Effect of Changing Disinfectants on Distribution System Lead and Copper Release

Part 1—Literature Review

Subject Area:
Infrastructure Reliability

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The Awwa Research Foundation (AwwaRF) is a member-supported, international, nonprofit organization that sponsors research to enable water utilities, public health agencies, and other professionals to provide safe and affordable drinking water to consumers.

The Foundation's mission is to advance the science of water to improve the quality of life. To achieve this mission, the Foundation sponsors studies on all aspects of drinking water, including supply and resources, treatment, monitoring and analysis, distribution, management, and health effects. Funding for research is provided primarily by subscription payments from approximately 1,000 utilities, consulting firms, and manufacturers in North America and abroad. Additional funding comes from collaborative partnerships with other national and international organizations, allowing for resources to be leveraged, expertise to be shared, and broad-based knowledge to be developed and disseminated. Government funding serves as a third source of research dollars.

From its headquarters in Denver, Colorado, the Foundation's staff directs and supports the efforts of more than 800 volunteers who serve on the board of trustees and various committees. These volunteers represent many facets of the water industry, and contribute their expertise to select and monitor research studies that benefit the entire drinking water community.

The results of research are disseminated through a number of channels, including reports, the Web site, conferences, and periodicals.

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Part 1—Literature Review

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FOREWORD

The Awwa Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the industry. The research agenda is developed through a process of consultation with subscribers and drinking water professional. Under the umbrella of a Strategic Research Plan, the Research Advisory Council prioritizes the suggested projects based upon current and future needs, applicability, and past work; the recommendations are forwarded to the Board of Trustees for final selection. The foundation also sponsors research projects through the unsolicited proposal process; the Collaborative Research, Research Applications, and Tailored Collaboration programs; and various joint research efforts with organization such as the U.S. Environmental Protection Agency, the U.S. Bureau of Reclamation, and the Association of California Water Agencies.

This publication is a result of one of these sponsored studies, and it is hoped that its finding will be applied in communities throughout the world. The following report serves not only as a means of communication the results of the water industry's centralized research program but also as a tool to enlist the further support of the nonmember utilities and individuals.

Projects are managed closely from their inception to the final report by the foundation's staff and large cadre of volunteers to willingly contribute their time and expertise. The foundation serves a planning and management function and awards contracts to other institutions such as water utilities, universities, and engineering firms. The funding for this research effort comes primarily from the Subscription Program, through which water utilities subscribe to the research program and make an annual payment proportionate to the volume of water they deliver and consultants and manufacturers subscribe based on their annual billings. The program offers a cost-effective and fair method for funding research in the public interest.

A broad spectrum of water supply issues is addressed by the foundation's research agenda: resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide the highest possible quality of water economically and reliably. The true benefits are realized when the results are implemented at the utility level. The foundation's trustees are pleased to offer this publication as a contribution toward that end.

Walter J. Bishop   Robert C. Renner, P.E.
Chair, Board of Trustees   Executive Director
Awwa Research Foundation   Awwa Research Foundation

ACKNOWLEDGMENTS

PREFACE

The objective of this research is to determine the effects of changing disinfectants (from free chlorine to chloramines and vice versa) on levels and rates of leaching from lead, brass, and copper components in the distribution system. This project will also study the effects of changing disinfectants on galvanic coupling on metals release and existing scales, and will advance our understanding of the nature of lead and copper solids.

Part 1 of this report (Literature Review) summarizes existing information regarding the effects of changing disinfectants on rates and concentrations of metals leaching from distribution system components. Workshop participants requested early publication of the literature review as a resource for utilities currently undergoing or considering a disinfectant change.

Part 2 of this report (Laboratory Studies, Pipe Loop Testing, and Field Sampling) will update the literature review and summarize laboratory studies, pipe loop testing, and field-sampling results. Part 2 will include pipe loop testing to determine the metal-release and galvanic-corrosion effects associated with a change in disinfectant. The chemistry of water provided by utilities will be modified for testing to span the range of water qualities found in the United States. The report will include scale analysis and characterization and how it relates to the nature of protective scales. Part 2 will include leaching levels of representative distribution system component parts and will verify the laboratory results by comparing field sample testing collected during routine operational change in disinfectant at participating utilities.

Knowing that within the next five years, over 100 sizeable utilities will undergo disinfection conversion to chloramines, AwwaRF chose to publish the results of this research in two parts. Part 1 (Literature Review) was published within a few months of the start of the project in order to provide timely information to utilities concerning the effects of changing disinfectants and compliance with the Lead and Copper Rule. Part 2 (Laboratory Studies, Pipe Loop Testing, and Field Sampling) should be available by early 2009, after the completion of the laboratory and field sampling that will be conducted through May of 2008.

EXECUTIVE SUMMARY

More and more utilities are using chloramines in place of free chlorine because of their greater stability for better compliance with both the Total Coliform Rule and more stringent requirements of the Disinfectants/Disinfection By-Products Rule. However, new information about disinfectant-induced changes in oxidation reduction potential (ORP), lead chemistry, scale formation and scale destabilization involving NOM have contributed to greater understanding of the factors influencing increased corrosion and metals release associated with a change in disinfectant. The objective of this research is to determine the effect of changing disinfectants from free chlorine to chloramines and vice versa on metals leaching rates and leaching levels from lead, brass, and copper components in the distribution system. This literature review aims to build upon the water industry's limited understanding of the potential consequences of changing disinfectants by posing the following questions:

- How does a change in disinfectant impact lead release?
- How does a change in disinfectant affect copper release?
- Does galvanic coupling affect metals release with the change in disinfectant?
- How does the change in disinfectant affect the nature of protective scales formed on plumbing materials?
- Historically, what have been the effects of various forms of treatment on galvanic coupling corrosion and metals release after disinfectant changes in the distribution system?
- What effect does background water chemistry have on metals release and galvanic coupling?
- What effect does a change in disinfectant have on redox?

The findings of this literature review indicate the importance of chemical and electrochemical properties that are fundamental to our understanding of the response of corroding metals and alloys to transitions from free chlorine to chloramines, and vice versa. Some of these properties include the following:

- The electrochemical behavior of unpassivated surfaces of lead-bearing materials (elemental lead) is substantially different than passivated surfaces.
- Of the common distribution system oxidants, only free chlorine oxidizes Pb(II) solids to form PbO_2 and possibly other Pb(IV) solids.
- The solubility of Pb(IV) species is low and their formation and presence under conditions (e.g. ORP) that promote their stability may be beneficial in controlling lead release.
- The oxidation of Pb(II) by free chlorine exhibits a lag time, which is affected by water quality and possible hydrodynamic conditions.
- The reverse process of PbO_2 reduction to Pb(II) can also involve NOM and appears to be kinetically slow.
- Comparative effects of free chlorine and chloramines on the release of copper and zinc from lead-bearing and copper materials remain largely unknown.
- The influence of galvanic coupling or other external electrochemical perturbations on passivated lead-bearing surfaces relative to lead release is likely to be minimal.

