorphous aluminosilicates are observed in the surface layer of lead corrosion scales that formed in distribution systems with low concentrations of aluminum and silicates. We suggested that water pH and concentration of silicate might control the interaction between aluminosilicates and trace heavy metals in water. Aluminum is also a major element accumulated in the iron corrosion scales formed in DWDS. A comprehensive review on characteristics of both lead and iron corrosion scales collected from additional municipalities could be performed, and links with the corresponding drinking water quality to gain a better understanding of the influence of water quality on formation and stability of surface layer of corrosion scales.

Based on the study in this thesis and lessons learned from lead water crises, sudden change of water quality will disturb the equilibrium that established over decades between solid lead phase and drinking water. The morphology and stability of lead corrosion scales are highly site-specific. To develop an effective corrosion control strategy, a comprehensive characterization of scales needs to be performed. Meanwhile, it is necessary to analyze the characterization results in the context of historical water quality data. Before implementation of a potential control strategy, a simulation system with real lead service lines, e.g., pipe loop system, needs to be used to test the proposed strategy.

In this thesis, a solid aging effect is observed to play an important role in the stability, electronic structure, and surface properties of PbO$_2$. This effect may also be observed in other lead compounds (e.g., lead carbonates) that commonly present in lead corrosion scales. Since the corrosion scales is formed under drinking water conditions, the solid phases in scales rarely experience the aging effect that commercial chemical commonly has. Thus, freshly prepared lead compounds should be used as starting material to perform future studies.
For the reaction of PbO$_2$ and NH$_2$Cl, we proposed two reaction regimes for this surface reaction based on PbO$_2$/NH$_2$Cl molar ratio, and proton-containing species in PbO$_2$ as the active species enhancing NH$_2$Cl decomposition through a general acid catalyzed mechanism. But two main questions remain. First, there is no direct evidence of the presence of proton-containing species in PbO$_2$. Moreover, the reaction pathway of NH$_2$Cl decay in the regime with high PbO$_2$/NH$_2$Cl molar ratio was not addressed. Further studies could be performed to address these two questions using solid proton monitoring techniques such as NMR.

Chlorinated PbO$_2$ was prepared and spiked with monochloramine to simulate a sudden switch in disinfectant. Surprisingly, no elevated dissolved lead concentrations were observed under high PbO$_2$/NH$_2$Cl molar ratio conditions. But elevated dissolved lead concentrations are still possible to occur under low PbO$_2$/NH$_2$Cl molar ratio conditions. This scenario needs to be further explored. The NH$_2$Cl spike experiments of chlorinated PbO$_2$ could be performed under low PbO$_2$/NH$_2$Cl molar ratio conditions to address this point.

An effect linked to crystallite size on the activity of PbO$_2$ for NH$_2$Cl decomposition was observed in this thesis. Particularly, PbO$_2$ with small crystallites reveals quantum size effects on its electronic spectra and stability in water that differ from its bulk solid counterpart. However, only the effect of NH$_2$Cl on lead dissolution process was evaluated. Other naturally present or artificially added ions or chemicals in drinking water could also play a role in PbO$_2$ stability and dissolution. The impact of these ions or chemicals on the dissolution of small crystallites PbO$_2$ needs to be addressed in further work. This information might be particularly relevant for municipalities developing corrosion control strategies.
Appendix A

Physical properties of lead bearing corrosion scales

The P3 scale sample collected from the City of London, contains four different layers. The outermost layer, L1, is the layer in direct contact with drinking water. A rusty brown solid was observed in L1 with a porous texture and covering about 30% of the inner pipe surface. Underneath this deposit, two inner layers were observed, named L2 and L3, respectively. These two layers covered most of the pipe surface and consisted of an orange (L2) and yellowish (L3) solid. These layers account for most of the total mass of the overall harvested lead corrosion scale (~70%). The innermost layer, L4, is the phase in direct contact with the metallic pipe. A dark brown dense solid was observed for this layer.

For all the scale samples collected from Municipality B (B1-B5), their outermost layer, L1, was deep orange-red in color and covered the entire surface. This solid was porous with a thickness around 1 mm (the thickest among the three layers collected). The inner layer, L2, had similar color and texture as P3-L2 (City of London), and covered the entire surface. The innermost layer, L3, was primarily white in color, which contrasts with the inner most layer collected from P3 (City of London). This was the thinnest layer and was strongly bonded to the inner metallic pipe wall.

For the case of the scale samples (C1 and C2) harvested from Municipality C, both samples consisted of three layers. There was no detectable difference between the physical properties for the same layer. The L1 (C1-L1 and C2-L1) and L2 (C1-L2 and C2-L2) layers had a color and texture similar to P3-L1 and P3-L2 respectively; i.e. a porous rusty brown L1 loosely attached to L2, which in turn was sandy brown in color. Both layers covered the entire pipe surface. For both pipe samples (C1 and C2) L3 was the thinnest layer and was strongly adhered to the entire inner surface of the metallic pipe surface and was white in color. C1-L3 and C2-L3 were similar to the equivalent innermost scale harvested for Municipality B (B-L3). For the case of Municipality D, two lead pipe scale samples were analyzed (D1 and D2). Two distinct layers were separated and obtained successfully from pipe sample D1. The physical properties of the corrosion scales harvested from D1 are dramatically different from the scales collected for the other municipalities. The color of
the outermost layer obtained from D1 (D1-L1) was close to those L1 layer samples obtained from the pipes collected from the other three municipalities. However, compared to the smooth porous surface layer observed for the other three municipalities, a sandy texture was observed for the D1-L1 sample, showing the thinnest thickness among all other L1 samples. This D1-L1 layer covered about 60% of the pipe surface. A thin pale brown layer was observed in the inner layer (sample D1-L2). There were some white patches underneath L2, but they were strongly attached to pipe surface and not enough to be collected.

**Detailed IR results of scale samples**

The spectra obtained on the P3 sample (Figure 3.2a) show a major band centered around 1450 cm\(^{-1}\). This band is attributed to the asymmetric stretching of carbonates in different molecular configurations, indicating the presence of different forms of carbonates in this scale.\(^1\)\(^-\)\(^3\) Moreover, all spectra revealed carbonate vibrational bands/peaks centered around 1045, 850, and 680 cm\(^{-1}\), which are consistent with those present in hydrocerussite. However, for the surface layer sample (P3-L1), the intensity of these characteristic peaks was overwhelmed by the strong bands assigned to strongly adsorbed water, centered at 3450 and 1640 cm\(^{-1}\). Additionally, a band centered around 1600 cm\(^{-1}\) is observed, which is the characteristic vibration of bicarbonate.

For the B5 scale sample, hydrated compounds (band centered between 3500 and 3450 cm\(^{-1}\)) and aluminosilicate (Si-O-Si/Al stretching vibration at 1071/950 cm\(^{-1}\)) are abundant in the outermost layer (B5-L1) of the scale (Figure 3.2b). In contrast, lead carbonates (band centered in a range of 1400-1465 cm\(^{-1}\)) are the major phases in the intermediate layer (L2) with a concomitant decrease in the intensity of the band assigned to absorbed water. Lead carbonates characteristic peaks were also observed at 1737, 1045, 694 cm\(^{-1}\), indicating the presence of hydrocerussite in this sample (B5-L2). In terms of the innermost layer (B5-L3), lead carbonates are the most abundant phases observed by FTIR. Besides the characteristics peaks of carbonates in hydrocerussite, a peak at 686 cm\(^{-1}\) is also apparent, indicating the presence of cerussite. Figure A.3a shows the IR spectra of five outermost layer samples of Municipality B (B1-L1, B2-L1, B3-L1, B4-L1, and B5-L1). All of them
display characteristic adsorbed water and carbonates bands. However, low-intensity metal oxides bands were observed only for the case of the B3-L1 and B5-L1. For the case of all innermost layer samples (B1-L3, B2-L3, B3-L3, B4-L3, and B5-L3) their IR spectra display very similar characteristics (Figure A.3b).

The IR spectra obtained on the scale samples collected from Municipality C, C1 are shown in Figure 3.2c. For the case of equivalent layers, scale samples C1 and C2 displayed similar patterns (Figure A.4). Comparison of the IR spectra (Figure A.2) obtained for each equivalent layer of pipe sample C1 and other three samples indicates that C1-L1, P3-L1 and B5-L1 partially resemble each other, there are however some differences which are discussed in the main manuscript.