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- Treatment type or treatment changes such as coagulant, orthophosphate inhibitor addition and pH and alkalinity adjustment can, along with disinfectant change, potentially impact lead and copper corrosion
- Water quality background can potentially impact lead and copper corrosion
- The influence of electrical perturbations on copper surfaces could be important along with water quality parameters and treatment chemicals

The literature review has identified many of the key issues with regard to predicting effects of disinfectant change on lead and copper corrosion and metals release into drinking water supplies. Some of these issues will be explored further in Part 2 of this study.

CHAPTER 1 - BACKGROUND

Utilities are facing new challenges and concerns as they strive to comply with multiple simultaneous regulations, all aimed at enhancing drinking water quality (Neukrug, 2000; Gurian *et al.*, 2004). In some cases, treating for one contaminant can make it more difficult to comply with regulations for other contaminants. An example of this, one that will affect many utilities, is simultaneous compliance for corrosion control and disinfection in the distribution system. Since promulgation of the Lead and Copper Rule (LCR) in 1991, pH adjustment has become a commonly used treatment for corrosion control in the distribution system. Free chlorine also is used by many utilities as a secondary disinfectant in the distribution system, but raising pH for corrosion control also tends to increase formation of certain disinfection byproducts (e.g., trihalomethanes). More and more utilities are therefore using chloramines in place of free chlorine because of their greater stability for better compliance with the Total Coliform Rule and their reduced potential for forming disinfection byproducts for meeting more stringent requirements of the Disinfectants/ Disinfection By-Products Rule (Seidel *et al.*, 2005). However, the use of chloramines may impact the corrosive effect of the water on metals.

The evidence concerning effects of changing disinfectants on corrosion of metals is incomplete. In a recent survey (Kirmeyer *et al.*, 2004), 31 utilities that converted from free chlorine to chloramines after 1980 were asked to report their experience with corrosion in the distribution system. Forty one percent of the respondents indicated that there was no increase in pipe corrosion; one respondent indicated that there was an increase in corrosion in galvanized pipes, and the remaining respondents (55 percent) did not know whether or not chloramines increased pipe corrosion in the distribution system. In Washington DC, the transition from chlorine to chloramines in drinking water has been shown to cause a dramatic increase in lead release, as will be discussed in more detail in the sections that follow.

The aim of this research therefore is to determine the effect of changing disinfectants from free chlorine to chloramines and vice versa on metals leaching rates and leaching levels from lead, brass, and copper distribution system components. In addition, this project will study the effects of the change on galvanic coupling on metals release and existing scales.

To better define our proposed approach, we posed the following questions:

- How does a change in disinfectant impact lead release?
- How does a change in disinfectant affect copper release?
- Does galvanic coupling affect metals release with the change in disinfectant?
- How does the change in disinfectant affect the nature of protective scales formed on plumbing materials?
- Historically, what have been the effects of various forms of treatment on galvanic coupling corrosion and metals release after disinfectant changes in the distribution system?
- What effect does background water chemistry have on metals release and galvanic coupling?
- What effect does a change in disinfectant have on redox?

In the chapters below we summarize our understanding of work completed to date, summarize preliminary findings and identify areas where additional research is needed.

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CHAPTER 2 - HOW DOES A CHANGE IN DISINFECTANT IMPACT LEAD RELEASE?

In recent years, our understanding of lead solubility and the impact of chloramines on lead release has improved. Most of the guidance for lead control in drinking water per the LCR is based on the presumption that Pb(II) solids control lead solubility. However, recent research has shown that Pb(IV) oxides are also important species in the distribution system (Lytle and Schock, 2005). The formation and stability of lead (IV) oxides in the presence of chlorine was recently demonstrated in model experiments (Switzer *et al.*, 2006). The previous "conventional" understanding assumed that manipulation of basic water chemistry (pH, alkalinity) could produce stable mineral forms (cerussite, $PbCO_3$, and hydrocerussite, $Pb_3(OH)_2(CO_3)_2$) that would passivate a corroding lead surface. What was not fully understood is that in many cases Pb(II) solids were not necessarily controlling, and that changing redox conditions could affect the dominant mineral forms, potentially destabilizing existing corrosion scales and producing metal release rates that represent both a regulatory and public health concern. The role of naturally occurring organic matter (NOM) in the source water is also becoming clearer, and the effects of NOM are likely to be especially important when the change in disinfectant from free chlorine to chloramines (or vice versa) takes place. Because many large utilities are now considering conversion to chloramination, the scope of this problem is national.

There are three major components in our new understanding of lead release in the presence of chlorine or chloramine. These include (1) the formation of Pb(II) and Pb(IV) solids and their distribution on surfaces of corroding metals, (2) the role of chlorine and chloramines in establishing the redox conditions that determine the nature of predominant lead species, and (3) the role of chloramines and NOM in destabilizing existing corrosion scales and accelerating lead release. Figure 2-1 provides a schematic of the new conceptual relationship suggested by these competing factors (Korshin and Ferguson, 2005).
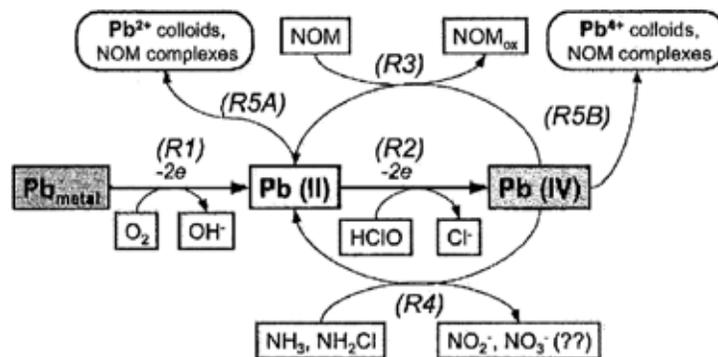

Figure 2-1. Simplified schematic of electrochemical and chemical redox processes that involve Pb(0), Pb(II) and Pb(IV) in the presence of chlorine, chloramines and NOM (Ref: Korshin and Ferguson, 2005).

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The District of Columbia Water and Sewer Authority (DCWASA) is an example of a large water system faced with distribution system conditions and water quality characteristics that illustrate the importance of understanding Pb(IV) oxides in complying with the LCR (Reiber and Giani, 2005; Renner, 2004). Prior to 2001, DCWASA, as well as other retailers of Aqueduct water, had achieved optimal corrosion control, and their lead-release levels were below the action limits of the LCR. The bulk of compliance sampling sites were located at residences connected to lead service lines.

In November 2000, DCWASA converted from a free chlorine disinfectant residual to a combined (chloramines) residual. The disinfectant change was brought about by more stringent federal regulations limiting the acceptable concentrations of DBPs (Disinfectant By-products) produced by chlorination of NOM in the raw or treated water. In an effort to comply with regulations simultaneously, the more stringent requirements of the Disinfection By-Products Rule essentially provided a motivation for the water treatment provider to utilize a disinfectant with a lower oxidation reduction potential (ORP) relative to free chlorine – hence the application of chloramines. The change in disinfectant unexpectedly caused a substantial change in lead release from the lead service lines (potentially attributed to a change in ORP) and thus destabilization of PbO_2 solids with an ensuing increase in lead levels at the tap.