In contrast with the IR spectra of scale samples P3, B5, and C1, D1-L1 revealed a distinct IR spectrum (discussed in the main manuscript) while the IR spectrum D1-L2 is comparable to L2 series obtained in other pipe samples. Based on the IR spectra, it can be concluded that for D1-L2 sample hydrocerussite is the dominant phase, with a minor contribution of metal oxides.
Figure A. 1 FTIR reference spectra for hydrocerussite, cerussite, PbO, and Pb₃O₄.
Figure A. 2 Comparison of IR spectra obtained on equivalent layers of scale samples collected from four municipalities. L1 layer (a), L2 layer (b), and L3 layer (c).
Figure A. 3 IR spectra of the outermost layer (a) and the innermost layer (B) obtained for five scale samples of Municipality B.
Figure A. 4 IR spectra for three different layers collected from the scale samples obtained from Municipality C.
Figure A. 5 UV/Vis reference spectra obtained for hydrocerussite and cerussite (a), PbO, Pb$_3$O$_4$ and PbO$_2$ (b).

Figure A. 6 UV/Vis reference spectrum of allophane.
Figure A. 7 UV/Vis spectra obtained on the outermost layer (L1) of five scale samples from Municipality B.

Figure A. 8 UV/Vis spectra obtained on the innermost layer (L3) of five scale samples from Municipality B.
### Table A. 1 Basic information of lead pipe samples.

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<tr>
<th>Sample</th>
<th>Year of installation</th>
<th>Sampling (MM/YYYY)</th>
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<tr>
<td>P3</td>
<td>1880</td>
<td>04/2009</td>
</tr>
<tr>
<td>B1, B2, B3, B4, and B5</td>
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<td>N/A/2012</td>
</tr>
<tr>
<td>C1 and C2</td>
<td>1908</td>
<td>08/2013</td>
</tr>
<tr>
<td>D1 and D2</td>
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<td>05/2014</td>
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### Table A. 2 Drinking water treatment process for the four municipalities in this study.

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<th>System B</th>
<th>System C</th>
<th>System D</th>
</tr>
</thead>
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<td>Lake Huron</td>
<td>Lake</td>
<td>River</td>
<td>River</td>
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<tr>
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<td>pre-chlorinated</td>
<td>screens</td>
<td>screens</td>
</tr>
<tr>
<td></td>
<td>mechanical screens</td>
<td>travelling screens</td>
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<td>screens</td>
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<tr>
<td></td>
<td>diffused chlorine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>coagulation</strong></td>
<td>fast-stirring with acidified</td>
<td>pre-chlorination</td>
<td>sulphuric acid + alum</td>
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<tr>
<td></td>
<td>alum</td>
<td>(adding chlorine to the</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>water before filtration) +</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>alum</td>
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<td>activated silica as a</td>
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<td></td>
<td></td>
<td>coagulant aid</td>
<td></td>
<td></td>
</tr>
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<td>Yes</td>
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<td>sand and gravel</td>
<td>sand/anthracite</td>
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<td>sodium hypochlorite</td>
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Table A. 3 Pearson correlation coefficients obtained for elemental concentrations in water (obtained from water quality data) and elemental concentrations in the solid corrosion scales. Data for all municipalities and corrosion solid samples were included.

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<tr>
<th>Element</th>
<th>Al</th>
<th>Fe</th>
<th>Pb</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Cu</th>
<th>Zn</th>
<th>V</th>
<th>B</th>
<th>Ba</th>
<th>Ni</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
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<tr>
<td>Pearson correlation coefficient</td>
<td>0.70</td>
<td>-0.17</td>
<td>-0.26</td>
<td>0.98</td>
<td>0.08</td>
<td>-0.95</td>
<td>0.99</td>
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<td>-0.31</td>
<td>0.85</td>
<td>0.89</td>
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Table A. 4 Pearson correlation coefficients between elemental concentrations in the solid corrosion scales of all municipalities.

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<th>Al</th>
<th>Fe</th>
<th>Pb</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Cu</th>
<th>Zn</th>
<th>V</th>
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<tr>
<td>Fe</td>
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<tr>
<td>Mn</td>
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<td>Mg</td>
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<td>Zn</td>
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<td>V</td>
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<tr>
<td>B</td>
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<td>0.82</td>
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<td>-0.01</td>
<td>0.73</td>
<td>-0.13</td>
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<td>0.03</td>
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<td>Ba</td>
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<td>Cd</td>
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<td>0.27</td>
<td>0.58</td>
<td>0.84</td>
<td>0.84</td>
<td>0.09</td>
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<tr>
<td>Cr</td>
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<td>0.06</td>
<td>0.00</td>
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<td>-0.19</td>
<td>0.20</td>
<td>0.06</td>
<td>0.08</td>
<td>0.21</td>
<td>0.18</td>
<td>0.42</td>
<td>0.51</td>
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Note: the bold values means statistically significant (p-value < 0.05).
References