Figure 2-2 illustrates the electrochemical potential - pH diagram that is helpful in understanding lead release events in DCWASA (Schock and Giani, 2004; Lytle and Schock, 2005). The numbered boxes show how the sequence of treatment changes formed and then destabilized the PbO_2 passivating film associated with Pb(IV). Point 1 represents the initial conditions of the early 1990s when there were some lead release problems. Initiation of high free chlorine residuals and flushing in 1994 moved the system chemistry to the predominance of PbO_2 (approximately point 2). The change to chloramines for secondary disinfection in 2001 moved the ORP back into approximately the area of point 3, thus causing PbO_2 to transform and cause lead levels to increase at the tap. DCWASA currently provides orthophosphate treatment with the chloramines disinfectant. The most recent LCR compliance monitoring met the 90th percentile compliance level of 15 µg/L for lead. Additional studies are ongoing to determine the reaction behavior between the various forms of lead, orthophosphate, and scales (Giani *et al.*, 2005a).
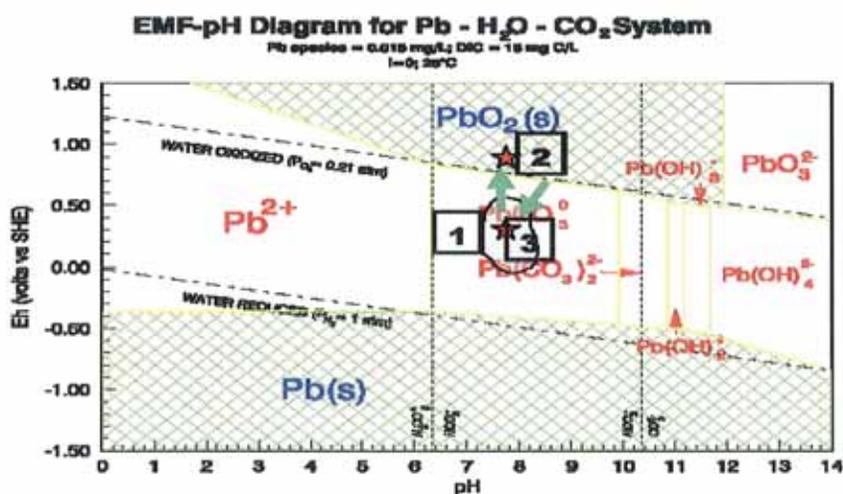

Figure 2-2. Potential-pH diagram for the lead system corresponding to DC WASA water (Ref: Giani *et al.*, 2005b; Schock and Giani, 2004).

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The redox transition from Pb(II) to Pb(IV) (and vice versa) in drinking water distribution systems can be considered analogous to the well-known system of different solubilities and scale-formation properties of ferrous versus ferric iron (Lytle and Schock, 2005). The higher oxidation state forms of the iron oxide or oxyhydroxide pipe scale phases, Fe(III), have much lower solubility than those of Fe(II). For lead, the redox potential required for the transformation of Pb(II) to Pb(IV) is much higher than for the ferrous to ferric iron transformation. In drinking water, free chlorine is the sole agent capable of driving the lead redox system towards the predominance of PbO_2. Conversely, the removal or replacement of free chlorine is likely to be accompanied by PbO_2 reduction and destabilization.

The presence of Pb(IV) in drinking water distribution systems is not unique to DCWASA, as polymorphs of PbO_2 (plattnerite, β-PbO_2 and scrutinyite, α-PbO_2) have been found in other systems (Schock *et al.,* 1996; Schock *et al.,* 2001; Lytle and Schock, 2005). For example, in lead service-line deposits from Cincinnati, Ohio, the pipe scales were in contact with relatively high disinfectant concentrations for long periods of time, elevated pH (8.5 - 9.2) for corrosion control, and granular activated carbon and free chlorine treatment. Only traces of cerussite ($PbCO_3$) were found in these pipes. In another example reported by Schock and colleagues, lead service-line specimens from Madison, Wisconsin had a thick layer of continuous PbO_2 at the water interface, with $PbCO_3$ making up the bulk of the underlying scale. In another study (Boozarpour *et al.*, 2005), the San Francisco Public Utilities Commission reported 90th percentiles of 5.2 - 6.7 µg/L Pb in 2000-2001 while using free chlorine and 11.5 µg/L Pb in 2004 following the change in disinfectant to chloramines, with no known lead service lines in the distribution system.

The results discussed above point to the occurrence of events of major importance for plumbosolvency (and possibly for cuprosolvency) specifically controlled by free chlorine, or its absence. More research is needed to understand how a change in disinfectant, in combination with system-specific water quality conditions and other relevant characteristics, can affect lead and copper release in drinking water distribution systems.

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CHAPTER 3 - HOW DOES A CHANGE IN DISINFECTANT AFFECT COPPER RELEASE?

As part of a study aimed at understanding effects of chloramines on distribution system materials, Reiber (1993) exposed copper, brass and bronze to varying levels of pH (6 - 8), chlorine (0.5 and 5.0 mg/L), chloramines (0.5 and 5.0 mg/L), and ammonia (<10 mg/L). Corrosivity was measured using weight loss, electrochemical and galvanic current measurement on coupons and pipe segments. Based on these tests, Reiber (1993) concluded that both free chlorine and chloramine disinfectants accelerate corrosion of copper and its alloys at pH 6, but cause minimal corrosion at pH 8. It was also concluded that water with an equal concentration of free chlorine is slightly more corrosive towards copper and its alloys than the same water with chloramine. In a recent case study (Boozarpour *et al.*, 2005), the San Francisco Public Utilities Commission (SFPUC) reported LCR 90th percentiles of 0.08 - 0.12 mg/L for copper in 2000 - 2001 while using free chlorine, and 0.09 mg/L Cu in 2004 following the change in disinfectant to chloramines. Generally, SFPUC concluded that the change in disinfectant had not significantly impacted copper compliance with the LCR.

In other studies, free chlorine has been shown to cause an increase in corrosion rates (Reiber, 1989; Stone *et al.*, 1987) and copper leaching (Atlas *et al.*, 1982; Hong and Macauley, 1998; Boulay and Edwards, 2001). Copper corrosion also can be affected by water quality in the presence of free chlorine (Edwards and Ferguson, 1993; Edwards *et al.*, 2000) and behave differently for certain copper alloys (Tuthill *et al.*, 1998). Chloramines also have been shown to increase corrosion rates and copper leaching (Zhang *et al.*, 2002).

Recent research on copper release has focused on understanding reports of pinhole leaks forming in copper tubing in residential water distribution systems in suburban Washington DC and elsewhere (Veazey, 2004). Possible explanations for these pinhole leaks include tubing defects, stray electrical currents, lightning, microbiologically influenced corrosion, and changes in water quality (such as lower levels of NOM and increased levels of aluminum). In a recent study, Rushing and Edwards (2004) tested the hypothesis that high chlorine residuals and aluminum solids were contributing to copper pitting problems. Aluminum is commonly present in water distribution systems originating predominantly from aluminum-based coagulants and cement-based distribution system materials (Miller *et al.*, 1984; Leroy *et al.*, 1996; Edwards *et al.*, 2004). Consequently, aluminosilicate solids can precipitate and assumedly cause higher levels of copper to be released at elevated pH (Kvech and Edwards, 2001). Rushing and Edwards (2004) demonstrated that a synergistic reaction might exist between chlorine and aluminum solids when exposed to copper as evidenced by increased chlorine decay rates, increased non-uniform copper corrosion, and rising corrosion potentials. More research is needed to understand this synergistic effect and the impact of the change in disinfectant on copper release in the distribution systems for representative water quality conditions.

CHAPTER 4 - DOES GALVANIC COUPLING AFFECT METALS RELEASE WITH THE CHANGE IN DISINFECTANT?

Members of our project team recently conducted laboratory studies to demonstrate whether or not galvanic coupling in the DCWASA system could generate lead release (HDR and CADMUS, 2005). Galvanic coupling occurs in distribution systems when a portion of a lead service line is replaced with copper piping and the dissimilar pipe materials are connected to restore drinking water service. The electrochemical effects of galvanic coupling are described in the paragraph below. The study was conducted under conditions that were specific to DCWASA and designed to exacerbate lead release. Additional testing was conducted to demonstrate whether or not grounding current could generate lead release.

The coupling of a new copper surface with lead theoretically should produce a substantial galvanic impact as illustrated by the Evan's diagram (Figure 4-1). The diagram shows the observed polarization behavior of uncoupled copper and lead surfaces, as well as the theoretical polarization behavior of the surfaces that would occur if they were coupled. The uncoupled surfaces are relatively un-scaled and un-passivated, and hence represent practical worst-case scenarios. Relative to lead, the coupling of the two surfaces results in a theoretical initial increase in the anodic (lead) exchange current (corrosion process) greater than an order of magnitude, which, of course, would have a profound impact on corrosion and metal release rates.
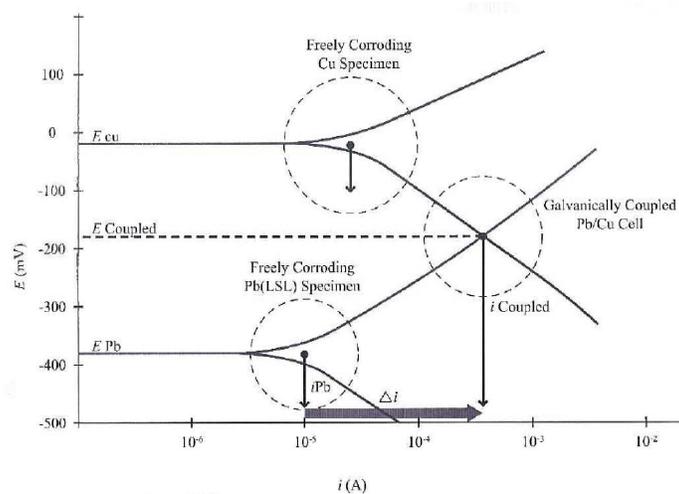
Figure 4-1. Polarization (Evan's) diagram of coupled lead and copper surfaces (Ref: HDR and CADMUS, 2005).

Preliminary results of this study (HDR and CADMUS, 2005) indicate that the magnitude of galvanic impacts on aged and passivated surfaces of lead service lines and new copper surfaces is minimal, but galvanic impacts can be substantial on un-passivated, newly-exposed lead surface. These results therefore indicate that the long-term impacts associated with partial lead service line replacement likely are inconsequential in the DCWASA distribution system.

The preliminary findings of this study showed that a chlorine residual (free or combined) elevated the galvanic effect in a lead-copper couple by accelerating the cathodic current exchange process. However, the overall impact was largely limited to the galvanic influence on

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the copper service line. Further, these preliminary findings were based on waters with low mineral content. In comparison, water conductivity had a more important effect on the galvanic process than chlorine residual. As such, galvanic impacts in systems having waters with substantially higher mineral content could be more extensive and possibly more prolonged than observed for the DCWASA system. More research therefore is needed to extend these preliminary conclusions to systems with other water quality conditions, specifically mineral content.

CHAPTER 5 - HOW DOES THE CHANGE IN DISINFECTANT AFFECT THE NATURE OF PROTECTIVE SCALES FORMED ON PLUMBING MATERIALS?

Recent studies by Korshin *et al.* (submitted 2006) of interactions between chlorine or chloramine and, on the other hand, lead solid phases (for instance, hydrocerussite $Pb_3(CO_3)_2(OH)_2$, and cerussite $PbCO_3$) typically found on the surfaces of lead-bearing materials (LBM) have demonstrated these processes are widely different for chlorine and chloramine. Chloramine has been determined to be largely inactive towards hydrocerussite and cerussite. In contrast with that, free chlorine oxidizes Pb(II) solids to form PbO_2. The main features of transformations associated with interactions between chlorine and hydrocerussite are shown in Figure 5-1. It shows that the platy hexagonal crystals of hydrocerussite (Figure 5-1A) are transformed in the presence of free chlorine into prismatic crystals of cerussite (Figure 5-1B). Why this transformation occurs is unknown, but while it is happening, almost no chlorine consumption takes place. This incipient or "lag" phase of the reaction is followed by a phase in which substantial chlorine consumption occurs (Figure 5-1). Morphologically, the chlorine oxidation is accompanied by gradual "dulling" of the distinct edges between crystalline planes of cerussite (Figure 5-1C), development of step-type structures on its crystalline planes, and the appearance of disperse crystals of PbO_2 that are either formed on the Pb(II) surfaces or embedded into them (Figure 5-1D). The microcrystals of PbO_2 have sizes <100 nm and exhibit tetragonal symmetry. Independent X-ray absorbance (XAS) and X-ray diffraction (XRD) measurements confirmed that the observed transition is indeed a change from solid Pb(II) phases to the predominance of PbO_2.
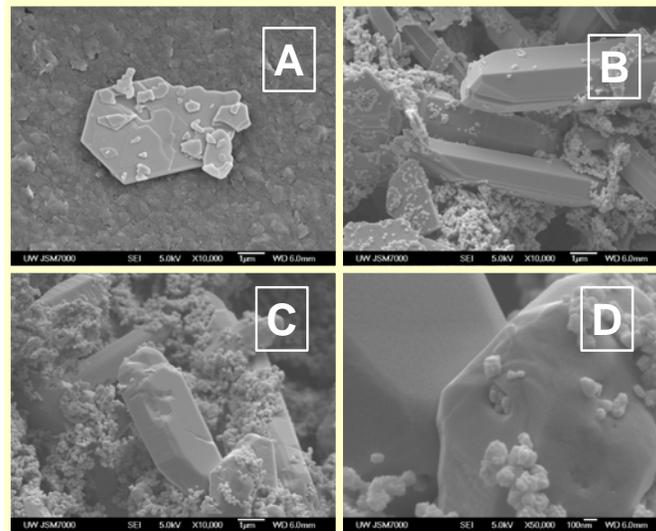
Figure 5-1. SEM data showing morphological changes that accompany the oxidation of hydrocerussite by chlorine. (A) Initial morphology of hexagonal crystals of hydrocerussite. (B) Change of predominant phases from hydrocerussite to orthorhombic crystals of cerussite in the presence of free chlorine (exposure time 8 hours). (C) Disappearance of hydrocerussite and formation of dispersed crystals of lead dioxide. (D) Growth of PbO_2 microcrystals on the surface of cerussite. (Ref: Korshin *et al.*, 2006)

The kinetics of Pb(II) solids' oxidation is a complex function of water quality parameters. The duration of the lag phase has been determined to be inversely proportional to the concentration of free chlorine. In model experiments with chlorine concentrations <4 mg/L, it can last for several days (Figure 5-2A). For actual corroding lead pipe, the duration of the lag phase can be longer, as indicated by the behavior of the electrochemical (EC) potential and lead release shown in Figure 5-3. The duration of the lag phase increases nearly linearly with the concentration of carbonate (Figure 5-2B) and pH. As a result, the minimum duration of exposure to chlorine that is necessary to initiate the conversion of Pb(II) to Pb(IV) species may vary from one distribution system to another, and it can also be affected by past accumulations of Pb(II) solids on corroding surfaces and the hydrodynamic conditions that affect mass transfer of chlorine to corroding surfaces.

(A)   (B)
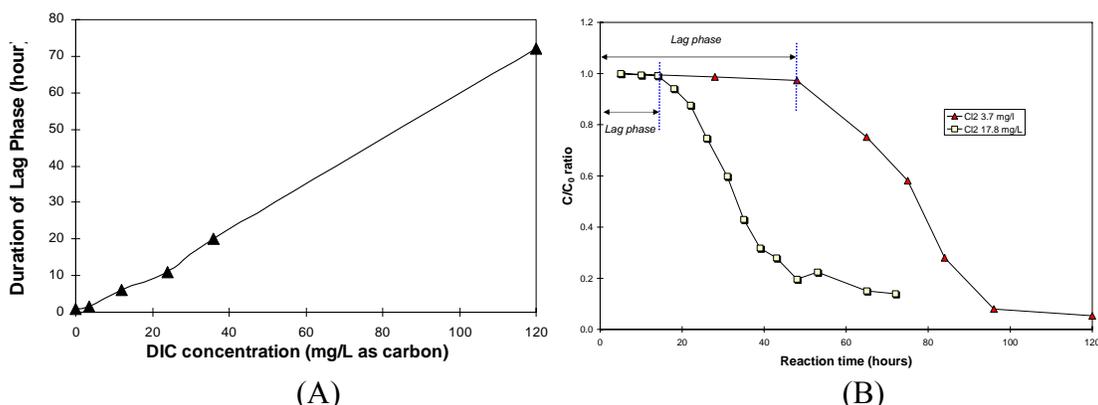
Figure 5-2. (A) Chlorine consumption profiles for the oxidation of hydrocerussite by chlorine. Initial pH 7.0, hydrocerussite concentration 0.1 g/L, total carbonate 0.001 M. (B) Effects of carbonate concentration of the duration of the lag phase of hydrocerussite oxidation by free chlorine. Concentration of $Pb_3(CO_3)_2(OH)_2$ 0.5 g/L, initial chlorine dose 55 mg Cl_2/L, initial pH 7.0. (Ref: Korshin et al., 2006)

As discussed in some detail above, the occurrence of Pb(IV) solids on the surface of corroding LBM is important for several reasons. The solubility of PbO_2 at pH < 13 is extremely low. If it forms a dense surface layer, the rate of lead release is likely to decrease dramatically. The EC and metal release data obtained for the DCWASA strongly support this conclusion. When a piece of lead pipe that had been exposed to chloraminated DCWASA drinking water and exhibited lead concentrations exceeding the action level (AL) of 15 µg/L by more than an order of magnitude was exposed to the same water containing dissolved chlorine instead of chloramine, it was observed that the EC potential of lead slowly increased from ca. –0.2 V to +0.4 V (Figure 5-3). At the same time metal leaching initially increased somewhat (this is likely to correspond to the hydrocerussite/cerussite transition described above) and then decreased to levels comparable with the AL or below it.

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Figure 5-3. Effects of switch from chloramine to chlorine on lead release and corrosion potential of lead pipe exposed to Washington DC drinking water. Chlorine concentration 4.0 mg/L. (Ref: Korshin and Ferguson, 2005)
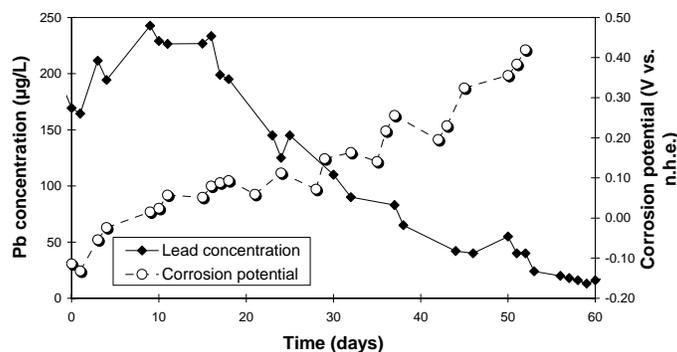
The results presented in Figure 5-1 to Figure 5-3 show that free chlorine causes LBM surfaces to undergo passivation. However, PbO_2 is likely to be intrinsically unstable when the disinfectant is changed from chlorine to chloramines. Most tellingly, the increase of Pb leaching in treated Potomac River water that occurred after chlorine disinfection was superseded with chloramine indicates that the stability of the Pb(IV) solids was lost.

Experiments performed by Korshin (2005) show that NOM plays a role in the reduction of Pb(IV) species. The behavior of PbO_2 particles suspended in Potomac River water and water from Lake Washington was also examined (Figure 5-4). The black color of PbO_2 particles was observed to be stable in the presence of chlorine, but it acquired a reddish hue in the absence of oxidants and even more so with chloramine.

(A)   (B)
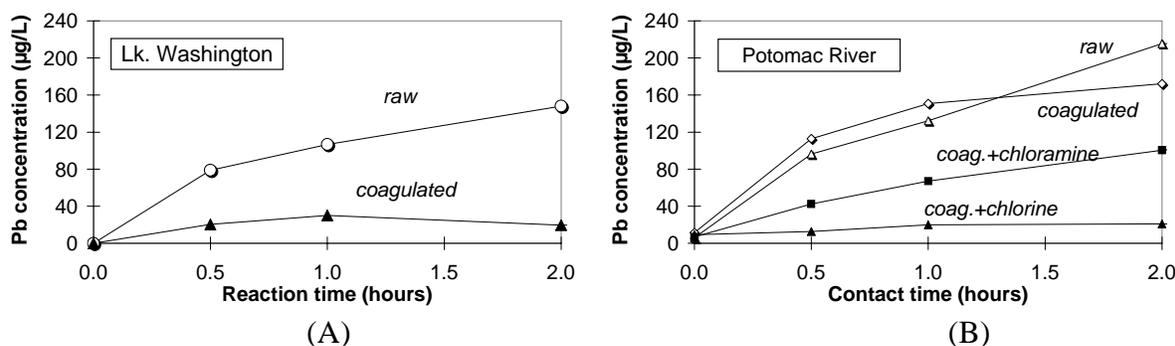
Figure 5-4. A and B: Comparison of effect of chlorine and chloramine on the release of soluble lead from suspension of 0.2 g/L PbO_2 in Lake Washington and Potomac River water. Concentration of chlorine or chloramine 4 mg/L, concentration of dissolved organic carbon 3.0 mg/L. (Ref: Korshin and Ferguson, 2005)

Simultaneously with the visually discernible changes, the concentration of soluble lead measured for PbO_2 suspensions in untreated Potomac River water increased in the absence of chlorine from 10 to 220 µg/L within two hours of exposure (Figure 5-4A). Chloramine partially suppressed lead release in Potomac River water, but chlorine drove lead levels to < 20 µg/L. The release of lead in the untreated, coagulated and ozonated Potomac River NOM was similar, while for Lake Washington water, NOM coagulation prevented PbO_2 reduction/mobilization

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(Figure 5-4B). The nature of differences in the behavior of NOM from Potomac River water and Lake Washington water is unclear. It is possible that activated aromatic and quinone functional groups potentially active in reactions of NOM with Pb(IV) are associated with both hydrophobic, transphilic and hydrophilic fractions of Potomac River NOM, while for other sources they may be associated mostly with hydrophobic NOM fractions. It was also determined that the kinetics of PbO_2 reduction by NOM may be slow. For instance, SEM measurements showed that a two-month exposure of PbO_2 model phase to raw Potomac River water was accompanied by the decrease of crystallinity of PbO_2 tetragonal structures and appearance of numerous sub-structures with low symmetry (Figure 5-5), but no formation of Pb(II) solids could be documented.

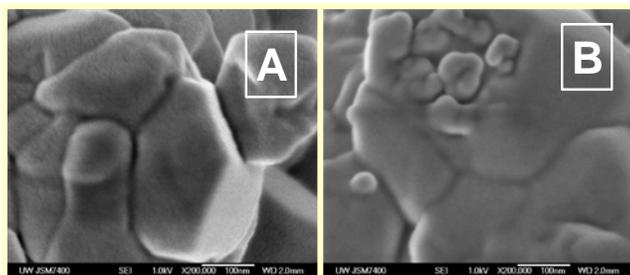**Figure 5-5. SEM data showing morphological changes that accompany the reduction of PbO_2 model phase by Potomac River NOM. (A) High resolution image of the initial morphology of clusters of tetragonal crystals of PbO_2 (B) high-resolution images showing changes of the morphology of PbO_2 crystals in the presence of Potomac River NOM. Exposure time 2 months. (Ref: Korshin, 2005)**

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CHAPTER 6 - HISTORICALLY, WHAT HAVE BEEN THE EFFECTS OF VARIOUS FORMS OF TREATMENT ON GALVANIC COUPLING CORROSION AND METALS RELEASE AFTER DISINFECTANT CHANGES IN THE DISTRIBUTION SYSTEM?

Different forms of treatment can affect galvanic coupling corrosion and metals release. However, far less information exists in the literature regarding how treatment related changes, in conjunction with disinfection changes in the distribution system, affect galvanic corrosion and metals release. Based on a review of the literature, pH, alkalinity and orthophosphate were identified as amongst the most important treatment related parameters, in conjunction with different disinfectants and disinfection changes.

PH AND ALKALINITY

pH and alkalinity adjustment are widely used as part of corrosion control treatment strategies to meet OCCT (Optimum Corrosion Control Treatment) and OWQP (Optimum Water Quality Parameters) requirements of the Lead and Copper Rule. Increasing pH above 8 can significantly reduce lead release (Schock, 1989; Boffardi, 1995; Johnson et al., 1993). Alkalinity addition can also decrease lead release particularly in waters with poor buffering capacity (Vik *et al.*, 1996; Tang *et al.*, 2006). In pilot scale distribution studies, Taylor *et al.*, (2005) acknowledged the importance of pH and alkalinity on lead release based on other work on lead corrosion scales, but did not clearly observe the relationship in pilot studies. Taylor attributes this observation to either the confounding effect of stabilization or the dominant effect of chloride and sulfate masking the pH and alkalinity impact on lead release. Additional field study confirmed that lead concentration decreased with increasing pH and alkalinity (Tang *et al.*, 2006). Copper release increases with increased alkalinity and decreasing pH (Taylor *et al.*, 2005.)

ORTHOPHOSPHATE INHIBITOR

Orthophosphate has been used successfully for corrosion control. Most studies show orthophosphate is an effective corrosion inhibitor when used within an appropriate pH range (Reiber *et al.*, 1997). In lead pipe loop studies after orthophosphate addition to chlorinated water that was significantly above the AL, there was a reduction in lead levels to below the AL after approximately one year of operation (Cantor, 2003). Identical pipe loops without orthophosphate were run with both chlorinated and untreated water. The chlorinated and untreated water loops also showed reduced lead levels to below the AL, but not to the extent of the loop with orthophosphate. The untreated water still showed the highest lead levels over the other treatment scenarios. Lin *et al.* (1997) observed that phosphate corrosion inhibitor appeared to show slightly lower corrosion rates on lead coupons in water treated with free chlorine compared to chloramines, but noted there was not a clear difference between the two disinfectants. Recent studies by DCWASA show a decrease in lead both in pipe loops and the distribution system after an initial increase in lead with the changeover from free chlorine to chloramines (Giani *et al.*, 2005a; 2005b). However the DCWASA study also points out the data gaps in the role of the orthophosphate in terms of lead speciation and scale formation.

AMMONIA FROM MONOCHLORAMINE

Free ammonia can be present as a result of the decomposition of monochloramine in the distribution system, due to the ammonia feed ratio or from source water. Monochloramine decomposition can occur predominantly by oxidation of NOM and also by reactions with pipe walls and by autodecomposition. The ammonia generated can lead to nitrification and further chloramines decomposition (Kirmeyer *et al.*, 2004).

FLUORIDE

Static tests on lead, copper/lead solder and brass coupons using water from the Potomac treatment plant were conducted to include sodium fluoride addition (Lin *et al.*, 1997). The study concluded that adding fluoride led to an increase in dissolved lead, however data appear inconclusive. A literature review by Urbansky and Schock (2000) concludes that that there are many factors and water quality parameters at play that can affect lead corrosion and that there is no credible evidence to support that fluoride increases lead solubility.

COAGULATION WITH ALUMINUM-CONTAINING COAGULANT

Treatment processes such as coagulation can influence copper corrosion. The presence of aluminum solids in the distribution system, after coagulation with an aluminum-containing coagulant, appears to contribute to pitting corrosion of copper indicating a possible synergistic corrosion effect with both chlorine and chloramines (Rushing and Edwards, 2004). The investigators report rising corrosion potentials over the exposure period, increased chlorine decay and non-uniform corrosion as evidence of the synergistic effect leading to pit corrosion. Generally water treated with chloramines showed higher corrosion potential, attributed to the higher residual. However visual inspection of the copper indicated that the chloramines, even at higher levels were similarly as aggressive as the free chlorine. The investigators conclude that chloramines are no more beneficial than free chlorine in terms of both non-uniform corrosion and copper pitting.

COAGULATION WITH FERRIC CHLORIDE COAGULANT

Recent reports suggest that ferric chloride may play a role in lead corrosion, the degree to which, and relationship to disinfectant change, is not clear. Several utilities reported higher lead levels after both changing to ferric chloride as a coagulant and switching to chloramine disinfection at around the same time (Renner, 2004). Investigators suggest that ferric chloride may affect corrosion by increasing the chloride to sulfate ratio and potentially causing an increase in galvanic corrosion in lead-containing solder.

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CHAPTER 7 - WHAT EFFECT DOES BACKGROUND WATER CHEMISTRY HAVE ON METALS RELEASE AND GALVANIC COUPLING?

CHLORIDE AND SULFATE

Chloride and sulfate are important water quality parameters for lead release (Schock *et al.*, 1996). In case studies of 12 utilities (Reiber *et. al.*, 1997) lead release increased with increasing chloride, and utilities with chloride/sulfate ratios below 0.58 all met the 90th percentile AL for lead. The study found that 40 percent of utilities with ratios greater than 0.58 did not meet the AL, and that as the chloride/sulfate ratio increased, generally higher 90th percentile lead release was observed. Similar findings have been reported in other work (Oliphant, 1983; Taylor *et al.*, 2005; Tang *et al.*, 2006).

In a study of Pb(IV) formation in chlorinated water, Lytle and Schock (2005) noted a slight increase in formation of Pb(IV) from Pb(II) possibly due to the presence of sulfate, but indicated a need for further study under controlled conditions to verify the relationship.

Chloride and sulfate both induce copper pitting corrosion, and sulfate appears to be more aggressive (Duthil *et al.*, 1996) This study showed that low chloride concentrations appear to accelerate pitting rate by sulfate and inhibit it at higher chloride concentrations. At even higher concentrations chloride appears to be largely responsible for the pitting formation.

CONDUCTIVITY

Conductivity is an important parameter that can result in an increase in lead release (Tang *et al.*, 2006). A recent study (HDR and CADMUS, 2005) indicated that conductivity has a significant effect, more so than chlorine residual, on the galvanic process of coupled lead and copper. However the study results show galvanic impacts are only significant on newly exposed lead pipes.

TEMPERATURE

Temperature is also important but seemingly less so than other parameters. Several studies show enhanced lead corrosion with increasing temperature (Boffardi, 1988; Johnson *et al.*, 1993). In a pipe loop study (Cantor *et al.*, 2003) temperature changes didn't appear to significantly affect lead or copper levels unlike iron where temperature impact was significant. In the Cantor *et al.* (2003) study, site specific factors for the test waters such as the alkalinity, disinfection and application of chemicals for corrosion control had a far greater influence on lead and copper levels than temperature.

CALCIUM AND SILICA

In blended waters, Tang *et al.* (2006) showed that calcium did not appear to have any effect on lead concentrations where pH<7.9. However the study observed a reduction in lead concentrations for pH>7.9 suggesting this may be due to either formation of a solid film or enhancing an existing film at the lead surface, thus resulting in the observed decrease in lead release. The investigators found silica reduced lead release for the range of pH evaluated, noting that silicate compounds are often cited as metal corrosion inhibitors. In a large-scale pilot

distribution study Taylor *et al.* (2005) found that calcium and silica appeared to show inhibitory effects on lead release, but that it was difficult to confirm the correlation because of the confounding effect of the other water quality parameters.

DISSOLVED OXYGEN

Dissolved oxygen can affect lead and copper release but with less impact on copper (Cantor *et al.*, 2003). Based on thermodynamic considerations (Lin *et al.*, 1997), both lead and copper should corrode in the presence of oxidants including oxygen, chlorine and chloramines. This study and others discussing DO note that it is difficult to quantify the DO effect on lead corrosion in the presence of a disinfectant residual (Cantor *et al.*, 2003). DO is less important to cuprosolvency, especially when a chlorine residual is present (Schock, 2001).

NATURAL ORGANIC MATTER

The presence of natural organic matter (NOM) is an important factor in corrosion studies both due to reactions with disinfectants including both free chlorine and chloramines, and interaction with the metal surfaces. Recent studies on lead and Pb/Sn solder indicate that NOM influences both type of scale formation as well as increasing the quantity of soluble lead and tin. Although the mechanisms are more detailed than described here, the conclusions of this study are that NOM is an important consideration alongside pH, alkalinity and other parameters considered in corrosion studies (Korshin *et al.*, 2005b). In another study, Broo *et al.* (2000) considered NOM influence on copper corrosion, concluding that NOM increases both the corrosion rate and copper concentration in the water after only one night of stagnation.

NITRIFICATION

When nitrification occurs some of the water quality parameters important to corrosion are impacted such as reduced alkalinity and reduced pH especially in poorly buffered waters. Nitrifying bacteria can also release nitric acid thereby increasing corrosion (Kirmeyer *et al.*, 2004).

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CHAPTER 8 - WHAT EFFECT DOES A CHANGE IN DISINFECTANT HAVE ON REDOX?

Recent studies have highlighted both the importance of ORP and the data gaps in relation to disinfection change and the impact on lead scales and lead release (Lytle and Schock, 2005, Switzer *et al.*, 2006, Vasquez *et al.*, 2006). This information is important to this research because it adds to the developing body of knowledge about the redox conditions established by free chloramines and chloramines and the dominant lead mineral forms that result.

In the Switzer *et al.* (2006) study, Pb(s) films were exposed to chlorine or monochloramine to determine the effect of each disinfectant on lead dissolution. In free chlorine, there was very little lead mass loss and XRD showed a PbO_2 passive layer, composed primarily of α-PbO_2 and some β-PbO_2, had formed over the Pb(s). In contrast, monochloramine completely dissolved the lead film yielding a solution with a high concentration of lead. The remaining film contained only hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, which has a much higher solubility than PbO_2, thus explaining the higher lead levels.

Switzer *et al.* (2006) analyzed the results of the study in terms of the ORP of the two disinfectants. The discussion notes that both monochloramine and free chlorine are thermodynamically capable of oxidizing Pb(s) to Pb(IV), based on formal reduction potentials at pH 8: NH_2Cl/Cl^-, $HOCl/Cl^-$, OCl^-/Cl^- and PbO_2/Pb^{2+} are 1.0, 1.25, 1.17 and 0.72 V respectively versus the NHE (Normal Hydrogen Electrode). However Switzer *et al.* (2006) suggest there may be error in their standard reduction potential calculated for NH_2Cl. This uncertainty is because monochloramine was estimated based on equilibrium constant calculations from earlier work by Margerum (1994), whereas the other formal reduction potentials at pH 8 are calculated from standard reduction potentials from the literature.

The study then conducted direct measurements of the equilibrium potentials of monochloramine and free chlorine at pH 8 yielding 0.65 and 1.02 V respectively. The results show a lower potential than as predicted above for NH_2Cl, and which was more consistent with the observed results for the Pb(s) films.

Other factors may also explain the differences in theoretical electrochemical potentials and those observed in practice. The study by Margerum (1994) showed that NH2Cl oxidizes NO_2^- by first forming NO_2Cl as an intermediate by acid catalyzed transfer of Cl^+. Switzer *et al.* (2006) suggest the Pb(s) to Pb(IV) oxidation is similarly complex requiring more than one step, but the mechanisms of this oxidation processes have not been ascertained. Potentially, these mechanisms can be affected by both the lower oxidation potential of chloramine and also by kinetic changes associated with the conversion of the kinetically active free chlorine species to chloramine, a much slower oxidant. Similar to the observations by Switzer *et al.* (2006), Lytle and Schock (2005) suggest formation of precursor Pb(II) mineral phases may be part of overcoming kinetic barriers before eventual formation of PbO_2, based on their results from long-term lead precipitation experiments in free chlorine.

The behavior of theoretically predicted standard electrochemical potentials of a realistic system (2 mg/L chlorine or chloramine, 10 mg/L chloride) is shown in Figure 8-1. This figure shows that the formation of monochloramine decreases the standard EC potential in a wide range of pH, most prominently for pH from 7 to 10, where the oxidation potential of chlorine is expected to decrease, when chlorine is converted to chloramine, in the presence of ammonia, by ca. 60 mV. Although this chart refers to conversion of chlorine to chloramines, direct

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application of either chlorine or chloramines would correspond to the same theoretical differences in EC. The actual difference between redox potentials measured for the same concentrations of total chlorine, but in one case when it exists as free chlorine and in another when it is converted to chloramine, may be significantly different from that predicted theoretically (Figure 8-2 and Vasquez *et al.*, 2006). The reason for that is not yet completely understood, but this is likely to be caused by contributions of other factors that affect the overall redox state of the system, and possibly limitations of the performance of redox electrodes per se at relatively low concentrations (<4 mg/L) of chlorine or chloramine that are typical for drinking water.
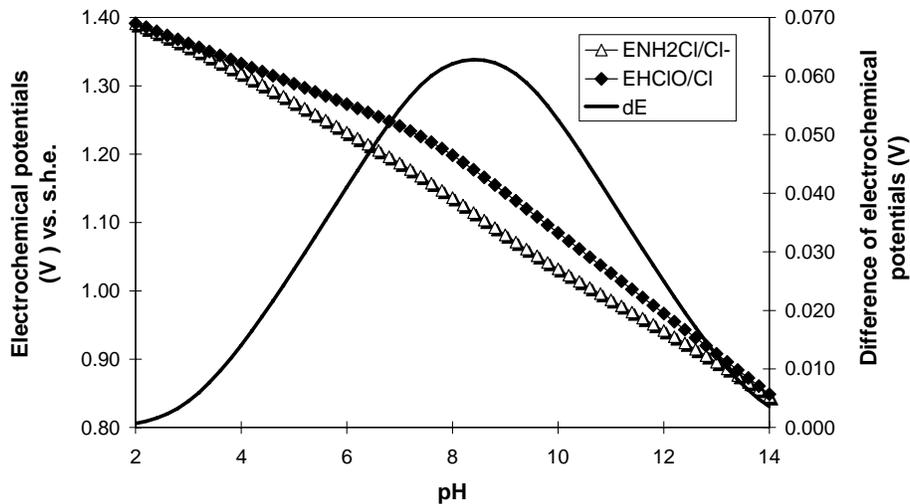

Figure 8-1. Results of theoretical calculations of standard electrochemical potentials of water containing 2mg/L of chlorine or chloramine and 10mg/L of chloride. (Ref: Korshin, 2006a)
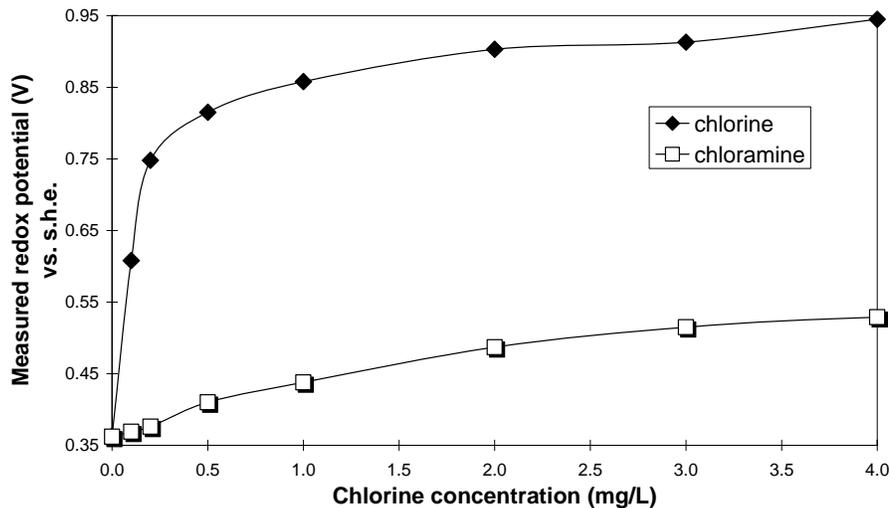

Figure 8-2. Comparison of experimental measurements of the redox potential in organic-free synthetic water at pH 7 and varying concentrations of chlorine and chloramine (Ref: Korshin, 2006b)

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CHAPTER 9 - SUMMARY OF PRELIMINARY FINDINGS AND KEY RESEARCH ISSUES

The discussions above indicate the existence of chemical and electrochemical properties that are fundamentally important to our understanding of the response of corroding metals and alloys to transitions from free chlorine to chloramines, and vice versa. Some of these properties are listed below:

- The electrochemical behavior of unpassivated LBM surfaces (elemental lead) is substantially different from passivated surfaces. Recognizing that the distribution system LBM surfaces at issue in this study are all heavily passivated, what are in question are the cycling of the mineral solids that make up the passivation scales and the varying solubilities of the solids and their interactions.
- Of the common distribution system oxidants, only free chlorine oxidizes lead (II) solids to form PbO_2 and possibly other Pb(IV) solids. Their solubility is low and their formation is beneficial for lead release control.
- The oxidation of Pb(II) phases by free chlorine involves an initial slow transformation that occurs without discernible chlorine consumption. The duration of the lag phase is affected in complex but quantifiable ways by water quality parameters and, possibly, hydrodynamic conditions.
- The reverse process of PbO_2 reduction to Pb(II) involves NOM and appears to be kinetically slow. Chloramine does not prevent PbO_2 reduction but it is not clear whether it accelerates it.
- Comparative effects of free chlorine and chloramine on the release of copper and zinc from LBM and copper per se remain largely unknown. It can be hypothesized that free chlorine can suppress the formation of Cu(I) films and promote that of Cu(II) oxyhydroxides. The importance of changes in the Cu(I)/Cu(II) predominance for copper and zinc release is to be explored.
- The influence of galvanic coupling or other external electrochemical perturbations on passivated LBM surfaces relative to lead release is likely to be minimal. However, the influence of internal galvanic currents relative to lead inclusions in lead bearing alloys has not been well studied. Also, the influence of electrical perturbations on copper surfaces may be of importance, and is likely strongly influenced by water quality parameters such as redox potential and conductivity.
- Treatment chemicals such as coagulants may increase copper and lead corrosion and metals release, and their involvement may be influenced by a change in disinfectant.
- pH and alkalinity change can impact lead and copper corrosion, and other water quality variables or treatment changes can modify or confound their effect.

The above findings lead to key issues that will be explored in this study to predict effects of disinfectant change on corrosion and metals release into drinking water.

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