Appendix B

7.3
7.5
7.7
7.9
8.1
8.3

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<td>8.1</td>
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<td>8.3</td>
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<table>
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<td>30</td>
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<td>40</td>
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48m-aged-PbO₂ + NH₂Cl=3.57 mg/L
Control, NH₂Cl=3.39 mg/L

12m-aged-PbO₂ + NH₂Cl=1.58 mg/L
12m-3mH₂O-PbO₂ + NH₂Cl=1.45 mg/L
Control, NH₂Cl=1.44 mg/L
Figure B. 1 pH values measured for monochloramine decomposition of a) 48m-aged-PbO$_2$ with initial monochloramine concentration of 3.5 mg/L, b) unaged-PbO$_2$, 12m-aged-PbO$_2$, and 12m-3mH$_2$O-aged-PbO$_2$ c) chlorinated PbO$_2$ with initial monochloramine concentration of 1.5 mg/L, and d) 12m-aged-PbO$_2$ with an initial monochloramine concentration of 1.5 and 15 mg/L. In each plot, the corresponding control NH$_2$Cl auto-decomposition profile obtained is also included.
Figure B. 2 XRD patterns of 12m-aged-PbO₂ solid before and after 30 days dissolution in the presence of an initial NH₂Cl concentration of 15.4 mg/L.
Normalized Kubelka unit

Wavelength (nm)

- 12m-aged-PbO₂ + Cl₂°=1.1 mg/L_90 days (12m-Cl₂°-PbO₂)
- 12m-Cl₂°-PbO₂ + NH₂Cl=1.5 mg/L_1 day
- 12m-Cl₂°-PbO₂ + NH₂Cl=1.5 mg/L_3 days
- 12m-Cl₂°-PbO₂ + NH₂Cl=1.5 mg/L_10 days
- 12m-Cl₂°-PbO₂ + NH₂Cl=1.5 mg/L_30 days
- unaged-PbO₂ before dissolution
- control test_unaged-PbO₂_4 days
- control test_unaged-PbO₂_10 days
- control test_unaged-PbO₂_33 days
Figure B.3 NIR spectra obtained before and after dissolution in the presence of monochloramine for a) unaged-PbO$_2$, b) 12m-Cl$_2^\circ$-PbO$_2$ and c) 12m-aged-PbO$_2$ in experiment with 15 mg/L NH$_2$Cl. Results for control tests carried in the absence of monochloramine are also included for reference.
Table B. 1 Calculated optical band gap values for four PbO$_2$ samples.

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<tr>
<th>sample</th>
<th>$E_g$ (eV)</th>
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<tbody>
<tr>
<td>unaged-PbO$_2$</td>
<td>1.69</td>
</tr>
<tr>
<td>12m-aged-PbO$_2$</td>
<td>1.75</td>
</tr>
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<td>12m-3mH$_2$O-PbO$_2$</td>
<td>1.78</td>
</tr>
<tr>
<td>48m-aged-PbO$_2$</td>
<td>1.79</td>
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</table>
Appendix C

Figure C. 1 Schematic plot of the gas flow system used for thermal treatments of PbO$_2$. 

158
Figure C. 2 a) NH\(_2\)Cl decomposition and b) pH profiles observed on experiments using solid n-PbO\(_2\) and the aqueous filtrate of the aged-n-PbO\(_2\) sample under depleting NH\(_2\)Cl conditions.
Figure C. 3 a) XRD patterns of n-PbO$_2$ before dissolution and after dissolution for 10, 30, 60 and 164 days in the absence of NH$_2$Cl, b) calculated average crystallite size of these samples. c) XRD patterns of n-PbO$_2$ before dissolution and after dissolution for 30 days in the presence of NH$_2$Cl.
Figure C. 4 NH₂Cl decomposition and corresponding pH profiles of n-PbO₂ in 1.5 mg/L NH₂Cl spike experiments with a, b) 0.88 g/L, c, d) 0.11 g/L, and e, f) 0.08 g/L solid concentrations.
Figure C. 5 Values for the observed 2\textsuperscript{nd}-order kinetic constants obtained from monochloramine decomposition experiments as a function of PbO\textsubscript{2} solid loading used.
Figure C. 6 XRD patterns of a) n-PbO$_2$ and thermally treated n-PbO$_2$ under b) nitrogen, c) air, d) steam, and e) hydrogen.

Figure C. 7 UV/Vis/NIR spectra of n-PbO$_2$ and thermally treated n-PbO$_2$ under nitrogen, air, steam, and hydrogen.
The image contains multiple graphs, each comparing Zeta-potential and pH over time for different conditions.

**Graph a:**
- Title: n-PbO₂ + NH₂Cl=1.44 mg/L
- Data points for n-PbO₂ and control n-PbO₂ over time.

**Graph b:**
- Title: pH
- Data points for n-PbO₂ and control n-PbO₂ over time.

**Graph c:**
- Title: I-n-PbO₂ + NH₂Cl=1.44 mg/L
- Data points for I-n-PbO₂ and control I-n-PbO₂ over time.

**Graph d:**
- Title: pH
- Data points for I-n-PbO₂ and control I-n-PbO₂ over time.

**Graph e:**
- Title: O₂-n-PbO₂ + NH₂Cl=1.44 mg/L
- Data points for O₂-n-PbO₂ and control O₂-n-PbO₂ over time.

**Graph f:**
- Title: pH
- Data points for O₂-n-PbO₂ and control O₂-n-PbO₂ over time.

The graphs indicate changes in Zeta-potential and pH with time for different treatments involving PbO₂ and NH₂Cl.
Figure C. 8 Zeta-potential values of n-PbO₂, I-n-PbO₂, H₂-n-PbO₂, and W-n-PbO₂ solids during monochloramine decomposition and their corresponding pH profiles.

Figure C. 9 XRD patterns of μ-PbO₂ and thermally treated μ-PbO₂ (I-μ-PbO₂ and H₂W-μ-PbO₂) before dissolution and after dissolution for 10 days in the presence of 1.5 mg/L of NH₂Cl.
Figure C. 10 UV/Vis/NIR spectra of a) $\mu$-PbO$_2$ and thermally treated $\mu$-PbO$_2$ (I-$\mu$-PbO$_2$ and H$_2$W-$\mu$PbO$_2$) before and dissolution for 10 days in the presence of NH$_2$Cl.
Figure C. 11 Zeta-potential values for μ-PbO₂, I-μ-PbO₂, and H₂W-μ-PbO₂ solids and their corresponding pH values obtained during monochloramine decomposition.
Table C. 1 Observed second order kinetic constants for monochloramine decomposition in experiments carried using commercial, chlorinated, and nano-sized synthesized PbO₂

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Solid reactant</th>
<th>Stock solution</th>
<th>Initial concentration of disinfectant (mg Cl₂/L)</th>
<th>Observed 2&lt;sup&gt;nd&lt;/sup&gt;-order kinetic constant* (mM&lt;sup&gt;-1&lt;/sup&gt;*day&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reactor size</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-1</td>
<td>n-PbO₂</td>
<td>NH₃Cl</td>
<td>1.44</td>
<td>18668</td>
<td>25ml</td>
</tr>
<tr>
<td>1-1</td>
<td>unaged-PbO₂</td>
<td>NH₃Cl</td>
<td>1.44</td>
<td>4.00</td>
<td>25ml</td>
</tr>
<tr>
<td>3-1-a</td>
<td>48m-aged-PbO₂</td>
<td>NaOCl</td>
<td>2.5</td>
<td>N/A</td>
<td>300 ml</td>
</tr>
<tr>
<td>3-1-b</td>
<td>following E3-1-a 48m-Cl₂&lt;sup&gt;0&lt;/sup&gt;-PbO₂</td>
<td>NH₃Cl</td>
<td>1.5</td>
<td>19.94</td>
<td>300 ml</td>
</tr>
</tbody>
</table>
Curriculum Vitae

Name: Daoping Guo

Post-secondary Education and Degrees:
University of Science and Technology Beijing, Beijing, China
2006-2010 B.E.

Western University, London, Ontario, Canada
2012-2014 M.Eng.

Western University, London, Ontario, Canada
2014-2018 Ph.D.

Related Work Experience:
Research Assistant
Western University, 2012-2018

Teaching Assistant
Western University, 2012-2018

Publications:
