IMPACT OF CHLORIDE:SULFATE MASS RATIO (CSMR) CHANGES ON LEAD LEACHING IN POTABLE WATER
IMPACT OF CHLORIDE:SULFATE MASS RATIO (CSMR) CHANGES ON LEAD LEACHING IN POTABLE WATER

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

and

U.S. Environmental Protection Agency
Washington, DC 20460

Published by:
Water Research Foundation
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FOREWORD

The Water Research Foundation (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 professionals. 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 organizations 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 findings will be applied in communities throughout the world. The following report serves not only as a means of communicating 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 who 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.

David E. Rager
Chair, Board of Trustees
Water Research Foundation

Robert C. Renner, P.E.
Executive Director
Water Research Foundation
ACKNOWLEDGMENTS

The authors of this report would like to thank Traci Case, the Water Research Foundation project manager, and the members of the Project Advisory Committee – Christopher Hill, France Lemieux, Joseph Marcinko, and Anne Spiesman. Thanks also to Alexander Vetrovs of HDR for maintaining the pilot study.

We also appreciate the assistance of the following water utilities and organizations for their cooperation and participation in this project: Davidson Water, City of Durham (NC), Greenville Utilities Commission (NC), Halifax Water (Nova Scotia), Jordan Valley Water Conservancy District (UT), Long Beach Water (CA), City of Minneapolis (MN), City of Montreal, Portland Water Bureau (OR), City of Raleigh (NC), City of Savannah, South Blount County Utility District, Ville de Laval (Quebec), Washington Suburban Sanitary Commission (MD), CDM, and the Copper Development Association, Ecole Polytechnique Montreal. We would also like to thank Jerry Lowry for assistance with the case study in Maine.
EXECUTIVE SUMMARY

The leaching of lead to potable water can sometimes be severely impacted by seemingly innocuous changes in water treatment including changes from one coagulant type to another. Case studies documented a few prior instances in which coagulant changes produced a higher chloride-sulfate mass ratio (CSMR) in the finished water that was linked to the onset of lead contamination problems. However, no mechanistic studies had been conducted to unambiguously demonstrate the precise sequence of events that can cause higher a CSMR to increase lead contamination.

The Water Research Foundation funded this project to determine the effects of CSMR on lead leaching to potable water. The work was performed in three phases. In Phase 1, the fundamental chemistry of galvanic corrosion attack on lead-copper joints was evaluated, and experiments examined impacts of high CSMR on the integrity of soldered joints. Utility case studies were evaluated in the second phase of work to examine effects of CSMR on galvanic corrosion in a number of potable waters. Specifically, questions regarding the effects of coagulant changeover, desalination, and anion exchange treatment on lead solder and leaded brass corrosion were evaluated. The roles of alkalinity, pH, and corrosion inhibitors to potentially mitigate corrosion in high CSMR waters were also examined. Finally, in a third phase of work, re-circulating loops were used to evaluate the impacts of chloride, sulfate, and flow rate on corrosion of lead plumbing materials.

A total of six conference papers on this work have been presented to date:

APPLICATIONS AND GENERAL GUIDANCE

Level of Utility Concern Relative to CSMR

The chloride-to-sulfate mass ratio (CSMR) is calculated based on effluent sample results. For example, for water with 10 mg/L Cl\(^{-}\) and 20 mg/L SO\(_4^{2-}\), the CSMR is 0.5:

\[
\text{Chloride to Sulfate Mass Ratio (CSMR)} = \frac{[\text{Cl}^{-}]}{[\text{SO}_{4}^{2-}]} = \frac{10 \text{ mg/L Cl}^{-}}{20 \text{ mg/L SO}_{4}^{2-}} = 0.5
\]

To judge whether the information in this report is of no concern, significant concern, or a serious concern, utilities can use the flow chart (Figure ES.1) and the calculated CSMR of their water. For example, if a utility has no lead solder or partially replaced lead pipe materials in the distribution system and the CSMR is below 0.2, in general this report would not predict lead problems from the mechanism of lead corrosion that is described herein. In contrast, if a utility has a CSMR greater than 0.5 and an alkalinity of less than 50 mg/L as CaCO\(_3\), then the utility could potentially have serious lead problems following treatment changes that increase the CSMR. The greatest concerns are at utilities with lead solder or partially replaced lead pipe, that are considering changes to their water chemistry that increase the water’s CSMR from below 0.5 (before) to above 0.5 (after). It is strongly recommended that utilities considering treatment changes that increase CSMR above 0.5 examine potential impacts on lead release using simple protocols described in this work. Most of the tests can detect adverse impacts after just a few weeks of bench scale testing.

![Flow Chart](image)
Guide to Using This Report Most Efficiently

A roadmap to the report is provided to assist utilities, regulators, and scientists in determining which portions of this work would be of greatest interest in their particular situation (Figure ES.2). Utilities with significant to serious lead concerns from CSMR, as determined from Figure ES.1, are strongly encouraged to consider the relevant portions of this work.

The key point of this work is that elevated chloride and reduced sulfate can sometimes markedly increase the lead leaching in consumers’ homes and 90th percentile lead values obtained through utility monitoring. Numerous treatment changes can increase the relative amount of chloride and sulfate in the water including: 1) switching from chlorine gas to hypochlorite generation using brine solutions, 2) changing from a sulfate-containing coagulant such as alum to a chloride-containing coagulant such as ferric chloride, 3) anion exchange for arsenic treatment, 4) desalination, and 5) increasing chloride in raw water due to road salt use. Methods that might reduce or eliminate the adverse effects of higher chloride (or lower sulfate) were also evaluated in this project. In general, water quality changes that mitigate most lead corrosion problems including phosphate dosing or modest adjustments to alkalinity/pH, were largely ineffective in controlling lead leaching problems from lead solder or lead pipe that is galvanically connected to copper. Thus, findings of this work may be viewed as a special manifestation of lead corrosion problems, which requires specialized considerations and expertise to solve.

BACKGROUND

Much of the prior research on lead leaching has focused on corrosion as it relates to bulk water parameters including pH, alkalinity and orthophosphate concentration. Utilities have had a great deal of success applying solubility concepts to mitigation of lead leaching from pure lead pipe, lead solder, and brass. Galvanic corrosion between dissimilar metals can cause a dramatic divergence from this conceptualization in some circumstances and have relatively little effect in others. Specifically, if there is little or no galvanic current between electrically connected dissimilar metals such as lead and copper, then the concentration of constituents at the surface of the solder will be close to that of the bulk water. In those circumstances, prior insights regarding the role of water chemistry on lead solubility under pH, alkalinity, and anion levels would directly apply and solve most problems (Schock et al. 1996). Although lead in water can be in particulate form as well as soluble form (McNeill et al. 2004), the general trends in lead solubility often serve as a useful guide for predicting changes in total lead concentration that will occur in drinking water.

However, if significant galvanic currents exist, localized conditions arise which can decouple the chemistry present at the lead surface from that present in the bulk water. Specifically, pHs at the surface of lead solder can be driven to as low as pH 2, and the local Cl\(^-\) and SO\(_4^{2-}\) levels in the water contacting the lead can be orders of magnitude higher than in the bulk water. Under such circumstances, conventional approaches to mitigating lead corrosion can be rendered almost completely ineffective. To address gaps in understanding and to provide a basis for responding to problems, this work attempted to: 1) extend prior practical research on lead solubility to the range of chemical conditions that may be present at lead anode surfaces, 2) unambiguously demonstrate mechanisms of the serious corrosive attack that can occur on lead
Figure ES.2 Applications decision tree. This tree is intended to provide direction for the reader in finding the relevant chapter(s) based on their individual situations and applications. If the reader determines that changes to treated water would affect the CSMR, and these changes could create a significant or serious level of concern, the tree can direct them to the applicable research and help them mitigate a potentially corrosive situation. Note: this tree is meant as a reference guide to find research information and not intended to be used as an absolute water treatment reference manual.
solder in waters with high CSMR, and 3) systematically evaluate a range of water treatment changes that might alter CSMR through case studies at participating utilities.

At the outset it is important to note that CSMR impacts on galvanic corrosion and associated lead contamination of potable water can be controlled by a number of factors that may include but are not necessarily limited to: 1) type of lead plumbing material, 2) type of passivating film coating the lead or copper surface, 3) frequency of water flow patterns in the building, 4) plumbing connections to other pipe materials including iron, 5) workmanship of the plumber who originally installed the lead:solder joints, which controls the mass of solder exposed to the water, and 6) history of water chemistry in the plumbing system. Moreover, although this work did not identify specific trace water chemistry constituents that could be present (or added) to water that could completely stop this type of attack, it is also quite possible that such trace constituents exist in certain systems. Considering these factors, trends found in this work are not expected to apply universally to lead contamination events in individual homes/buildings, or even at specific water utilities, because additional research is needed to better understand the practical circumstances when severe lead contamination from galvanic corrosion is triggered. However, based on prior research and the case studies presented herein, it is clear that the discoveries presented in this work do apply to lead corrosion problems at some utilities.

APPROACH

Static dump-and-fill experiments were conducted in triplicate for the first phase of work examining fundamental chemistry and solder corrosion. Effects of water chemistry on total, soluble, and complexed lead were determined. Lead, tin, antimony, pH and chloride near the solder (anode) surface, galvanic currents, and peak structural loads before joint failure were measured. A quality assurance and quality control (QA/QC) plan was developed, approved, and followed for all laboratory work in this project.

In a second phase of work, water was shipped from participating utilities to Virginia Tech. The waters from the utilities were treated at bench scale to simulate the full-scale treatment to the extent possible using coagulation, sedimentation, filtration, and disinfection. For the case studies where the coagulant type was evaluated, attempts were made to treat the waters exactly the same as they would be in practice, except for the type of coagulant used. Although there were some differences in finished water turbidity and organic carbon levels (as would occur in practice), the major difference in the treated finished water was almost always the amount of counter-ion added to the water from the coagulant (i.e., sulfate from coagulants such as alum or ferric sulfate, and chloride from coagulants such as PACl or ferric chloride). A range of inhibitor types, alkalinity levels, and pHs were also examined to see if they mitigated or exacerbated the corrosion and resulting lead contamination (Table ES.1). Solder-copper coupons and sometimes brass were exposed to fresh test water twice per week, but water was otherwise stagnant. Total lead in water and pH near the solder surface were amongst the measurements used to track practical impacts resulting from treatment.

In the final phase of the work, water was recirculated through pipe loops containing lead plumbing materials and copper pipes while exposed to low and high CSMR water. The water in the reservoir for each loop was changed weekly. Total lead was measured weekly in the reservoir for each condition and from pipes before and after stagnation periods. The galvanic current flowing between the copper pipe and the lead plumbing material was measured at least
Table ES.1

Variables investigated in each bench scale test.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Utility Case Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td></td>
</tr>
<tr>
<td>Anion Exchange</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{2}Cl vs. Cl\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>Cl- Leak from Chlorine Generation</td>
<td></td>
</tr>
<tr>
<td>Coagulant Type</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>Phosphate Inhibitors</td>
<td></td>
</tr>
<tr>
<td>Road Salt</td>
<td></td>
</tr>
</tbody>
</table>

| Chapter in Report | 1 | 4 | 5 | 6 | 6 | 7 | 8 | 9 | 10 | 11 |

Completed as part of the Water Research Foundation Project 4088

weekly for the loops containing two dissimilar metals. The lead and current data were used to examine the effects of high and low CSMR water on a range of lead plumbing materials with more frequent flow conditions compared to the second phase of work.

RESULTS

Lead leaching from lead plumbing materials increased when the chloride-to-sulfate mass ratio (CSMR) of the water was increased for almost all of the cases evaluated in this report. As CSMR increased towards the ratio of 0.4-0.6, changes in the CSMR had particularly strong impacts, consistent with prior experiences and experiments. If CSMR was well above 0.4-0.6, then further increases in CSMR were detrimental but did not produce large percentage increases in lead leaching. Experiences of utilities were synthesized and documented, illustrating that substantive increases in CSMR and lead problems can be triggered by the following:

1) changing from a sulfate-based coagulant to a chloride-based coagulant,
2) using anion exchange (resin in chloride form),
3) using desalinated or membrane treated water,
4) road salt runoff from roadways, and
5) chloride leaks from hypochlorite generation system using brine.
Mechanistic Effects of CSMR

The key reactions occurring at the lead surface were examined using a combination of solubility tests and macro-cell arrangements. Sulfate in water can be beneficial because it reacts with lead in the water to form relatively insoluble PbSO$_4$ solids, even at pHs as low as 2 to 5. In contrast, chloride does not tend to form insoluble lead solids at these pHs, but instead enhances the dissolution of lead by forming soluble complexes such as PbCl$^+$. The net result is that sulfates mitigate lead contamination from lead surfaces galvanically coupled to copper, by reducing the magnitude of the galvanic current and also by forming a relatively low solubility scale layer. In contrast, chloride increases the magnitude of the galvanic current and prevents formation of a protective scale layer. The net result is that under conditions found at lead anode surfaces, SO$_4^{2-}$ is beneficial in reducing lead release, and Cl$^-$ is detrimental. This is the mechanistic basis for the CSMR ratio in predicting lead contamination from galvanic corrosion. A higher CSMR has relatively little effect on corrosion of lead pipe or lead solder that is not galvanically connected to copper.

Coagulant Changeover Case Studies

In practical case studies, coagulation with a chloride-based coagulant (e.g., ferric chloride) tended to increase lead leaching from simulated copper joints containing 50:50 Pb/Sn solder compared to coagulation with a sulfate-based coagulant such as alum. The differences between lead contaminants caused by coagulant selection were most dramatic when the CSMRs of the treated waters were below the threshold value of 0.5 before the switch, and were raised to greater than 1.0 after the switch. In this project, a wide range of chloride-based, sulfate-based, and blended coagulants were evaluated (Table ES.2).

For one utility in NC (Utility G) simulated solder-copper joints exposed to ferric chloride or a ferric sulfate/aluminum chlorohydrate blend leached at least 3 times more lead than the sulfate-based coagulants (e.g., alum). Further evidence of the positive correlation between CSMR and lead release was observed for two utilities in NC (Utilities B and E), where ferric chloride-treated water released 3 times and 6 times more lead from brass and solder, respectively, than ferric sulfate-treated water. Consistent with expected trends, the ferric sulfate/chloride blended water that had a CSMR of 0.3 leached significantly less lead from solder than the water with the highest CSMR (ferric chloride) and released more lead from solder than ferric sulfate, which had the lowest CSMR.

Similarly, PACI-treated water for Greenville in NC released 50 times more lead from 50:50 Pb/Sn solder than alum-treated water after 23 weeks. However, when the coagulant was changed for Greenville from alum to PACI at bench scale, the lead leaching did not increase markedly until after 2 weeks of exposure. Therefore, dosing PACI during storm events for a few days at the plant should not have major negative consequences for lead leaching in this system.

The effect of CSMR was not as obvious for a utility in Maryland (Utility I) and a utility in Nova Scotia (Utility D). This may be attributed to the consistently high CSMR of the treated water, regardless of which coagulant was used, because the CSMR was always well over the critical range of 0.5. No significant difference was observed for Utility I comparing alum and PACI in terms of lead leaching from brass and 50:50 Pb/Sn solder in this water. However, there
Table ES.2
Summary of coagulants evaluated in the EPA/Water Research Foundation Project 4088.

<table>
<thead>
<tr>
<th>Utility</th>
<th>Chapter in Report</th>
<th>Coagulants Evaluated</th>
<th>CSMR Tested</th>
<th>Summary of Findings and Other Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenville Utilities Commission (GUC), NC</td>
<td>4</td>
<td>Alum</td>
<td>0.4</td>
<td>After switching from alum to PACl, it took 1.5 weeks for lead leaching to increase. Coupons exposed to low and high CSMR waters for 2 years showed no differences between the CSMRs. For this water, blending coagulants to achieve a CSMR of approximately 0.7 did not significantly increase lead leaching, and changes in alkalinity did not have a large effect on lead leaching compared to the effects of CSMR.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alum/PACl Blends</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PACl</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>B &amp; E, NC</td>
<td>6</td>
<td>Ferric Sulfate</td>
<td>0.2</td>
<td>Water treated with ferric chloride consistently had more lead leaching from solder and brass than water treated with ferric sulfate. Anion exchange treatment in conjunction with ferric chloride coagulation resulted in the highest lead levels, and phosphate corrosion inhibitors made lead leaching worse for that CSMR condition.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Sulfate/ Ferric Chloride Blends</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Chloride</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>D, Nova Scotia, Canada</td>
<td>7</td>
<td>Alum</td>
<td>0.9</td>
<td>Lead release from Pb/Sn solder was not significantly different among the three water conditions tested. This might be because all waters were above the 0.5 CSMR threshold. At levels of CSMR above the 0.5 threshold, other factors such as alkalinity and organic carbon may control lead release.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Sulfate</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PACl</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>G, NC</td>
<td>5</td>
<td>Alum</td>
<td>0.4</td>
<td>Chloride-based coagulants, which had CSMRs &gt;1, had significantly higher lead levels than sulfate-based coagulants (CSMR of 0.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Sulfate</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Sulfate Polymer Blend</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Sulfate/ Aluminum Chlorohydrate Blend</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric Chloride</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>I, MD</td>
<td>1</td>
<td>Alum</td>
<td>1.4</td>
<td>Both CSMR levels that were evaluated resulted in high lead release from brass and solder. Because of the high CSMR of the waters evaluated, no significant differences were seen between PACl and alum in terms of lead leaching. However, PACl water dosed with simulated road salts (CSMR 8.4) resulted in about two times more lead than PACl or alum waters (with no road salts).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PACl</td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>
was evidence that a very high CSMR could result in some increase in lead leaching. Specifically, when PACI-treated water was dosed with 20 mg/L Cl to simulate the upward trend in raw water chloride from road salt runoff (CSMR 8.4), lead leaching doubled compared to the other two conditions with no simulated road salt runoff. Similarly, the CSMR for Utility D water was always relatively high (CSMR > 0.9), and therefore other factors such as organic carbon and alkalinity had a greater effect on lead leaching than did changes in CSMR. It is hypothetically possible that in systems with high CSMR, much of the solder that was exposed to water has been released over decades of corrosion. A substantial fraction of the simulated solder from worst-case joints leached to the water over a period of months to years. Hence, such systems might not be adversely impacted by higher CSMR water, relative to systems that passivated rapidly in a low CSMR water when first installed and abruptly subjected to high CSMR water. This might also explain compliance with 90th percentile lead levels in systems that have historically had high CSMR water.

Case Studies Evaluating the Effect of CSMR from other Treatment Changes

Desalinated water tends to contain relatively low levels of sulfate but high amounts of chloride, since the treatment process more efficiently removes sulfate from the water than chloride. Blending desalinated water with the current distribution water (groundwater) used at Utility K increased lead release from lead solder galvanically connected to copper by 18 times when the blended water consisted of 25% desalinated water in bench scale tests. In the highest blend evaluated, lead release increased more than 40 times when the blend contained 75% desalinated water. Further testing indicated that the detriments of high CSMR could not be countered by higher alkalinity or phosphate corrosion inhibitors in this water.

Another treatment change that impacted the CSMR of treated water is anion exchange, which is used to remove contaminants such as arsenic and organic matter from water. For one utility in Maine (Utility F), treating with anion exchange increased the CSMR of the water from 1.1 in the distribution water to 7.8 after anion exchange treatment. The lead release from 50:50 Pb/Sn solder reflected the impact of the CSMR, since an average of 47 times more lead was released from the coupons exposed to anion exchange treatment over the six-week study period compared to the coupons with no treatment. The dramatic increase in lead observed in practice in this water system after starting anion exchange treatment may also be attributed to the decrease in pH and alkalinity after anion exchange treatment. However, a major contributor to the problem, even in the absence of a pH drop, was the higher CSMR.

Effect of Alkalinity

Increasing the alkalinity for waters from Utilities A, E, and I decreased the lead released to the water. Thus, from this perspective alkalinity was beneficial as was predicted. However, adding alkalinity to a very low conductivity water from Utility J exacerbated lead release. Furthermore, the combination of orthophosphate and increased alkalinity made lead leaching much worse. Additional research is needed to better understand when alkalinity will have beneficial or detrimental effects.
Corrosion Inhibitors

The effects of phosphate are complex and were dependent on the water tested. Dosing orthophosphate to the water from Utility J, which had very low conductivity, reduced lead leaching from 50:50 Pb/Sn solder. However, when the alkalinity of the water was increased and orthophosphate was dosed, the lead release increased dramatically. Those results are inconsistent with accepted theory, and further research is needed to determine when phosphate would be beneficial or detrimental.

Based on prior field experience, it was known that dosing of phosphate for 18 months to 20 years did not stop problems from lead contamination when CSMR was subsequently increased. However, in bench scale testing for this work, phosphate seemed beneficial in mitigating problems in some cases. For example, addition of orthophosphate at a dose of 1 mg/L P (3 mg/L PO₄) was more effective in reducing lead leaching than polyphosphates or adding no inhibitor in Greenville, NC (Edwards and Triantafyllidou 2007). Lead solder coupons were exposed for at least 3 years to Greenville water containing orthophosphate, most likely with little or no dissolved oxygen during that exposure, and the coupons leached at least 3.5 times less lead than equivalent coupons never exposed to orthophosphate.

In another water tested for Utilities B and E, dosing of orthophosphate also dramatically decreased lead leaching to 25% of the lead release observed in the same water with no inhibitor. Benefits of dosing silicate polyphosphate inhibitor in terms of lead leaching was also achieved for Utilities B and E, but the extent of the decrease in lead release per equivalent amount of phosphate dosed was lower than with orthophosphate.

CONCLUSIONS

Key conclusions that can be taken from this work include:

- A simple bench-scale test protocol was developed that provides insights to changes in lead leaching to water from galvanic connections between solder/lead pipe and copper. This simple dump and fill protocol was successfully used to rapidly screen for significant changes in lead leaching that resulted from various water treatment changes. In most cases, short-term tendencies as measured by the test were in qualitative agreement with practical utility experiences and longer-term test results.

- pH drops at the surface of lead solder or lead pipe, if there is a galvanic connection to copper pipe. pHs as low as 3.3 were measured at the surface of the lead bearing material even when the bulk water pH was 8.0 or higher. (Chapter 1)

- At pH 3, pH 4, and pH 5, the concentration of soluble lead decreased with the addition of high levels of sulfate. Changes in pH in the pH 3-5 range have little effect on the solubility of lead sulfate. The migration of sulfate to lead anode surfaces can therefore serve to limit lead leaching. (Chapter 1)

- At pH 3, 4, and 5, the uncomplexed or free lead concentration decreases with the addition of chloride, consistent with formation of a PbCl⁺ lead chloride complex. The migration of chloride to lead anode surfaces, therefore, can exacerbate problems with lead leaching. (Chapter 1)
The net effect of chloride and sulfate migration to lead anode surfaces depends on their relative concentration. Higher chloride tends to increase lead solubility whereas higher sulfate tends to decrease lead solubility; hence, the usefulness of the CSMR in explaining trends in lead contamination when galvanic corrosion of lead is significant. (Chapter 1)

The corrosion rate of and the release of lead and/or tin from solder alloys was greater in high CSMR water. The pH at the solder surfaces were measured to be as low as pH 3.0. (Chapter 2)

Simulated joints with 97/3 Sn/Cu solder had the greatest reduction of joint strength after one year of exposure to high CSMR water. (Chapter 2)

The 95/5 Sn/Sb had the most desirable characteristics of the solders evaluated in this project. The solder had the lowest reduction in joint strength after one year of exposure to high CSMR water, did not release harmful levels of antimony, and had less tin corrosion compared to other solder alloys. (Chapter 2)

For the utilities evaluated in this project, leaded brass leached relatively low levels of lead to the water, even in situations with high CSMR. In contrast, corrosion of lead solder in simulated copper joints contributed to very high amounts of lead in test waters. Thus, while leaded brass is impacted somewhat by CSMR, the issues associated with lead solder can occasionally achieve hazardous waste levels (>5,000 ppb) of lead in water under worst-case scenarios. As a result, lead solder and lead pipe galvanically connected to copper are the primary concern when effects of higher CSMR are considered.

Generally, increasing the chloride-to-sulfate mass ratio (CSMR) of the water results in higher lead levels in water when copper:lead solder or copper:lead pipe galvanic couples are present. There could be higher chloride and lower sulfate in the water due to a range of scenarios:

- Road salt entering the water supply from runoff, especially into open reservoirs (Chapter 1)
- Coagulant type (chloride-based vs. sulfate-based) (Chapters 4, 5, 6, and 7)
- Desalination (Chapter 8)
- Chloride-based anion exchange treatment (Chapter 6 and 9)
- Brine leak from hypochlorite generation system (Chapter 10)

A combination of low pH and high CSMR at the solder surface drive the long-term galvanic corrosion of the lead solder, as demonstrated by local measurements of very high chloride, sulfate, and lead near the lead solder anode. There is no evidence that the lead solder can passivate in such circumstances.

It is hypothetically possible that in systems with high CSMR, much of the solder that was exposed to water has been released over decades of corrosion. A substantial fraction of the simulated solder from worst-case joints leached to the water over a period of months to years. Hence, such systems might not be adversely impacted by higher CSMR water, relative to systems that passivated rapidly in a low CSMR water when first installed and...
abruptly subjected to high CSMR water. This might also explain compliance with 90\textsuperscript{th} percentile lead levels in systems that have historically had high CSMR water.

- Increasing alkalinity of the water can be effective in mitigating the low pH at the lead solder surface and eventually causing decreased lead levels. However, in some circumstances where conductivity of the water is very low, increasing the alkalinity (and conductivity) can make lead leaching much worse. Dosing orthophosphate was more effective than polyphosphate in reducing lead release. However, in rare circumstances, dosing orthophosphate could make lead leaching worse. Hence, the effects of phosphate and alkalinity need to be determined on a site-specific basis. With additional experience, it might be discovered that the adverse effects of higher alkalinity and higher phosphate are limited to certain waters, such as those with extremely low conductivity. (Chapters 6 and 10)

- The effect of CSMR was confirmed in flowing conditions that are typical in home systems. Higher CSMR water resulted in higher lead leaching from lead pipe, bronze pipe, and solder galvanically connected to copper. (Chapter 11)

- The galvanic connection of copper to the lead materials evaluated in the study significantly increased lead leaching when compared to the situation when there was no electrical connection to copper pipe. In some waters, however, galvanic connections had little effect on lead leaching. (Chapter 11)

**RECOMMENDATIONS**

A key finding was that problems that occur in coagulant changeovers could usually be mitigated by controlling the type of coagulant and keeping CSMR below about 0.5. However, this is not always an option when CSMR was increased via arsenic treatment via anion exchange or desalination. For these case studies, adding orthophosphate when the CSMR was high did not reduce lead leaching or the extent of the problem. Therefore, more work is needed to determine what treatment(s) could counter the adverse consequences of higher CSMR.

This work also focused on making comparisons among treatment methods in terms of leaching from lead solder under worst-case conditions of long stagnation times, and these changes were dramatic. However, it is not completely certain how the lead levels measured in these “worst case” scenarios would translate to 90\textsuperscript{th} percentile lead in practice. Better understanding would require consideration of many factors including plumbing materials in the distribution system, variability in plumbing jobs, and other factors. That is, in some situations, even a 20\% increase in lead leaching from solder or lead pipe connected to copper due to higher CSMR might translate to a relatively modest increase (+/- 0.1 to 1 ppb) in 90\textsuperscript{th} percentile lead. In these cases, even though galvanic corrosion of lead bearing materials is worsened, the public health concern might be of relatively low significance.
ORGANIZATION OF THE REPORT

This report is organized as follows:

- Chapter 1 defines the mechanism by which high chloride and low sulfate can increase lead release from solder using a macrocell configuration. A case study with one utility in Maryland demonstrated the impacts of chloride, sulfate, disinfectant type, and alkalinity on lead leaching, pH at the lead surface, and real-time corrosion rates for a simulated lead joint.

- Chapter 2 describes the impact of chloride and sulfate on the durability of simulated copper joints comprised of various solder alloys, including lead solder and lead-free solders. Some types of solder were more resistant to attack in high CSMR waters than others.

- Chapter 3 presents an overview of the factors evaluated in the case studies for this project and provides a framework for the remainder of the report.

- Chapter 4 describes results from the Greenville Utilities Commission (GUC) in North Carolina (NC), where lead in drinking water has been a problem in the past. The impact of short-term changes in coagulant from a sulfate-based coagulant to a chloride-based coagulant was evaluated. Additionally, blends of alum and PACl coagulants were reviewed, as a potential approach to realizing benefits of PACl coagulation while maintaining a lower level of chloride in the water.

- Chapter 5 is a case study using water from another utility in NC (Utility G), where 5 potential and past coagulants were evaluated for the effects on simulated copper joints and on brass.

- Chapter 6 describes a case study for two utilities in NC that were close in proximity. Coagulants, corrosion inhibitors, and lime (versus caustic) were evaluated.

- Chapter 7 summarizes the impacts of coagulant changes for a utility case study in Nova Scotia, Canada.

- Chapter 8 describes the implications of desalinated water use on lead leaching for one utility in California.

- Chapter 9 describes a case study in Maine where arsenic treatment and low pH both contributed to high levels of lead in water.

- Chapter 10 presents a case study for a utility in Tennessee that has very low conductivity water, and the standard practices for reducing lead in water actually made lead leaching much worse.

- Chapter 11 summarizes the results from the pipe loop study conducted at the HDR ARTC facility. Flow rate, chloride, sulfate, and various lead plumbing materials were evaluated.
CHAPTER 1: MECHANISMS OF ATTACK ON LEAD SOLDER

Caroline Nguyen, Kendall Stone, Brandi Clark, and Marc Edwards

Keywords: Coagulants, polyaluminum chloride, alum, chlorine, chloramines, road salt

INTRODUCTION

Lead corrosion is sometimes severely impacted by seemingly innocuous changes in water treatment. For example, several utilities observed lead contamination problems that arose after changing coagulants from aluminum sulfate to ferric chloride or polyaluminum chloride (PACl). In some cases, the addition of orthophosphate, a standard tool for mitigating many lead problems did not resolve the much higher lead in water produced from this changeover.

A literature review documented numerous prior cases in which higher chloride-to-sulfate mass ratio (CSMR) was linked to lead problems (Edwards and Triantafyllidou 2007). However, no mechanistic studies have ever unambiguously demonstrated the precise sequence of events that could explain the problem. Clearly, galvanic corrosion of lead pipe:copper or lead solder:copper connections is key as demonstrated by Oliphant (1983). Dudi predicted that the pH at the surface of lead materials would dramatically decrease in poorly buffered waters when connected to copper (2004). Edwards and Triantafyllidou confirmed Dudi’s prediction and measured pH as low as 3.4 at the solder surface in PACl-treated water compared to pH 7.6-7.8 in the bulk water (2007). In addition, if alkalinity is low enough, pHs as low as 3.0 have been measured at the lead plumbing material surface during stagnation, allowing the attack on the lead-bearing material to proceed indefinitely without passivation (Edwards and Triantafyllidou 2007). Using the findings of prior research, it is possible to conceptualize and anticipate the possible mechanisms by which high CSMR can trigger serious lead galvanic corrosion problems (Figure 1.1).

Considering the galvanic corrosion scenario and associated non-uniform corrosion, there are problems in applying prior research experience to prediction of lead leaching at the lead solder surface. Specifically, if there is no galvanic current between lead and copper in Figure 1.1, then the concentration of constituents at the surface of the lead solder will be that of the bulk water and prior insights regarding the role of water chemistry on lead solubility under pH, alkalinity, and anion levels are relevant (Schock et al. 1996). Although lead in water can be in particulate form as well as soluble form (McNeill et al. 2004), trends in lead solubility often serve as a useful guide for predicting changes in lead concentration that will occur in drinking water as a function of water chemistry. However, if significant galvanic currents exist, which might drive the solder surface pH to 2-5, the prior guidance from the solubility models does not extend to the conditions present at the lead anode surface during stagnation under galvanic corrosion. In those circumstances, the pH can be as low as 2.0, and local Cl\(^-\) and SO\(_4\)\(^{2-}\) levels in the water contacting the lead can be orders of magnitude higher than in the bulk water.
This work attempts to 1) extend prior practical research on lead solubility to the range of chemical conditions that may be present at lead anode surfaces, and 2) unambiguously demonstrate mechanisms of the serious corrosive attack on lead solder in waters with high CSMR. Bench scale tests were first conducted to examine the solubility behavior of lead in the unusual chemical environment (i.e., lower pH, higher chloride, and higher sulfate) that may be present near the surface of the lead solder when significant galvanic corrosion is occurring. Thereafter, a bench scale case study for Utility I in Maryland was conducted for eight weeks using a specially designed apparatus to mechanistically study the effect of coagulant selection, future water quality trends, and treatment process modifications on lead leaching. After the first two months of the utility case study, additional work was performed to gain confidence in the trends and to evaluate the effects of higher alkalinity and solder orientation in a pipe.

MATERIALS AND METHODS

Lead Solubility and Complexation Studies

Lead speciation for the low pH lead solubility and complexation studies were quantified by a variety of techniques. Soluble lead was operationally defined as the portion of lead that passed through a filter of 0.45 μm nominal pore size syringe filters. Particulate lead was determined as the difference between the total lead and the measured soluble lead, or by dissolution of the solids collected from the water on the surface of the membrane filter. Total, soluble, and particulate lead were quantified via measurements using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) according to Standard Method 3125. All chemicals were added as reagent grade salts.
Sulfate Addition

All solutions were prepared by first dissolving 0.48 mM Pb(NO\textsubscript{3})\textsubscript{2} in distilled and deionized water and adding HNO\textsubscript{3} to adjust the solution to pH 3, 4, or 5. The sulfate concentrations in these solutions were varied from 0 to 2.66 mM SO\textsubscript{4}\textsuperscript{2-} by adding Na\textsubscript{2}SO\textsubscript{4}. NaNO\textsubscript{3} was added in variable amounts to maintain a constant ionic strength of 0.01 M for each solution (Table 1.1). The pH was then re-adjusted to the target value of pH 3.0, 4.0, or 5.0 ± 0.05 using HNO\textsubscript{3} or NaOH. After 24 hours, unfiltered and filtered (through 0.45 μm pore size nylon filters) samples were collected for each solution and preserved with 2% nitric acid. The lead and sulfate concentrations were measured using ICP-MS.

Chloride Addition

All solutions were prepared by first dissolving 0.48 mM Pb(NO\textsubscript{3})\textsubscript{2} in distilled and deionized water and adding HNO\textsubscript{3} to bring the solution to pH 3, 4, or 5. The chloride concentrations in these solutions were then varied from 0 to 8 mM Cl\textsuperscript{-} by adding NaCl. NaNO\textsubscript{3} was added in variable amounts to maintain a constant ionic strength of 0.01 M for each solution (see Table 1.2). The final pH was adjusted to 3.00, 4.00, or 5.00 ± 0.05. After 24 hours, the free Pb concentration was measured, and a sample was collected and preserved with 2% nitric acid to determine the total soluble Pb concentration. Free Pb was measured using a Pb\textsuperscript{2+} ion specific electrode (ISE) manufactured by Cole Parmer, Inc, catalog number 27502-25. The electrode was calibrated using six standards with concentrations ranging from 1 to 300 ppm Pb\textsuperscript{2+} as lead nitrate. The ionic strength of all the standard solutions was maintained at 0.01 M using NaNO\textsubscript{3}. Measurements were taken immediately following calibration, and the 100 ppm standard was measured periodically to compensate for drift.

<table>
<thead>
<tr>
<th>Na\textsubscript{2}SO\textsubscript{4} added (mM)</th>
<th>NaNO\textsubscript{3} added (mM)</th>
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<tbody>
<tr>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>0.33</td>
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<td>1</td>
</tr>
<tr>
<td>2.66</td>
<td>0</td>
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</tbody>
</table>
Table 1.2
Chloride and Nitrate Concentrations in Complexation Study

<table>
<thead>
<tr>
<th>NaCl added (mM)</th>
<th>NaNO₃ added (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>0.5</td>
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<tr>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
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<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
</tr>
</tbody>
</table>

Mechanistic Study of Lead Corrosion

**Apparatus**

**Brass.** New brass fixtures, such as faucets, are considered major contributors to lead contamination of tap water (Kimbrough 2001, Lytle and Schock 1996, Mariñas et al. 1993). One of the most common types of brass used in faucets is C36000, an alloy with a lead content of 3% by weight. In this test C36000 brass coupons of 0.64 cm (0.25 in) diameter and 0.97 cm (0.38 in) height were fabricated from brass rods. The coupons were epoxied to the bottom of 46-mL glass vials to study corrosion of brass by itself. Each vial was filled with 40 mL of test water in order to achieve a brass surface area to water volume ratio of 8.7 x 10⁻³ in²/mL. The brass coupons were tested in triplicates and studied only during the first part of the Utility I testing (Part 1).

**Solder.** Solder wire (50:50 lead:tin) of 0.32 cm (0.125 in) in diameter and with a height of 6.35 cm (2.5 in) was exposed to water in a copper-solder connection (Figures 1.2 and 1.3). The copper portion of the couple consisted of a ¾” diameter copper pipe and a ½” diameter copper pipe, which were connected by clear tubing with an approximate 2-mm gap between the copper pipes. The smaller diameter (½”) copper pipe was used to investigate localized effects around the anodic solder. The large diameter (¾”) copper had the dual purpose of allowing electrode measurements inside the pipe and providing a large copper-to-solder surface area of approximately 30:1 Cu:Pb total. To simulate the galvanic connection between copper pipes and solder at joints, the solder and the copper pipes were externally connected with copper wires (Figure 1.2). The connection was broken at strategic times throughout the study to place an ammeter in-line electrically to measure the galvanic current and potential drop between the solder and the copper pipes. The schematic and dimensions of the apparatus are provided in Figure 1.2. Three replicates were tested for each water condition in Part 1.

**Test Water for Utility I, MD**

**Part 1.** Test water from Utility I in Maryland was obtained at Virginia Tech by shipments of raw water from the Patuxent River reservoir. Collected water was separated and subjected to two simulated treatments, which were otherwise identical except for the type of
coagulant used. Treatment involved coagulation with PACl or alum, filtration, phosphate corrosion inhibitor addition, disinfection with free chlorine or chloramines, and final pH adjustment. The pH for both treatments was adjusted to the same initial value, ranging from 7.6 to 7.8. Since PACl adds chloride to the water, it increases the ratio of chloride to sulfate whereas alum adds sulfate thereby decreasing the ratio. The PACl coagulant was provided by Utility I. Doses, timing of addition and duration of treatments were selected to simulate the full-scale treatment practice to the extent possible.

To simulate future reservoir water quality conditions when road salts enter the source water at higher concentrations, 20 mg/L Cl was added to PACl-treated water in the form of NaCl. An overall upward trend has been observed for raw water chloride concentrations at Utility I over the last 15 to 20 years, with an increase in Cl\textsuperscript{-} from approximately 10 mg/L in 1990 to 20 mg/L in 2007. Therefore, a total of three CSMR levels were evaluated in this study (Table 1.3).

In addition to the evaluation of CSMR, free chlorine and chloramines disinfectants were also evaluated. For the testing, the two lead materials (lead:tin solder coupled with copper and brass alone) were exposed to six different water conditions (Table 1.3). Each water had a free chlorine or chloramines dose of 3.5 mg/L Cl\textsubscript{2}, and all waters were dosed with orthophosphate at a concentration of 1 mg/L P. The alkalinity was approximately 25 mg/L as CaCO\textsubscript{3}.

![Figure 1.2 Schematic of solder-copper pipe couple used in mechanistic study](image-url)
Part 2. Since each test was performed in triplicate, 36 tests \((6 \times 3 \times 2 = 36\) with 18 in glass vials and 18 in copper pipes) were conducted overall. During the last ten weeks of the study, the conditions for two of the three replicates of the solder-copper couples were altered. The alkalinity for one replicate was increased from 25 mg/L to approximately 100 mg/L as CaCO₃ by the addition of NaHCO₃, and for another replicate, the solder-copper couple was turned upside down so that the solder was oriented at the top of the pipe. The last replicate remained at the same condition throughout the entire duration of the experiment and was referred as the “control” for the second part of work. Otherwise, all other parameters including pH, disinfection, and orthophosphate dose remained the same as in the first part of the study. All tests were kept at room temperature throughout the testing period.

Measurements

Exposure of the plumbing materials to water was via a static “dump and fill” protocol three times per week (Monday, Wednesday, and Friday). Therefore, the stagnation time was 48 hours after the Monday and Wednesday water changes, and the stagnation time was 72 hours after Friday until the water change on Monday. The water from each test condition was collected throughout the week, and the unfiltered composite was analyzed for metals at the end of each week. Metals analysis was performed via Induced Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with Standard Method 3125.

<table>
<thead>
<tr>
<th>Water Conditions</th>
<th>Chloride (mg/L Cl)</th>
<th>Sulfate (mg/L SO₄)</th>
<th>CSMR (mg Cl/mg SO₄²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum-treated, free chlorine</td>
<td>27</td>
<td>20</td>
<td>1.4</td>
</tr>
<tr>
<td>Alum-treated, chloramines</td>
<td>27</td>
<td>21</td>
<td>1.3</td>
</tr>
<tr>
<td>PACl-treated, free chlorine</td>
<td>30</td>
<td>6</td>
<td>5.3</td>
</tr>
<tr>
<td>PACl-treated, chloramines</td>
<td>32</td>
<td>6</td>
<td>5.3</td>
</tr>
<tr>
<td>PACl-treated, road salt (+20 mg/L Cl), free chlorine</td>
<td>48</td>
<td>6</td>
<td>8.5</td>
</tr>
<tr>
<td>PACl-treated, road salt, chloramines</td>
<td>48</td>
<td>6</td>
<td>8.4</td>
</tr>
</tbody>
</table>
In addition to metals analysis, pH and chloride measurements were taken for the water near the brass, solder, and copper surfaces using an MI-406 flat membrane pH microelectrode (Microelectrodes, Inc) and a Lazar electrode, respectively. The measurements were taken by slowly lowering the microelectrode from the top of the copper joint, making pH or chloride measurements at 1” and 3” from the top of the pipe. After measuring at the cathode (i.e., top of the joint), the large copper pipe piece was disassembled at the plastic tubing, which connected the large copper section with the small copper. The pH was then measured in the disassembled joint at the solder surface within the smaller copper pipe section. The pH microelectrode was calibrated before each set of measurements, and the localized pH was measured for each triplicate more than three times during the duration of the study. Trends in pH were consistent throughout the study. While it is possible, even likely, that making the measurement disturbed the water, this would manifest itself in making the pH less acidic and closer to the bulk water pH.

Galvanic measurements including current, potential drop, and corrosion potential were performed at least once monthly for the solder-copper couples. Currents and potential drops were measured 1 hour, 24 hours, and 48 hours after a water change 2 or 3 times per month while monthly $E_{corr}$ measurements were performed 1 hour after water was replaced in the pipes.

RESULTS AND DISCUSSION

Low pH Solubility Studies – Effect of Sulfate Addition

The addition of sulfate at pH 3, 4, and 5 caused a large decrease in soluble lead as the amount of sulfate added increased (Figure 1.4). This decrease in lead solubility occurred concurrent with a visible solid that was 100% PbSO$_4$ (ratio of Pb:SO$_4$ of 0.93 ± 0.09). Formation of PbSO$_4$ was completely consistent with the predictions using default constants in chemical equilibrium modeling software (MINEQL+). Likewise, the pH did not control lead solubility under these conditions, which is expected because the formation of PbSO$_4$ does not involve either H$^+$ or OH$^-$. To identify the composition of the precipitate, samples were dissolved and analyzed by ICP-MS to determine the molar ratio of lead to sulfate. This analysis revealed a molar ratio of lead to sulfate in the precipitate of 0.93 ± 0.09, which is consistent with the predicted formation of PbSO$_4$. Combining these two pieces of evidence, the precipitate is assumed to be PbSO$_4$(s), which has a $K_{sp}$ expression,

$$K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

The data collected from the experiment was used to calculate an optimized solubility product constant for lead sulfate with a value of $1.54 \times 10^{-8}$ as determined by fitting data on soluble lead and sulfate (Figure 1.5). This is in good agreement with the default $K_{sp}$ value in the MINEQL database of $1.62 \times 10^{-8}$. 

Low pH Solubility Studies – Chloride Addition

When the concentration of chloride was varied at pH 3, 4, and 5, no detectable precipitate or decrease in soluble lead occurred. However, the free lead as determined by ion specific electrode decreased with increasing chloride (Figure 1.6). The explanation is that chloride reacts with Pb(II) to form soluble complexes with lead. Using the free and total lead concentrations measured, a K-value can be determined for the formation of PbCl$^+$. The molar concentration of the lead chloride complex was assumed to be equal to the difference between the total soluble lead and the Pb$^{2+}$. The formation reaction:

$$\text{Pb}^{2+} + \text{Cl}^- \rightarrow \text{PbCl}^+$$

has an equilibrium expression:

$$K = [\text{PbCl}^+] / [\text{Pb}^{2+}][\text{Cl}^-]$$

An optimized constant of 59.5 was calculated by combining the data at pH 3, 4, and 5 (Figure 1.7). This value is in reasonable agreement with the default value in the MINEQL database, which was 39.8. The somewhat higher constant suggests that chloride complexation is more significant than previously predicted under these conditions, which have greater practical relevance to conditions found at lead surfaces in potable water.

![Figure 1.4 Effect of Sulfate Addition on Soluble Lead](image-url)
Figure 1.5 Determination of the Solubility Product for Lead Sulfate

Figure 1.6 Effect of Chloride Addition on Free (Uncomplexed) Lead
Practically, when chloride complexes with lead to form soluble complexes, then the ultimate soluble lead in the water increases. Although previous studies that considered bulk water conditions of pH and Cl\textsuperscript{−} rightly determined these complexes were insignificant under normal circumstances, this work demonstrates that they can be highly significant in the thin layer of water near the lead pipe or solder during galvanic corrosion because the pH drops and Cl\textsuperscript{−} is concentrated. Considering the equilibrium equation: \( \text{Pb} \rightarrow \text{Pb}^{2+} + 2e^- \), when the free lead (\( \text{Pb}^{2+} \)) decreases in the water as \( \text{Pb}^{2+} \) becomes complexed with chloride, then at equilibrium lead metal would corrode to form more \( \text{Pb}^{2+} \). This cycle continues, and soluble lead increases, where soluble lead includes \( \text{Pb}^{2+} \), \( \text{PbCl}^+ \), and other soluble complexes.

**Effect of CSMR – Utility I, MD**

*Overall Summary*

In the first 8 weeks of the study, for both brass and solder-copper couples, lead leaching was very high in all cases in the test rig. This is probably because the CSMRs of all waters were above the critical threshold of 0.5–0.58 identified by other studies as triggering rapid galvanic corrosion (Table 1.3). The raw water CSMR was around 5 (24 mg/L Cl\textsuperscript{−} \( \div \) 5 mg/L SO\textsubscript{4}\textsuperscript{2−}). After alum coagulation followed by sedimentation and filtration, the CSMR was approximately 1.3 while the CSMR was around 5.3 after the PACl treatment (Table 1.3). Lead leaching from lead solder was significantly higher for the projected future condition simulating higher Cl\textsuperscript{−} from road salt.

![Figure 1.7 Calculation of the Formation Constant for PbCl\textsuperscript{+}](image.png)
**Brass**

For the amount of brass and the volume of water in each glass vial, the lead concentrations were consistently below 15 ppb for all water conditions (Figure 1.8). A slight trend of increasing lead with increasing CSMR from brass was observed when the water was chloraminated (Figure 1.9). However, differences in lead concentrations were not statistically significant, and the 90% confidence intervals overlapped for all conditions.

**Solder-Copper Couples**

*Lead in water.* The lead concentrations measured in the solder-copper couples remained very high (>2,000 ppb) throughout the 8-week duration of the first part of work (Figure 1.10). Even the very high dose of orthophosphate inhibitor (1 ppm P) applied to all water conditions did not protect the solder-copper couples from corrosion. The apparatus was designed to maximize the geometric and physical conditions that are believed to contribute to lead solder corrosion caused by high CSMR, and the results demonstrate that success was achieved in this regard. Specifically, it was believed that localized low pH and high CSMR generated at the lead anode surface was the culprit for the persistent lead release, and the apparatus was designed to replicate and measure this worst-case scenario. In addition, the orientation of the lead solder at the bottom of the pipe is also believed to represent the worst-case scenario in real systems, since a build-up

![Figure 1.8 Lead released from brass during Part 1. No significant difference was observed among the water conditions for lead leaching from brass.](image)
Figure 1.9 Average lead from brass with 90% confidence intervals during Part 1.

Figure 1.10 Lead released from solder-copper couples during Part 1. The alum- and PACl-treated waters behaved similarly, except when extra chloride was in the water (water types H and I). However, chloramines disinfectant appears to be more corrosive to the lead solder compared to free chlorine.
of chloride and other salts near the anode are suspected to prevent lead passivation, and this buildup would not be broken up by density gradients when the saline water is at the bottom.

As expected, higher chloride in the water (PACl with additional 20 mg/L Cl) correlated with an increase in lead leached, which was on average two times higher than the other two conditions (Figure 1.11). However, variability in lead leaching was so high that no statistical difference was found between the waters in which only the coagulant was different (alum-treated versus PACl-treated waters). This may be explained by the relatively short duration of the test and the already high CSMR of the raw water and the finished water (CSMR>1 compared to the 0.58 referenced threshold ratio). A decision was made to continue the test for additional months to allow time to obtain confidence in key trends. On average, the CSMRs for alum- and PACl-treated waters were approximately 1.3 and 5.3, respectively, while the CSMR for the projected future condition with high Cl− due to road salt was approximately 8.4 (Table 1.3). The peak observed during Week 7 is likely due to disturbance while taking pictures of the lead solder.

**Galvanic measurements.** The galvanic currents were measured for the solder-copper couples and were clearly related to the trends observed in lead levels (Figure 1.12). The galvanic current is a direct measure of the instantaneous rate of galvanic corrosion between the lead solder and the copper pipe. A higher magnitude of current indicates a higher rate of galvanic corrosion.

All of the values measured for this study were negative, which indicates the lead solder was being sacrificed and its corrosion was accelerated by connection to the copper. For instance, for the future watershed condition in which the CSMR was highest, the corrosion rate was 1.5 times higher than the rate for either alum- or PACl-treated waters without extra chloride (Figure 1.12). This is consistent with trends from Figure 1.11 in which the future watershed condition had about twice the lead release compared to either alum- or PACl-treated waters. The common trends between the real-time current measurements and the lead levels demonstrate that currents are relatively accurate indicators of corrosion and lead leaching was largely galvanically driven. For instance, for the future watershed condition in which the CSMR was highest, the corrosion rate was 1.5 times higher than the rate for either alum- or PACl-treated waters without extra chloride (Figure 1.12). This is consistent with trends from Figure 1.11 in which the future watershed condition had about twice the lead release compared to either alum- or PACl-treated waters. In addition, the observed trend throughout the study was that the galvanic currents decreased between water changes, most likely due to the dissipation of the oxidizing disinfectant.

In the redox reaction, the electrons produced at the leaded surface (anode) are consumed at the copper pipe surface (cathode) by the reactions depicted in Figure 1.1.

**Role of Disinfectants on Lead Corrosion**

**Brass**

In general, chloramines appeared to be slightly more aggressive than free chlorine for brass. However, similar to the effects of CSMR, the differences were not statistically significant in the first part of study (Figure 1.9).
Figure 1.11 Average lead released in Part 1 from solder for the three CSMR levels. Increasing CSMR of alum (CSMR of 1.3), PACl (CSMR of 5.3), and PACl + 20 mg/L Cl (CSMR of 8.4) had similar amounts of lead released to the water, except in the case with the highest CSMR. Data from free chlorine and chloramines waters were averaged to obtain the comparisons in this figure. The error bars indicate the 90% confidence intervals.

Figure 1.12 Average galvanic currents for each CSMR condition in Part 1. Each condition is an average of all measurements performed at least monthly for chlorine and chloramines disinfectants at each CSMR level. Similar to the lead levels in Figure 6, the future watershed condition (highest CSMR) was significantly greater than the other treatment types.
**Solder-Copper Couples**

Generally, chloramines were somewhat more aggressive than free chlorine regardless of the coagulant used for treatment. For example, the PACl-treated water with chloramines released an average of 6,300 ppb Pb while the same water but with free chlorine released 4,200 ppb Pb, which is a 30% difference (Figure 1.13). The average CSMRs of the PACl-treated water with free chlorine and chloramines were 5.3. The disinfectant had more impact on the PACl-treated water in projected future conditions with additional chloride—in that case, the water with monochloramine leached approximately 50% more lead than the water with free chlorine. The alum-treated water was not as impacted by the disinfectant type because nearly the same amount of lead was released in the presence of either free chlorine (3,800 ppb Pb) or monochloramine (4,400 ppb Pb). This result is consistent with the theory that sulfates (ex., from aluminum sulfate) in water protect lead from potentially corrosive conditions. Statistical analyses for the last three weeks of Part 1 before alkalinity or pipe orientation changes suggested that chloramines was more aggressive than free chlorine for PACl-treated water (p-value < 0.13) and PACl-treated water with road salts (p-value < 0.10). Due to the variability of corrosion, a p-value (p) below 15% or 0.15 was chosen for this study to indicate statistical confidence that results were different.

![Figure 1.13 Average lead released during Weeks 6 through 8 from solder. Lead levels were slightly increased by chloramines disinfectant for PACl-treated water (p-values of 0.13 and 0.10 for PACl and future watershed conditions, respectively). The 90% confidence intervals are shown.](image)
Galvanic current measurements were consistent with lead data from Figure 1.13. Both types of measurements, lead concentrations and galvanic currents, indicate that the future water condition could have more lead corrosion with chloramines than with free chlorine ($p < 0.02$). The effect of the disinfectant was not as obvious based on the currents for the alum-treated or PACl-treated water (Figure 1.14).

**Part 2: Long-Term Trends and Effects of Alkalinity and Solder Orientation**

*Long-term Trends*

After completing the work described in the original Water Research Foundation RFP, extra testing was performed to examine other conditions and to obtain greater confidence in key trends. One replicate for each of the six water conditions was continued with no water quality changes in the second part of this study.

The main observed trend was that the alum-treated water had dramatic decreases in lead levels compared to the PACl-treated waters, with the exception of the chloraminated PACl-treated water. Three of the four PACl-treated waters had the same amount of lead release throughout the second part of the work (Figure 1.15). In fact, the future water quality condition with road salts and either chlorine or chloramines disinfection increased at least 30% during Part 2 (Figure 1.16). The alum-treated water conditions with chlorine or chloramines had at least a 90% decrease in lead release. For example, alum with free chlorine decreased from approximately 1,000 ppb down to 70 ppb while alum with chloramines decreased from 4,200 ppb to 140 ppb (Figure 1.16). The PACl-treated water with chloramines had an 80% decrease in lead from approximately 1,300 ppb to 260 ppb (Figure 1.16). With enough time, it is possible that all water conditions would have much lower lead levels, but decreases did not occur during

![Figure 1.14 Average galvanic currents during Weeks 6 through 8 from solder. The current measurements are consistent with the trends in lead release in Figure 1.13. The 90% confidence intervals are shown.](image-url)
Figure 1.15 Lead concentration of water in the solder-copper couples during Part 2 for the control conditions. The replicate in which this data summarizes is for the replicate condition where no alkalinity or pipe orientation adjustments were performed. For most of the PACl conditions, the lead levels remained the same throughout the experimental run. The alum-treated waters had dramatic decreases in lead over time.

Figure 1.16 Average lead during the first and last three weeks of Part 2 for the control conditions. Alum-treated waters had significant decreases in lead levels during the second part of the work while three of the four PACl conditions had lead levels that did not change or even increased.
the 4.5-month duration of this study for the future water condition with road salts and PACI-treated water with free chlorine.

Effect of Alkalinity

One of the objectives for Part 2 was to determine if higher alkalinity could reduce lead release. Low pH occurs at the lead solder metal surface because of corrosion reactions; however, increased alkalinity provides pH buffering that prevents the low pH and the dissolution of metals such as lead into the water. When possible, the replicate for each of the six water conditions that was thought to have the highest lead level was altered in Part 2 to have high alkalinity (100 mg/L as CaCO₃ compared to 25 mg/L as CaCO₃) at Week 9. As a result, benefits of higher alkalinity were tested on the “worst case” test rig.

Additionally, during Part 2 solder orientation was evaluated. Copper joint failures in the field have suggested that corrosive attack on solder may be worst when solder is at the bottom of the joint. To investigate this theory, the solder was located at the bottom of the pipe until Week 8, and then at Week 9 one solder-copper replicate from each of the six water treatment types was oriented upside down. The lead levels, local pH measurements, and galvanic currents were then compared during the second part of the study.

At Week 8 before alkalinity and pipe orientation changes, the average lead release for the control pipe was approximately 5,400 ppb Pb for all three conditions (Figure 1.17). The data from Week 8 (“before”), which is summarized in Figure 1.13, includes the average of six data points for Week 8 for each of the three conditions – control, high alkalinity, and inverted pipe. The “after” data consists of averages of the lead data from the last 9 weeks of the experiment.

![Figure 1.17 Average lead release before and after changes in alkalinity or pipe orientation. Each condition had lead level decreases of at least 20% over 10 weeks; however, the higher alkalinity conditions had decreases of approximately 70%. The “before” data were averages of all pipes destined to be the control, high alkalinity, or inverted conditions for week 8. The “after” data is the average lead levels for the same pipes from weeks 9-18. The error bars represent the 90% confidence intervals.](image-url)
Between weeks 9 through 18, the lead levels dropped an average of 20% or more for all three conditions including the control (Figure 1.17). An even greater drop of 70% occurred for the higher alkalinity conditions between weeks 9 through 18 (Figure 1.17). Furthermore, the galvanic current measurements also subsided along with the lead levels. The currents for the high alkalinity condition decreased from an average of -23 µA to -9 µA, which is a 60% decrease (Figure 1.18). The control conditions and inverted pipes only decreased from around -20 µA to -15 µA and -12 µA, respectively, which equates to a 25% and 40% decline. Thus, substantial benefits were attributed to higher alkalinity in preventing this type of lead corrosion.

An explanation for the observed decrease in lead corrosion in the high alkalinity conditions is that while lower pH occurred at the lead anode surface for the control conditions, pH buffering due to alkalinity prohibited acidic conditions. Hence, the dissolution of metals such as lead into the water was reduced. In fact, in the high alkalinity waters, the pH ranged between 6.8 and 8.5 throughout the depth of the copper pipe and at the solder surface. In contrast, the pH near the bottom of the solder in the low alkalinity control conditions plummeted sharply to pH 5.0 and was measured to be as low as pH 3.3 throughout the study (Figure 1.19). Buffering clearly helped to prevent development of this adverse local condition.

The declining lead levels over time for higher alkalinity were especially apparent for the higher CSMR conditions when PACI treatment was used. For the control conditions, where the solder orientation and water quality was unchanged from Part 1 of the study, the alum-treated waters exhibited decreases in lead throughout Part 2 of the study (Figure 1.20). However, the PACI control conditions, except for PACI with chloramines, remained at the same lead levels throughout (>3,600 ppb lead). In contrast, the lead concentrations measured in the waters with high alkalinity decreased from Week 8 to Week 18. For instance, the future higher Cl⁻ watershed condition with chloramines disinfectant, which was one of the most corrosive waters in the control set, decreased from 10,400 pb to 2,900 ppb lead (Figure 1.20).

![Figure 1.18 Average galvanic currents for the solder-copper couples before and after alkalinity or solder orientation changes. The currents were consistent with the trends from the lead levels in the water. The greatest drop was from the high alkalinity conditions, followed by the inverted pipes and the control conditions.](image-url)
Figure 1.19 pH along the profile of the solder-copper couple in Part 2 of study. See Figure 1.2 for identification of measurement locations. A pH gradient between pH 8.5 and 5.0 was measured with depth in the control pipes.

Figure 1.20 Lead release from the solder-copper couples during Part 2 for the high alkalinity conditions. For all conditions, the lead levels decreased from Week 8 to Week 18. The alum-treated waters had dramatic decreases in lead over time.
For all but one condition, the high alkalinity waters had lower lead levels than the low alkalinity conditions during the last 5 weeks of the study (Figure 1.21). The exception was the solder-copper connection exposed to alum-treated water and free chlorine, which was shown to be the least aggressive condition in this study. This particular replicate consistently had one of the highest lead levels throughout the study, and the entire wire corroded completely at the solder-silicone interface at the end of the study. This is an example of the variability of corrosion and indicates the importance of replicate samples to provide a representative picture. The attack on this wire also illustrates how devastating galvanically driven lead corrosion can be.

**Effect of Solder Orientation**

At the surface of the lead material, salts such as H\(^+\), Cl\(^-\), and SO\(_4\)\(^{2-}\) are present at very high concentrations. Salt water has a higher density than water with less salt, so if the water with concentrated salts is ever on top of bulk water with dilute salts, the difference in density will induce natural mixing (Figure 1.22). In contrast, if the water with concentrated salts is ever below the less dense water with dilute salts, the system is stable and resists mixing.

To the extent mixing of water near the anode occurred with the bulk water, the lower pH and high level of Cl\(^-\) at the anode would decrease, similar to what would occur if the water was not stagnant. So if the solder were ever at the top of the pipe (unlikely due to the fact it flows with gravity), the impacts of CSMR would be less severe.

**Lead release.** In terms of lead leaching, the inverted pipes with solder located at the top of the copper pipe had similar lead levels as the control conditions, where the only difference was that the solder was located at the bottom of the pipe (Figure 1.23). Similar to the control conditions, the inverted pipes had lead levels that averaged 5,400 ppb Pb before the orientation
Figure 1.22 Diagram of effect of solder orientation in pipe

Figure 1.23 Average lead during the last 5 weeks for the control and inverted solder-copper couples. The lead levels in the inverted pipes were similar to the levels in the controls in this short-term study.
change but then decreased to an average of 4,000 ppb Pb after the change while the control had an average of 4,200 ppb Pb at the same period (Figure 1.17). Furthermore, statistical analysis demonstrated that the inverted condition was not statistically different from the control (p = 0.79). For most of the second part of study, the lead concentrations in the water decreased but increased during the last three weeks for unknown reasons (Figure 1.24).

**Galvanic measurements.** The galvanic currents or real-time corrosion rates were slightly lower than the rates for the control conditions but were considered statistically different with a p-value of 0.15 (Figure 1.18). While the control conditions had a high corrosion rate of -15 µA, the inverted pipes had lower currents that averaged -11 µA. Prior to Part 2, the currents were statistically the same (p = 0.68). The explanation is that internal mixing occurred within the pipe as the dense lead and salts settled from the solder at the top to the bottom of the apparatus. The conclusion is that inverting the pipe lessened galvanic corrosion markedly but did not dramatically reduce lead leaching in the short-term. It is expected that benefits would have occurred in the long term. This result has practical relevance in that solder connected to copper at the bottom of the pipe is more prone to problems from this type of corrosion than solder connected to copper at the top of a pipe.

![Figure 1.24 Lead in water during Part 2 for the inverted solder-copper couples. The lead levels were similar to the levels in the controls and declined for the majority of the second part of the work.](image-url)
Mechanistic Insight in Lead Corrosion: Local Measurements

The worsened corrosion of lead solder at higher CSMR is explained by the localized high chloride and low pH near the lead surface. Previous research has shown that sulfate is very effective in forming insoluble lead sulfate solids at pHs as low as pH 3. As a result, the precipitated lead sulfates form a protective layer around the leaded metal, thereby explaining benefits from sulfate in water. Chloride at the low pHs near the lead solder anode can form soluble complexes with lead. This explains why chloride is detrimental to lead and can increase lead leaching. Additionally, the concentration of salt at the bottom of the pipe indicates that internal mixing could be a factor in limiting corrosion, if the solder is located at the top of the pipe. The localized corrosive attack was visible (Figure A.1) and even resulted in solder wire being corroded through (Figure A.2).

Chloride and Sulfate

Localized chloride micro-measurements throughout the depth in the solder-copper pipe couples were performed periodically during Part 1 of the Utility I case study. The chloride concentration tended to be higher toward the bottom of the pipe and at the solder surface (Figure 1.25). The trend was most apparent in the water with additional chloride. A salt water layer was essentially formed near the lead at the bottom of the pipe near the silicone stopper. For example, the chloride concentration at the very bottom of the pipe was as much as 10 times the
concentration at the top of the copper pipe when free chlorine was present. This is expected based on the galvanic cell reactions depicted in Figure 1.12. The concentration of chloride and the high effective CSMR at the bottom of the pipe could explain the large amounts of lead released from the solder. This supports the hypothesis that chloride migration and build-up near the lead anode is a contributing factor in lead release for high CSMR waters.

ICP-MS analysis of water sampled in the top and bottom of the ¾” copper pipe and ½” pipe, respectively, further indicated a buildup of high chloride and sulfate concentrations at the bottom of the pipe near the solder (Figure 1.26). The sulfate concentration was consistently approximately two times higher at the bottom than at the top of the pipe. The chloride concentration was also higher at the bottom than at the top, but a higher ratio of the chloride residing at the bottom was measured for the higher CSMR conditions. The CSMR was measured to be as high as 10.8 for one of the future watershed condition replicates with chloramines when the overall CSMR was approximately 8.4. The disinfectant type appeared to have no effect on the distribution of chloride and sulfate. The chloride and sulfate anion concentrations confirm reactions shown in Figure 1.12 in which anions migrate toward the anode. In this case, the anode is the lead solder, and measurements support that the anion concentrations were higher at the bottom where the solder was located.

**pH Measurements**

Throughout Part 1 of the study and for the control conditions in Part 2, the pH decreased (i.e., was more acidic) toward the bottom of the pipe where the solder was located, consistent with expectations for reactions near the anode (Figure 1.12). The initial bulk water pH was 7.7±0.1, but the pH at the top of the pipe was generally around pH 9, which is expected because the copper is the site of the cathodic reaction (Figure 1.27). During Part 1, the average pH at the bottom of the solder-copper couple was pH 5 but was measured to be as low as pH 3.9 for individual solder-copper couples. When lead is connected to copper, the anodic and cathodic reactions are separated (Figure 1.12). The water near the lead-bearing material surface becomes acidic, whereas the cathodic reactions occur over the surface of the copper. In this situation, lead leaching to water could be increased by a higher corrosion rate and/or a lower pH at the surface of the leaded material. Since lower pH tends to prevent passive film formation on lead surfaces, high galvanic currents are somewhat self-perpetuating.

The pH was lowest at the anode for the treatment types with higher CSMR. For instance, the pH was 5.9 at the deepest point in the alum-treated water while the PACI-treated water had pHs as low as pH 5.0 (Figure 1.28). The future watershed condition, which has the highest CSMR, had an even lower average pH of 3.9 for the water contacting the solder. This further suggests the importance of low pH in conjunction with high chloride in accelerating lead release in galvanic corrosion reactions between copper pipe and lead solder. It also explains why even a high dose of orthophosphate cannot control lead corrosion since orthophosphate is only effective for lead down to about pH 5.0. The fact that the pH was so highly acidic demonstrates the desired mechanistic insight, even if some mixing occurred.
Figure 1.26(a-b) Sulfate and chloride concentrations at the top and toward the bottom of the pipe during Part 1. The sulfate (a) and chloride (b) anions had higher concentrations at the bottom of the pipe than at the top. Migration of anions to the anode is expected to occur and as diagramed in Figure 1.8.
CHAPTER 1: MECHANISMS OF ATTACK ON LEAD SOLDER | 27

Figure 1.27 Average pH throughout the depth of the solder-copper pipe couples in Part 1. The pH increased at the top of the pipe from pH 7.7 and decreased to around pH 5 at the lowest point on the solder. The error bars represent the 90% confidence intervals.

Figure 1.28 Average pH in solder-copper pipe couples for the three CSMR levels with free chlorine in Part 1. The general trend is that pH decreased with depth and with closer proximity to the solder. Lower pH was measured with increasing CSMR. The error bars represent the 90% confidence intervals.
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Lead Concentrations at Top and Bottom

The entire volume of water in the smaller diameter copper pipe portion was analyzed for metals and compared to an aliquot of water from the top of the solder-copper couple during Part 1 of the study. The lead concentration at the bottom of the pipe was at least 85 times and as much as 250 times greater than the concentration in the upper section of the pipe (Figure 1.29). This is expected given the lack of mixing in the pipe, the lower pH in the bottom of the apparatus, and the proximity to the lead anode.

![Figure 1.29 Lead concentrations at the top of the copper pipe and at the solder (“Bottom”). The concentration of lead is at least 85 times greater at the bottom of the pipe than at the top of the pipe. This is due to lead particles settling to the bottom of the vertical copper pipes. The dark bars represent the lead concentration at the top of the pipe and the light grey bars represent the lead concentration at the bottom of the pipe. The error bars are shown as 90% confidence intervals.](image-url)
CONCLUSIONS

- At pH 3, pH 4, and pH 5, the concentration of soluble lead decreased with the addition of sulfate.

- Over the pH range of 3-5, changes in the pH had little effect on the solubility of lead sulfate.

- In the presence of sulfate, PbSO₄ formed with the solubility product constant (K_{sp}) value 1.54×10⁻⁸, which is in very good agreement with accepted models.

- At pH 3, 4, and 5, the uncomplexed or free lead concentration decreased with the addition of chloride, presumably as a lead chloride complex formed.

- An optimized constant was calculated for the formation of PbCl⁺ of K = 59.5, which is in the range of that previously reported, but indicates that chloride complexes are slightly more significant in lead solubility than was previously realized.

- From the Utility I case study:
  - For the conditions studied, brass leached very low levels of lead to the water.
  - Even with relatively high orthophosphate inhibitor dose, 50:50 Pb/Sn solder wires connected to copper pipes released very high amounts of lead to the water.
  - A combination of low pH and high CSMR at the solder surface drove the long-term galvanic corrosion of the leaded solder, as demonstrated by local measurements of chloride, sulfate, and lead near the anode.
  - Increased alkalinity in the water was very effective in mitigating the low pH at the lead solder anode and eventually causing decreased lead levels.
  - The effect of CSMR on lead leaching was not statistically significant in the comparison of the alum- and PACl-treated waters in the first part of the utility case study, due to already high CSMRs in all waters.
  - However, the projected future watershed conditions with road salt, which had additional chloride in the water, had the highest amounts of lead released.
  - Overall, chloramines were more aggressive than free chlorine in lead corrosion for the current PACl-treated water conditions and the projected future watershed condition.
  - The lowest lead levels were observed for the alum-treated waters with either disinfectant and the PACl-treated water with free chlorine.
CHAPTER 2: IMPACT OF CSMR ON SOLDER ALLOYS AND JOINT FAILURE

Caroline Nguyen, Kendall Stone, and Marc Edwards

Keywords: solder alloys, lead, tin, antimony, silver, copper

INTRODUCTION

Failures at soldered joints in copper tubes are relatively rare events. The conventional wisdom is that solder quickly develops protective coatings even in highly corrosive potable water. If a failure occurs at a soldered joint in a copper plumbing system, it is often attributed to poor workmanship.

Recently, in Greenville and Durham, NC, lead solders in copper potable water plumbing systems suddenly started corroding at a very high rate and triggered problems with lead release. For decades in these systems, the lead solder joining the joints of copper tubes had not caused significant lead in water problems, but pieces of the solder started falling off into the water and were trapped in aerators. The cause of the sudden attack on solder joints was traced to a change in water treatment by the utility. Specifically, at both utilities, the water coagulant was changed in a manner that shifted the chloride-to-sulfate mass ratio (CSMR) ratio of the water. Subsequent studies proved that a high CSMR could trigger very rapid galvanic attack at joints with lead solder. During the period of high lead leaching, one of the utilities maintained high pH and orthophosphate while another switched to high levels of orthophosphate without mitigating lead leaching. According to conventional criteria, the water would have been deemed relatively non-corrosive.

During galvanic corrosion, the copper pipe and the solder form a galvanic cell (a battery) in which the solder is sacrificed, and the copper pipe is protected. The high Cl⁻ and low SO₄²⁻ content of the water acts as a “switch” that reverses prior passivation of the solder that occurred when the water had a low Cl⁻:SO₄²⁻ ratio. Other pre-conditions, such as low alkalinity and other factors, such as stagnation, might also be required for the severe galvanic attack between the copper pipe and lead solder to occur.

The potential adverse impacts of higher corrosivity at high CSMR are not just limited to lead contamination of the water. Some utilities have reported failures at copper and solder joints in systems where the coagulant has been changed, even when lead-free solder (< 0.25% Pb) is used. This is not unexpected, since galvanic corrosion that can cause pieces of solder to fall off into the water can also be expected to weaken joints. Even modern lead-free solders might not be immune to this problem because antimony and tin are also anodic to copper, and might be subject to galvanic corrosion under certain water quality conditions.

Due to the high cost of water damage from failed plumbing in homes and buildings, this chapter focused on examining the interplay between CSMR, solder alloy composition, and rate of attack on solder joints. In addition to the obvious value of this work to the water industry/EPA/plumbing industry in terms of understanding the longevity of premise plumbing systems, the research also improves the understanding of corrosion mechanisms as a function of solder alloy composition. Leaching of other metals of potential health concern, such as antimony, silver, and tin, were also explicitly examined in these experiments.
MATERIALS AND METHODS

Apparatus for Copper-Solder Joint Study

Six solder alloys were evaluated for Parts 1 and 2 of this study (Table 2.1). For Part 1, pure lead and tin wires were also evaluated.

Part 1

The first part of the work attempted to examine mechanistically the impacts of CSMR on solder corrosion. Simulated joints with solder wire pieces connected to copper pipes were exposed to low and high CSMR water (Figure 2.1). Each piece of wire had an exposed surface area of approximately 6.2 cm² inside the copper pipe. The solder wires were between 0.5 mm and 3 mm in diameter (Table 2.1) and were positioned in the apparatus to remain inside the ½” copper pipe (Figure 2.1).

The apparatus consisted of a ¾” diameter copper pipe and a ½” diameter copper pipe that were connected by clear tubing with an approximate 2-mm gap between the two copper pipes (Figures 2.1 and 2.2). The smaller diameter (½”) copper pipe was used to isolate water located near the surface of the anodic solder. The larger diameter (¾”) pipe had the dual purpose of allowing electrode measurements inside the pipe, and providing a large copper-to-solder surface area of approximately 31:1. To simulate the galvanic connection between copper pipes and solder at joints while having the ability to measure corrosion activity with an ammeter, the solder and the copper pipes were electrically connected with copper wires.

<table>
<thead>
<tr>
<th>Wire</th>
<th>Weight Composition</th>
<th>Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead/tin solder</td>
<td>50% (Pb), 50% (Sn)</td>
<td>3</td>
</tr>
<tr>
<td>Tin/copper solder</td>
<td>97% (Sn), 3% (Cu)</td>
<td>3</td>
</tr>
<tr>
<td>Tin/antimony solder</td>
<td>95% (Sn), 5% (Sb)</td>
<td>3</td>
</tr>
<tr>
<td>Tin/copper/silver solder</td>
<td>95.5% (Sn), 4% (Cu), 0.5% (Ag)</td>
<td>3</td>
</tr>
<tr>
<td>Tin/copper/selenium solder</td>
<td>Unknown</td>
<td>3</td>
</tr>
<tr>
<td>Nickel/silver/copper/tin/antimony solder</td>
<td>Unknown</td>
<td>3</td>
</tr>
<tr>
<td>Tin wire</td>
<td>99.9% (Sn)</td>
<td>0.5</td>
</tr>
<tr>
<td>Lead wire</td>
<td>99.9% (Pb)</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 2.1 Schematic of copper-solder couple

Figure 2.2 Lower portion of the Part 1 apparatus. The solder is suspended in the center of the lower portion by the silicone stopper.
Part 2

The second part of the work applied the knowledge gained in the first part to test simulated solder-copper joint failure. The joints were designed to allow corrosive attack to proceed in a narrow crevice, and to confirm whether the highly corrosive conditions could actually cause a joint failure. The apparatus (Figure 2.3 and 2.4) consisted of a large sheet of copper (7.75” wide x 7” tall x 0.062” thick), to which three squares of copper sheet were soldered. In each case, a small amount of solder was carefully weighed (0.011 g ±0.002) and used to attach small squares of copper (each 1” x 1” and 9.3 g ±0.4) to the larger sheet. The copper sheets and squares were 0.062-in thick, 14 gauge and consisted of alloy C11000 manufactured to ASTM-B152.

The aforementioned apparatus simulates: 1) the large amount of copper exposed to the water in a copper plumbing system, 2) a soldered connection between two pieces of copper, and 3) a natural crevice between the two pieces of copper, under which the solder structurally holds together the joints. New simulated solder-copper joints were also prepared at the end of Part 2 to compare the strength with the simulated joints exposed to water for 1 year.

Test Water and Measurements

Part 1

This part of the study lasted a total of 11 weeks. The simulated joints were tested in triplicate and were exposed to synthetic water with low and high CSMR, which were 0.2 and 16, respectively (Table 2.2). A CSMR of 16 was chosen to represent the worst-case scenario in terms of water corrosivity. CSMRs in excess of 16 have been measured for various communities,
and the project team wanted to select an extremely aggressive condition because the goal was to examine if some types of solders are more impacted by these problems than others. All waters were dosed with chloramines at a concentration of 4 mg/L as Cl₂ with a ratio of 4:1 mg Cl₂/mg N, and the pH of the water was adjusted to pH 8.3 ± 0.1 at each water change. The water was changed three times per week using a “dump and fill” protocol.

The water from each condition throughout the week was collected and analyzed for lead, tin, copper, and other metals using ICP-MS in accordance with Standard Method 3125. Additionally, sampling of individual replicates for each condition was conducted during Week 10 to obtain confidence intervals.

In addition to metals analysis, pH and chloride measurements were conducted twice during the study for the water near the solder and copper surfaces using an MI-406 flat membrane pH microelectrode (Microelectrodes, Inc) and a Lazar electrode, respectively. The measurements were taken by slowly lowering the microelectrode from the top of the copper joint, making pH or chloride measurements at 1” and 3” from the top of the pipe. After measuring at the cathode (i.e., top of the joint), the large copper pipe piece was disassembled at the plastic tubing, which connected the large copper section with the small copper. The pH was then measured in the disassembled joint at the solder surface within the smaller copper pipe section. The pH microelectrode was calibrated before each set of measurements, and the localized pH was measured for each replicate. Trends in pH were consistent throughout the study. While it is unavoidable to slightly mix the water during such measurements, any mixing would tend to make the measured differences in concentration less significant versus the conditions found in stagnant pipes.

Galvanic measurements including current, potential drop, and corrosion potential were performed monthly. The measurements were conducted 1 hour after a water change.
Part 2

The second part of the work was conducted for 12 months. Based on results from Part 1, the copper sheets with the simulated solder joints were exposed to 25 L of high CSMR water in a single reservoir (Table 2.2). A high CSMR water that had been determined to be much more aggressive to simulated soldered joints compared to low CSMR water was used for testing. Water was changed in the reservoir every other week. The pH was adjusted at least 5 times per week, and the chloramines concentration was maintained at 4 mg/L Cl₂ twice per week. At the end of the study, stress testing was conducted on the simulated copper joint sheets to determine the maximum load for each replicate joint. An MTS 4204 instrument with TestWorks 4.0 software was used to conduct the load test (Figures 2.5 and 2.6).

RESULTS AND DISCUSSION

In the first part of the work metals concentrations, pH, and galvanic currents were measured for solder-copper couples exposed to low and high CSMR water. In the second part of the work, simulated copper joints were exposed to high CSMR water, which was determined to be more corrosive than low CSMR water in Part 1, and subjected to stress testing at the end of 1-year exposure. There was no significant selenium released from solder; therefore, only tin, lead and antimony results are described in this report.

Review of Previous Studies and Synthesis of Data from Earlier Lead Work (Part 0)

Prior to the start of this study, a review of results from previous work related to tin solders was performed. This includes data collected by Nguyen (2005) and in other case studies conducted for this work. Hypothetically, because tin is found in most solder (Table 2.1), accelerated corrosion of tin may decrease the longevity of soldered joints. One important factor in tin solder corrosion appears to be the presence of orthophosphate. In one study, dosing of

<table>
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<th>Parameter</th>
<th>Concentration</th>
<th>Low CSMR</th>
<th>High CSMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>8.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Chloramines (mg/L Cl₂)</td>
<td></td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Chloride (mg/L Cl)</td>
<td></td>
<td>22</td>
<td>129</td>
</tr>
<tr>
<td>Sulfate (mg/L SO₄)</td>
<td></td>
<td>121</td>
<td>8</td>
</tr>
<tr>
<td>CSMR (mg/mg)</td>
<td></td>
<td>0.2</td>
<td>16</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td></td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Magnesium (mg/L Mg)</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
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<td>Potassium (mg/L K)</td>
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<tr>
<td>Nitrate (mg/L N)</td>
<td></td>
<td>1.3</td>
<td>1.3</td>
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Figure 2.5 Peak loading instrument to test simulated soldered joints at end of study.

Figure 2.6 Picture of 95/5 Sn/Sb simulated joint during stress testing at the end of the study (middle of photo). At left in the picture of a simulated joint after failure during the stress test.
1 mg/L PO₄-P increased the amount of tin released by as much as 10 times from 50:50 Pb/Sn solder connected to copper compared to the same condition without phosphate (Figure 2.7). This was observed for 1-ft long copper pipes dipped into 1-in of molten 50:50 Pb/Sn solder and exposed to simulated Potomac River water at two pH levels (7 and 9.5) and two levels of chloramination (0 and 5 mg/L Cl₂). The type of disinfectant (free chlorine and chloramines) appeared to have no effect on tin corrosion in the study for Utility I (Figure 2.8).

Another factor that affects the corrosion of tin in addition to other metals is the CSMR of the water, which was observed in three case studies. In the case of Greenville Utilities Commission in North Carolina (NC), using polyaluminum chloride (PACl) coagulant or a coagulant blend with PACl increased tin release from 50:50 Pb/Sn solder compared to when aluminum sulfate (alum) coagulant was used (Figure 2.9). In another case study in NC (Utilities B and E), ferric sulfate, ferric chloride, blends of ferric sulfate and ferric chloride, and anion exchange treatment were evaluated as strategies to treat water. Consistent with previous findings, increasing CSMR of the water resulted in increases in the tin release from galvanic connections of 50:50 Pb/Sn solder and copper (Figure 2.10).

The effect of CSMR on tin leaching was also seen with desalinated salt water, which had as much as 100 mg/L Cl⁻ and less than 5 mg/L SO₄ (i.e., high CSMR). Increasing the percentage of desalinated or nanofiltered water blended with groundwater for Utility K in California increased the tin released from 50:50 Pb/Sn solder that was connected to copper (Figure 2.11).

Figure 2.7 Tin release in water with and without orthophosphate. The water contained 0 or 5 mg/L chloramines as Cl₂ and had a pH of 7 or 9.5.
Figure 2.8 Tin release from a Maryland utility water treated with alum or PACl coagulants and disinfected with either free chlorine or chloramines. There was no evidence that the water conditions treated with free chlorine were any different from water disinfected with chloramines in terms of tin leaching.

Figure 2.9 Effect of CSMR on tin release from 50:50 Pb/Sn solder galvanically connected to copper for water from a utility in NC.
Figure 2.10 Tin release from water treated with sulfate-based coagulants, chloride-based coagulants, and anion exchange.

Figure 2.11 Effect of desalinated (nanofiltered or NF) water blends on tin release. Increasing blends of desalinated water, which has high CSMR, results in higher levels of tin released to the water.
Effect of Low and High CSMR Water (Part 1)

*Tin Release*

Samples collected during Week 10 illustrated that tin leaching was higher in water with high CSMR. For instance, the solder alloy with 97/3 tin/antimony had almost 7 times more tin released in high CSMR water than in low CSMR water (Figure 2.12). Overall, tin release increased between 3 and 11 times in high CSMR water compared to low CSMR water for the tin solder alloys tested. Clearly, the adverse galvanic effects of a high CSMR water are not limited to the lead:tin solder alloys.

During Week 10, tin release from pure tin wire appeared to be unaffected by the CSMR. However, the tin release from tin wire had been an average of 28 times worse in high CSMR water than low CSMR water during the first 10 weeks of the study (Figures 2.13 and 2.14). Additionally, tin leaching from all of the solder alloys and tin wire exposed to high CSMR water was more variable than in low CSMR water throughout the 11-week study (Figure 2.14).

*Lead Release*

High CSMR water significantly increased lead leaching at the 99% confidence level for pure lead wire and 50/50 Pb/Sn wire connected to copper pipes. For instance, the lead release from 50/50 Pb/Sn solder increased 35 times when the solder-copper couples were exposed to high CSMR water (Figure 2.15). Similarly, lead release from pure lead wire increased 18 times due to high CSMR. The results are consistent with theory since higher CSMR accelerates

![Figure 2.12 Tin release from high and low CSMR waters from each of the alloys during Week 10 in Part 1 of the study. The error bars represent the 95% confidence intervals among the 3 replicates at each condition.](image)
Figure 2.13 Tin release as a function of time for low CSMR water of 0.2 in Part 1 of this study.

Figure 2.14 Tin release as a function of time for high CSMR water of 16 in Part 1 of this study.
galvanic reactions that occur between lead and copper (Figure 2.16).

Comparing the lead materials, 50/50 Pb/Sn solder had similar levels of lead compared to pure lead wire in both low and high CSMR waters. In high CSMR water, the pure lead wire and the 50/50 Pb/Sn solder were not significantly different in terms of lead leaching (Figure 2.15). However, in low CSMR water, the lead leaching was about 1.5 times greater for pure lead wire than for 50/50 Pb/Sn solder and was statistically significant at the 99% confidence level during Weeks 5-9 but not at Week 10 alone. This suggests that higher CSMR could increase lead leaching for these two lead materials galvanically connected to copper.

**Antimony Release**

Antimony is a concern because it is considered a carcinogen after long-term exposure and causes health effects such as nausea and vomiting with short-term exposure. To protect the population, the US EPA has set the maximum contaminant level (MCL) for antimony to be 6 ppb. Due to this concern, a goal of this study was to determine the amount of antimony that may be released from plumbing materials, or in this study the 95/5 tin-antimony and Ni/Ag/Cu/Sn/Sb solders. Herrera et al. (1982) found that for tin/antimony solders, tin would become the sacrificial anode and protect antimony.

In contrast to the release of the lead and tin metals from solder, antimony release was worse for low CSMR water. Antimony is recognized as a metalloid that does not act chemically like a metal. In this study, antimony release from 95/5 Sn/Sb solder increased from undetectable levels in high CSMR water to 2.8 μg/L in low CSMR water (Figure 2.17). Similarly, solder containing Ni/Ag/Cu/Sn/Sb exposed to low CSMR water had an increase in antimony release from 0.1 μg/L to 1.3 μg/L, or a factor of 13 times. However, for this study, the antimony levels remained below the MCL of 6 ppb.

![Figure 2.15 Lead leaching from pure lead wire and 50:50 lead-tin solder in low (0.2) and high (16) CSMR water during Week 10 in Part 1. The error bars indicate the 95% confidence intervals.](image-url)
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Figure 2.16 Reactions at lead or tin anode and copper cathode surfaces

Figure 2.17 Release of antimony from 95/5 Sn/Sb solder and solder containing Ni, Ag, Cu, Sn, and Sb during Week 10 in Part 1 of the study. The CSMRs of the high and low CSMR waters were 16 and 0.2, respectively.
Galvanic Currents

The galvanic current measurements indicated that high CSMR water generally produced higher currents, or higher corrosion rates of the solders and wires, compared to low CSMR water (Figure 2.18). The currents reflected similar trends as the tin and lead leaching data in terms of the impact of CSMR. Any differences in currents and tin leaching may be explained by the release of other metals, such as lead, from the solders or wires.

The theoretical amount of metals release was also calculated based on the galvanic current. Because tin is a major component in all of the solders evaluated in this study, the theoretical and actual tin dissolution values were compared. The typical oxidation state of tin is +4. Therefore, as tin corrodes, 4 electrons ($e^-$) are released for each mole of tin leached ($Sn^{4+}$): $Sn_0 \rightarrow Sn^{4+} + 4e^-$. The maximum leaching of tin from the tin solders can be calculated from the following equation, assuming that the current measured at a given time remains constant, an average stagnation period of 2.33 days, and correcting for percent tin in the solder:

$$\text{Maximum Sn Leaching (g)} = \frac{I \left( \frac{\text{Coulomb}}{\text{sec}} \right) \times T \left( \text{sec} \right) \times 118.7 \left( \frac{g \ Sn\ mol}{mol \ Sn} \right)}{1.6 \times 10^{-19} \left( \frac{\text{Coulomb}}{e^-} \right) \times 6.023 \times 10^{23} \left( \frac{Sn\ mol}{mol \ Sn} \right) \times 4 \left( \frac{e^-}{Sn} \right)}$$

The calculated and actual tin release were correlated. However, actual tin leaching from solder was approximately 40 times lower than would be predicted based on the above galvanic current measurement (Figure 2.19). The discrepancy could be explained by a number of factors. For example, the galvanic current used for the calculation provides a snapshot in time of the

![Figure 2.18 Galvanic currents measured in the simulated joint apparatus during Week 5 one hour after a water change for the low and high CSMR water conditions in Part 1. The CSMRs of the low and high CSMR waters were 0.2 and 16, respectively.](image-url)
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

\[ y = 44.62x + 3288 \]

\[ R^2 = 0.792 \]

Figure 2.19 Comparison of theoretical versus actual tin release for the first part of the study. The theoretical tin release was calculated from the galvanic currents and was approximately 40X higher than the actual measured concentrations. The red line represents the hypothetical 1:1 relationship between the calculated and actual tin release.

corrosion rate while the tin leaching data is an average of the metal release during a given stagnation period. During stagnation, the galvanic current might tend to decrease somewhat as oxidants in the water are depleted. Regardless, there is a roughly linear correlation between the observed tin leaching and the calculated values.

**pH at Surface of Solder and Copper**

The pH of water near the surface of the copper cathode (i.e., upper portion of the copper pipe apparatus) and near the solder anode were measured. Generally, the pH decreased at the solder surface compared to the surface of the copper cathode (at least 7” away from the solder) consistent with theory. High CSMR exacerbated the pH difference between the solder or wire and the upper regions of the copper.

**Low CSMR water.** In low CSMR water, the pH was as low as 6.6 at the surface of the 50/50 Pb/Sn solder, which represented a pH drop 1.1 pH units compared to the pH at the copper cathode surface (Figure 2.20). The next largest pH drop was measured for the Ni/Ag/Cu/Sn/Sb solder, which had a pH drop of 0.5. The other solder alloys and wires had below 0.5 pH unit drops. The pH at the copper surface was an average of pH 7.3. Generally, the pH was not as acidic in low CSMR water compared to high CSMR water, which is expected given the trend in galvanic current.
**CHAPTER 2: IMPACT OF CSMR ON SOLDER ALLOYS AND JOINT FAILURE**

**High CSMR water.** For high CSMR water, the pH at the solder or wire surface was as little as 0.7 pH units and as high as 7 pH units lower than water at the top of the apparatus (Figure 2.21). The pH was as low as 3.0 at the surface of the 50/50 Pb/Sn solder and the 97/3 Sn/Cu solder. At the copper cathode surface, the pH was approximately pH 9.4 for all the solder alloys and wires, or 2 pH units greater than measured in the low CSMR water. The acceleration of galvanic reactions occurring at the surfaces of the solder and the copper pipe due to high CSMR (Figure 2.16) caused the pH to be lower at the solder anode and higher at the copper cathode.

**Local Chloride Measurements**

More chloride tended to accumulate at the solder alloy surfaces when exposed to high CSMR water than low CSMR water. For low CSMR water, the chloride concentration along the surface of the apparatus was the same, with the exception of the 97/3 Sn/Cu solder (Figure 2.22). In that case, the chloride concentration doubled from 22 mg/L Cl in the initial bulk water to 40 mg/L Cl at the solder surface.

For high CSMR water, which accelerates galvanic corrosion and reactions in Figure 2.15, the chloride concentration was depleted at the copper cathode surface (located 11” from the solder). The initial bulk water concentration was approximately 129 mg/L Cl but decreased to between 42 and 82 mg/L Cl at the cathode (Figure 2.23). The chloride increased to as high as 215 mg/L at the bottom of the solder surface. The three solder alloys with the highest chloride were 50/50 Pb/Sn, 95/5 Sn/Sb, and 97/3 Sn/Cu solders. In contrast, the pure lead and tin wires did not appear to have salt accumulation at the surface of the wires.
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Figure 2.21 pH measurements near the surface of the copper and solder for simulated joints exposed to high CSMR water in Part 1. The water had a CSMR of 16.

Figure 2.22 Microelectrode chloride measurements at the surface of the copper and solder for the simulated joints exposed to low CSMR (0.2) water in Part 1.
Load Testing (Part 2)

Based on results from Part 1, the high CSMR water was more corrosive for metals such as tin and lead, and corresponding with measurement of lower pH and higher chloride at the solder surface. Therefore, in Part 2 of the study, simulated soldered joints were prepared for tin wire and the six solder alloys and exposed to high CSMR water for 12 months (Figure 2.4). At the end of the 12-month exposure to high CSMR water, the strength of the simulated joints was tested by determining the maximum load that each joint could sustain before failing. The loads were compared to that which were present in new simulated soldered joints. In some cases the joint “failed” during testing without applying any load at all, as the soldered copper detached from the large copper sheet naturally. In these cases the load was recorded as “0” strength.

In each and every case, there was a significant reduction in the peak load for the simulated soldered joints after 1-year exposure to high CSMR water, and preliminary results indicate that significant amount of solder was lost via corrosion from the simulated joints. The loads decreased from 260-740 lbf before exposure to as low as 0-130 lbf after being exposed to high CSMR water for 12 months (Figure 2.24). The most significant reduction in load was observed for 97/3 Sn/Cu solder, where each joint replicate naturally failed or detached the end of the study (i.e., load reduction of 100%) (Figure 2.25). One replicate for the 97/3 Sn/Cu solder detached after approximately 10 months while the other two replicates for this condition detached as the apparatus was disassembled and prepared for load testing. Likewise, complete joint failure prior to load testing was also recorded for one replicate of the Sn/Cu/Se solder (after approximately 5 months) and one replicate of the nickel-bearing solder (after approximately 10
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Figure 2.24 Average peak loads for new and exposed simulated copper-solder joints at the end of the second part of the study.

Figure 2.25 Percent reduction in load at the end of Part 2 of the study for each simulated soldered joint exposed to high CSMR water compared to new joints not exposed to water.
months). Based on the average peak load, the solder performance is ranked (from best to worst) in the following order:

1) Ni/Ag/Cu/Sn/Sb
2) 50/50 Pb/Sn
3) 95/5 Sn/Sb
4) 95.5/4/0.5 Sn/Cu/Ag (tied)
4) Sn wire (tied)
4) Sn/Cu/Se (tied)
7) 97/3 Sn/Cu

After exposure to high CSMR water, all of the soldered joints evaluated in this study had load reductions of 70-100%. Pure tin wire had a load reduction of 92%; however, these results were only significant at the 85% confidence interval. The peak load for the 50/50 Pb/Sn and the 95/5 Sn/Sb soldered joints were significantly reduced by 86% and 88%, respectively, as a result of exposure to high CSMR water, and the results were significant at the 95% confidence level (Figures 2.24 and 2.25). The Ni/Ag/Cu/Sn/Sb solder had the lowest load reduction of 71% (p = 0.02) compared to the other solder types. However, one replicate for the nickel-bearing solder failed after 10 months of exposure to high CSMR water.

CONCLUSIONS

- Generally, higher chloride-to-sulfate mass ratio (CSMR) and dosing of orthophosphate increased tin release from 50/50 Pb/Sn solder connected to copper pipe.

- High CSMR water increased corrosion rates of the solder alloys and pure metal wires connected to copper.

- Increased corrosion was also reflected in higher tin and lead concentrations in water exposed to the simulated joints.

- Contrary to results for tin and lead, the release of antimony from the two solder alloys containing antimony was worse in low CSMR water. However, in this study, the antimony release remained below the MCL of 6 ppb.

- The pH was measured to be as low as 3.0 at solder surfaces exposed to high CSMR water. Given the difficulties in measuring pH at the surface, these values should be considered an upper bound to the actual pH.

- The chloride concentration measured at the solder surface generally increased during stagnation compared to the level in the bulk water. No significant change in chloride concentration was measured for the pure tin and pure lead wires.

- The 97/3 Sn/Cu solder wire had the greatest reduction in joint strength after 1 year of exposure to high CSMR water.
• Based solely on peak load and excluding the nickel-bearing solder (Ni/Ag/Cu/Sn/Sb), which had a failure at month 10, the two solder types with the least structural damage were 50/50 Pb/Sn solder and 95/5 Sn/Sb solder. Of the two, 95/5 Sn/Sb had the lowest measured tin release.

• The 95/5 Sn/Sb solder had the most desirable characteristics of the solders evaluated in this study. The solder had the lowest load reduction after exposure to high CSMR water, did not release harmful levels of antimony (or lead, as would be the case for 50:50 Pb/Sn solder) to the water, and had less tin corrosion compared to the other solder types.
CHAPTER 3: OVERVIEW OF CASE STUDIES

In this project, nine case studies were conducted for 10 utilities across North America. These studies focused on the impacts of treatment changes on the lead leaching from common lead plumbing materials (lead solder and brass). These treatment changes included dosing of corrosion inhibitors, finished water pH, and treatment processes that affect the chloride and sulfate concentrations in the water. It has already been established that the coagulant (chloride-based versus sulfate-based) is a major factor in controlling lead leaching from solder-copper galvanic couples (Edwards and Triantafyllidou 2007) and was also evaluated in a range of waters in this project (Table 3.1), but other pathways discovered in this work include the uses of desalinated water, arsenic treatment, and anion exchange. Increases in chloride have also been associated with run-off of road salt during the winter into the water supply and a chloride leak into treated water from a hypochlorite generation system.

The impacts of these treatment changes on lead leaching were investigated in case studies described in Chapters 1 through 10 using static dump-and-fill methods to replace water in test coupons (Table 3.2). The case study presented in Chapter 11 used recirculating flow through pipe loops to test the impacts of chloride and sulfate in flow conditions typical in homes.

For the utilities where coagulant type was evaluated (Chapters 1 and 4-7), bench scale treatment of the utility raw water source (i.e., river water in these cases) was conducted to simulate treatment at the plant to the extent possible. Optimal coagulant doses were provided by the plant for each batch of water received at Virginia Tech. Coagulation mixing speeds and times (rapid mix for one minute, 20 rpm for 20 minutes, and settling for 30 minutes) were selected to simulate full-scale treatment in jar tests. Filtration was conducted using glass wool filters with the exception of the Canadian case study in Chapter 7.

“Optimization” of coagulation is a science and an art in its own right. Virtually all the utilities that participated in this project have noted substantial differences in coagulant performance in terms of TOC and turbidity removal in practice. For example, Greenville Utilities Commission in NC desperately wanted to use PACl due to marked improvements in turbidity removal after settling and filtration. Qualitatively, a deep sand filter does a better job of removing particles than the glass wool filter used at bench scale in the lab tests, but the relative performance advantages in this work for glass wool in terms of turbidity removal were the same as those noted by the utilities in practice. In each study, data were scrutinized to determine whether factors other than CSMR could explain the differences in lead leaching performance. In general, results agreed with those from very well controlled laboratory studies, in that changes in CSMR were the primary controlling factor in determining the extent of lead leaching from galvanic connections between copper and lead bearing plumbing materials.
Table 3.1
Summary of coagulants evaluated in EPA/Water Research Foundation Project 4088.

<table>
<thead>
<tr>
<th>Utility</th>
<th>Chapter in Report</th>
<th>Coagulants Evaluated</th>
<th>CSMR</th>
<th>Summary of Findings and other Considerations</th>
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</thead>
<tbody>
<tr>
<td>Greenville Utilities Commission, NC</td>
<td>5</td>
<td>Alum</td>
<td>0.4</td>
<td>After switching from alum to PACl, it took</td>
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<td>1.5 weeks for the lead leaching to increase.</td>
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<td>Alum/PACl Blends</td>
<td>0.7</td>
<td>Coupons exposed to low and high CSMR</td>
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<td>waters for 2 years showed no differences</td>
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<td>between the CSMRs. For this water,</td>
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<td>blending coagulants to achieve a CSMR of</td>
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<td>approximately 0.7 did not significantly</td>
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<td>increase lead leaching, and changes in</td>
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<td>alkalinity did not have a large effect on</td>
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<td>lead leaching compared to the effects of</td>
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<td>CSMR.</td>
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<td>PACl</td>
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<td>B &amp; E, NC</td>
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<td>Ferric Sulfate</td>
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<td>consistently had more lead leaching from</td>
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<td>Ferric Sulfate/ Ferric Chloride Blends</td>
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<td>solder and brass than ferric sulfate (and</td>
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<td>the blend with CSMR 0.3). Anion exchange</td>
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<td>treatment with ferric chloride coagulation</td>
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<td>resulted in the highest lead levels, and</td>
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<td>leaching worse for that CSMR condition.</td>
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<td>Ferric Chloride</td>
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<td>D, Nova Scotia, Canada</td>
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<td>Alum</td>
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<td>Lead release from lead:tin solder was not</td>
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<td>significantly different among the three</td>
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<td>water conditions tested. This might be</td>
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<td>because all waters were above the 0.5</td>
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<td>CSMR threshold. At levels of CSMR above the</td>
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<td>0.5 threshold, other factors such as</td>
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<td>alkalinity and organic carbon may control</td>
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<td>lead release.</td>
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<td>Ferric Sulfate</td>
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<td>G, NC</td>
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<td>Alum</td>
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<td>levels than sulfate-based coagulants (CSMR</td>
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<td>of 0.4)</td>
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<td>1.4</td>
<td>Both CSMR levels that were evaluated</td>
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<td>resulted in high lead release from brass and</td>
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<td>lead leaching. However, PACl water</td>
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<td>resulted in about two times more lead than</td>
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<td>PACl or alum waters (with no road salts).</td>
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<td>Utility J, TN</td>
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<td>Utility H, WA</td>
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Completed as part of the Water Research Foundation Project 4088
INTRODUCTION

Lead corrosion is sometimes severely impacted by seemingly innocuous changes in water treatment. For example, several utilities observed lead contamination hazards that arose after changing coagulants from aluminum sulfate to ferric chloride or polyaluminum chloride (PACl). Other utilities switched from free chlorine to chloramine disinfection and triggered severe lead leaching to water, such as in Washington, D.C. (Lytle & Schock 2005; Edwards & Dudi 2004).

A recent literature review has documented numerous prior instances in which higher chloride-to-sulfate mass ratio (CSMR) was linked to lead problems (Edwards and Triantafyllidou 2007; Dodrill and Edwards 1995). The chloride-to-sulfate mass ratio is expressed as and can be computed, for example, for water with 10 mg/L Cl and 20 mg/L SO₄:

\[ \text{Chloride to Sulfate Mass Ratio (CSMR)} = \frac{[Cl^-]}{[SO_4^{2-}]} = \frac{10 \text{ mg/L } Cl^-}{20 \text{ mg/L } SO_4^{2-}} = 0.5 \]

The problems attributable to higher CSMR are manifested through galvanic corrosion of lead pipe: copper or lead solder: copper connections. If alkalinity is low enough, the galvanic corrosion has produced pHs as low as 3.0 at the surface of the lead plumbing material, allowing high lead leaching to persist indefinitely by preventing passivation (Edwards & Triantafyllidou 2007).

The Greenville Utilities Commission (GUC) in North Carolina (NC) has been treating water with aluminum sulfate (alum) with no lead problems. After months of using polyaluminum chloride (PACl) some lead problems were observed. Because PACl has some benefits in terms of particle removal during storm runoff events, the following strategies were tested in an attempt to utilize PACl without detrimental problems from lead. These include:

1) dosing PACl for a very short time period during storm events, and then switching back to alum before problems occur
2) blending alum and PACl coagulants to obtain benefits of the chloride-based coagulant while also maintaining a lower CSMR, and
3) increasing the alkalinity of the water to counter the higher corrosivity while using PACl coagulant.

Bench scale experiments were conducted to examine the above strategies using water from Greenville to: (1) determine the effects of a range of CSMR on lead leaching, (2) evaluate the impact of changes in alkalinity on lead release, (3) identify how quickly lead leaching is
worsened following a coagulant switch from alum to PACl, and (4) evaluate the effectiveness of passivation in reducing lead leaching from solder. To investigate Objective 4, coupons that had been passivated for two years were tested to determine if lead release had been reduced significantly.

In addition to the objectives of the study, other key parameters that affected lead leaching including nitrate and the addition of orthophosphate were identified for this water.

HISTORICAL

The utility receives its potable water from one treatment plant. Sampling events under the US EPA LCR from 1992 to 2001 clearly show that the plant was easily meeting the lead action limit throughout this period (Figure 4.1). However, sampling in 2004 indicated a problem with lead leaching, which was reinforced by two cases of elevated blood lead attributed to lead from potable water in early 2004 (Landers 2006; Allegood 2005; Norman et al. 2005). Tap water from the affected child’s faucet measured as high as 400 ppb lead, although lead was more commonly detected from this faucet at 40-60 ppb. The utility’s main distribution system does not include lead pipes; thus, the key sources of lead in water are therefore leaded solder and leaded brass.

For the year 2004 about 22% of LCR samples contained lead above the action level. This percentage increased to 27% for the year 2005. The 90th percentile lead concentration was relatively constant at 28-30 ppb in 2004 and 2005.

Like many other utilities across the US, the utility made a series of changes in their treatment process in order to better comply with stringent federal regulations. Theoretically, any of these changes, alone or in combination, could have contributed to the change in the water’s aggressiveness to lead. The utility began using chloramines rather than free chlorine as secondary disinfectant in December 2002, in order to comply with US EPA regulations regarding DBP formation. At the same time and due to the introduction of chloramines, finished water pH was increased from about 7.2 to 7.7, in order to optimize monochloramine formation. Later on,

![Figure 4.1 Compliance history with the LCR Action Level for lead, for Greenville, NC. Data from Edwards and Triantafyllidou (2007).](image_url)
in August 2003, the utility also switched from chlorine to ozone as primary disinfectant. Throughout these disinfection changes, the plant continued to follow optimal corrosion control as required under the LCR using a polyphosphate/phosphate blend. Following exceedence of the LCR action level for lead in August 2004, the plant started dosing an orthophosphate corrosion inhibitor to try to mitigate the lead corrosion problems.

In addition, the plant changed its coagulant from alum (aluminum sulfate) to polyaluminum chloride (PACl) in January of 2001, in order to achieve better organic matter and turbidity removal. The switch resulted in an increase of the CSMR of finished water leaving the treatment plant, as historical data demonstrate (Figure 4.2). This ratio increased well above the threshold of 0.58 mentioned in the Dodrill study, after the coagulant switch (Dodrill and Edwards 1995). More specifically, the CSMR averaged 0.50 for the year 2000 (just before the switch), but increased by a factor of 9X and up to a value of 4.50 during the year 2003 (Figure 4.2).

After considering recommendations from the bench-scale experiments reported in earlier work, the utility switched the coagulation chemical back to alum in April 2006 (Edwards and Triantafyllidou 2007). This change dropped the CSMR to 0.55 (Figure 4.2), and reduced the 90th percentile lead level to 18 ppb (38% reduction) during the first half of 2006 (Figure 4.1). The following LCR sampling event, during the second half of 2006, showed further reduction in the 90th percentile lead level to 8 ppb, which is below the action level (Figure 4.1).

**MATERIALS AND METHODS**

**Test Water**

Greenville raw water was shipped to Virginia Tech approximately every other week. Collected water was separated and subjected to simulated drinking water treatment. Treatment involved coagulation, filtration, phosphate corrosion inhibitor addition, disinfection with

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**Figure 4.2** Historical plant data of the chloride to sulfate mass ratio in Greenville, NC finished water. The numbers reported are the averages for any given year. Data from Edwards and Triantafyllidou (2007).
chloramines, and final pH adjustment. A summary of the treatment scenarios and water chemistry is provided in Table 4.1.

**Coagulant Type and CSMR**

The two coagulants used were aluminum sulfate (alum) and polyaluminum chloride (PACl). Different levels of chloride-to-sulfate mass ratios (CSMR) were achieved by mixing the two coagulants. The coagulant doses were based on the treatment plant doses. Coagulation mixing speeds and times (rapid mix for one minute, 20 rpm for 20 minutes, and settling for 30 minutes) were selected to simulate to the extent possible the full-scale treatment practice in jar tests.

**Alkalinity**

The alkalinity for the CSMR test conditions was consistent amongst the treated waters and was approximately 25 mg/L as CaCO₃. To determine the effect of increasing alkalinity on lead leaching, five levels of alkalinity were tested for water treated with PACl (Table 4.1). For those conditions, PACl-treated water was diluted to an alkalinity of 20 mg/L as CaCO₃ using deionized water to simulate a rain event. The alkalinity for each test condition was then increased to the target level between 20 mg/L as CaCO₃ and 40 mg/L as CaCO₃ by adding NaHCO₃. For the 50 mg/L as CaCO₃ alkalinity condition that was evaluated in the earliest stage

<table>
<thead>
<tr>
<th>Condition Evaluation</th>
<th>Coagulant</th>
<th>Chloride (mg/L Cl)</th>
<th>Sulfate (mg/L SO₄)</th>
<th>CSMR</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Ortho-phosphate (mg/L P)</th>
<th>Lead Materials Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSMR Blend</td>
<td>Alum and PACl</td>
<td>21</td>
<td>30</td>
<td>0.7</td>
<td>25</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>CSMR Blend</td>
<td>Alum and PACl</td>
<td>22</td>
<td>24</td>
<td>1.1</td>
<td>25</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>Alkalinity Evaluation</td>
<td>PACl, 50 mg/L alkalinity (Weeks 1-7)</td>
<td>21</td>
<td>14</td>
<td>1.6</td>
<td>50</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>Alkalinity Evaluation</td>
<td>PACl, 20 mg/L alkalinity</td>
<td>21</td>
<td>12</td>
<td>1.9</td>
<td>20</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>Alkalinity Evaluation</td>
<td>PACl, 25 mg/L alkalinity</td>
<td>21</td>
<td>12</td>
<td>1.9</td>
<td>25</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>Alkalinity Evaluation</td>
<td>PACl, 30 mg/L alkalinity</td>
<td>21</td>
<td>12</td>
<td>1.9</td>
<td>30</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>Alkalinity Evaluation</td>
<td>PACl, 35 mg/L alkalinity</td>
<td>21</td>
<td>12</td>
<td>1.9</td>
<td>35</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
<tr>
<td>Alkalinity Evaluation</td>
<td>PACl, 40 mg/L alkalinity (Weeks 8-35)</td>
<td>21</td>
<td>12</td>
<td>1.9</td>
<td>40</td>
<td>1</td>
<td>New solder/copper couples; Brass</td>
</tr>
</tbody>
</table>

Table 4.1
Test Conditions for Greenville, NC
of this study, NaHCO₃ was added to water treated with PACl that had an initial alkalinity of 25 mg/L as CaCO₃.

**Corrosion Inhibitor, Disinfectant, and Target pH**

Orthophosphate corrosion inhibitor was added to all waters at a dose of 1 mg/L P, except for the two conditions specifically evaluating the effect of no inhibitor (Table 4.1). The target chloramines dose was 3.5 mg/L Cl₂ at a chlorine-to-ammonia ratio of 4:1 mg Cl₂:mg N. The pH was adjusted to the target value of pH 7.7 within 0.1 pH units by bubbling CO₂ to decrease the pH or by adding 0.1 M NaOH to increase the pH prior to exposure of the water to the test coupons.

**Lead Plumbing Materials Evaluated**

Two common types of lead bearing plumbing materials were evaluated for lead leaching. Brass and 50:50 Pb/Sn solder (new and passivated) were exposed to the water conditions listed in Table 4.1. At least three replicates were tested for each condition to examine statistical confidence of key trends. Water exposed to the lead materials was changed twice per week (Tuesday and Friday) and was otherwise stagnant. All materials were kept at room temperature throughout the testing period.

**Passivated Non-Galvanic and Galvanic Solder-Copper Connections**

Solder wire pieces (50:50 lead:tin) of 0.125 inch diameter and 0.854 inch height were epoxied to the bottom of a 46 mL vial (Figure 4.3), which was then filled with 25 mL of test water. To simulate the galvanic connection between copper pipe and solder at joints, an identical piece of solder wire was melted onto the inside surface of a copper tube (Figure 4.3). These coupons were used in a prior study for the utility and were allowed to passivate in stagnant water for 2 years prior to the start of this study (Edwards and Triantafyllidou 2007). The coupons exposed to no inhibitor or Zn were used in this study as conditions with no orthophosphate, and the coupons previously used under conditions with orthophosphate or orthophosphate with Zn were grouped as orthophosphate in this study. These aged coupons were evaluated to determine

![Figure 4.3](image-url)  
**Figure 4.3** Passivated copper/solder coupons (left) and solder wire (right) were evaluated for effects of CSMR.
the effect of CSMR during the first 25 weeks of this study. During Weeks 4-6 of the study, a simulated coagulant switch occurred for a short period of time, and a coagulant switch was not re-evaluated later in the study for these coupons.

**New Galvanic Solder-Copper Connections**

Simulated lead-copper joints were prepared using a 1-inch in length copper coupling (½-inch diameter copper) with a 1-inch length of 50:50 Pb/Sn solder melted inside (Figure 4.4). The solder-copper couplings were exposed to 100 mL of all water conditions with orthophosphate listed in Table 4.1. After Week 23, the solder-copper coupons exposed to water with a CSMR of 0.7 were then exposed to water treated with 100% PACl (or CSMR 1.9) to determine the length of time PACl could be used before lead leaching increased significantly.

**New Brass**

Brass coupons (3% lead content) 1/4–inch in diameter were cut in 1-inch length and epoxied to the bottom of glass containers (Figure 4.5). The brass coupons were exposed to 50 mL of all water conditions listed in Table 4.1 for 18 weeks.

**Measurements**

The study lasted a total of 35 weeks for the new solder-copper coupons, but the brass coupons were evaluated for 18 weeks and the passivated solder coupons for 25 weeks during this study. The evaluation for each material ended once it appeared that the lead levels were stable and the study questions were answered to the extent possible. Composite weekly samples were routinely collected for each water condition (i.e., two water changes collected for each weekly sample) and lead material. The unfiltered composite samples were analyzed for metals with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with Standard Method

![Figure 4.4](image-url) New copper/solder couples were exposed to water to compare effects of CSMR and alkalinity.
RESULTS AND DISCUSSION

Effect of Coagulant Change

A key question for this study was: “How long could the utility switch from alum to PACl before lead levels would substantially increase?” The coupons used to evaluate this question were new solder-copper coupons, and a simulated coagulant switch occurred after Week 24 of the study. Throughout the first 24 weeks of testing, the 100% alum (CSMR of 0.4) and CSMR 0.7 conditions were not statistically different in terms of lead leaching and leached low relatively lead (Figure 4.6). These coupons were then abruptly exposed to 100% PACl (CSMR of 1.9) after Week 24 to simulate a switch, and to see how long it would take for lead leaching to worsen. Some coupons exposed to 100% PACl or 100% alum throughout the entire study period were used as a comparison (Figure 4.7).

Lead leaching from new solder-copper coupons that had been previously exposed to low CSMR water and leached low lead, began increasing after 2 weeks of exposure to 100% PACl-treated water (Figure 4.7). After the 3rd week of exposure to the higher CSMR water, the coupons previously exposed to CSMR 0.7 water had significantly higher lead release than the 100% alum condition (p-value < 0.05). In fact, the alum-treated water exhibited a decrease in lead release from 61 ppb to 37 ppb after week 24 while the coupons switched to 100% PACl had increased in the amount of lead in water from 298 ppb to 485 ppb after the coagulant switch (Figure 4.8). Even after 2.5 months of exposure to 100% PACl-treated water, the coupons (that were previously exposed to the CSMR 0.7 condition) reached only about 10% of the lead leaching of the coupons that were exposed to 100% PACl for the entire 35-week duration of the study. The results prove that it takes some time before coupons that were passivated begin to show higher lead leaching when exposed to higher CSMR.
Figure 4.6 Lead release as a function of time for 100% alum (CSMR 0.4), 100% PACl (CSMR 1.9), and CSMR 0.7 conditions throughout the entire testing period. Samples were exposed to water with nitrate from week 7 to week 12, causing a short-term spike in lead.

Figure 4.7 Lead release over time following a change to 100% PACl coagulant (CSMR 1.9) from a blended coagulant with a CSMR of 0.7. The 100% alum (CSMR 0.4) and PACl conditions in the plot were exposed to the coupons since the start of the study, or for 23 weeks prior to the coagulant changeover.
Effect of Blended Alum and PACl Coagulants on Lead Levels

New Solder-Copper Coupons

To obtain the benefits of PACl coagulant while maintaining a lower CSMR, one option for the GUC was to use a blend of PACl and alum coagulants. Consistent with theory and similar to the results for the passivated solder-copper coupons with no inhibitor after regular water changes, CSMR had a direct positive correlation with lead release from new lead solder-copper coupons in this water with 1 mg/L PO4-P (Figure 4.9). For instance, alum-treated water had the lowest lead release, and increasing the CSMR from 0.4 to 0.7 resulted in approximately 60% higher levels of lead (Figure 4.10). Increasing the CSMR to approximately 1.1 resulted in 25 times more lead in the water compared to alum-treated water with a CSMR of 0.4. Furthermore, at the highest CSMR level evaluated in this study (100% PACl), the lead concentrations were 50 times higher than the lowest CSMR condition (100% alum). The results were shown to be statistically significant (p-value < 0.05), except the comparisons between the two lowest CSMR test conditions and between the two highest CSMR test conditions. Therefore, these results suggest that higher blends of PACl with alum increases lead release, but the blended coagulant with a CSMR of 0.7 was not significantly different from the 100% alum condition and could be used by the utility without markedly increasing the lead in water.

Figure 4.8 Lead release from coupons exposed to CSMR 0.7 water before and after switching the condition to 100% PACl. The 100% alum (CSMR 0.4) and 100% PACl (CSMR 1.9) conditions are shown for comparison. After switching lead levels increased, but the increase took several weeks to become significant.
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

\[ y = 2799.0x - 1320.0 \]
\[ R^2 = 0.935 \]

Figure 4.9 Lead release from solder as a function of CSMR at week 23.

Figure 4.10 Lead release from new galvanic solder-copper coupons for a range of CSMRs during Weeks 22 and 23. Two replicate lead data points for CSMR 1.5 were discarded because the values (>8,800 ppb Pb) were more than 2.5 times the average for the condition.
Brass

T-testing indicated that there were no significant differences in lead leaching among the CSMR levels (Figure 4.11).

Effect of Alkalinity in High CSMR Water

New Solder-Copper Coupons

There was no conclusive evidence that increasing alkalinity reduced lead leaching from coupons exposed to 100% PACl-treated water (Figure 4.12). T-testing with a Bonferroni correction indicated that there were no significant differences between any of the conditions. Initially in this study, there was evidence suggesting that higher alkalinity significantly reduced lead leaching. For example, PACl-treated water with an alkalinity of 50 mg/L as CaCO₃ had 88% less lead than PACl-treated water with 25 mg/L as CaCO₃, and the result was significant at the 95% confidence level (Figure 4.13). However, after Week 7 nitric acid (nitrate) was added to all of the alkalinity test waters to consistently reduce the alkalinity and resulted in increased lead leaching.

Brass

Brass did not appear to be greatly affected by changes in alkalinity (Figure 4.14). T-testing with the Bonferroni correction indicated that there were no significant differences between any of the conditions.

Figure 4.11 Lead release from brass for a range of CSMRs during Weeks 17 through 20. Error bars represent 95% confidence intervals among the replicates for each condition for the sampling period.
Figure 4.12 Effect of alkalinity on lead leaching from new solder-copper coupons. Error bars show 95% confidence intervals.

Figure 4.13 Effect of increasing alkalinity from 25 mg/L to 50 mg/L as CaCO₃ before coupons were exposed to nitrate.
Figure 4.14 Effect of alkalinity on lead leaching from brass coupons. Error bars show 95% confidence intervals.

Impact of Nitrate

The coupons used to evaluate the effects of alkalinity were exposed for at least 5 weeks to a high level of nitrate (5 mg/L NO₃-N) when nitric acid was dosed to decrease the alkalinity to levels between 0 and 20 mg/L as CaCO₃ in the earliest stage of the study. For this water, even a low level of nitrate could increase lead release. For instance, the coupons originally exposed to 50 mg/L alkalinity as CaCO₃ were later exposed to water containing nitrate when the alkalinity was decreased to 40 mg/L as CaCO₃, and the lead release increased more than would be expected with an alkalinity decrease of 10 mg/L as CaCO₃ (Figure 4.15). An additional study was conducted to examine the effect of nitrate on lead leaching and demonstrated that nitrate dramatically increases lead release (Stone et al. 2009). No phosphate was added to the waters in the additional study, and consistent with prior experiences with copper pipe in those situations, no nitrite was detected, and there was no evidence of nitrification. Moreover, the pH of the bulk water did not drop as would occur with nitrification.

The surface of the solder coupon was irreversibly damaged by the presence of nitrate in the early stage of this case study. Increasing the alkalinity from 25 mg/L to 50 mg/L as CaCO₃ had no beneficial effects on lead leaching in the water with nitrate (Figure 4.16), in contrast to the initial results before the coupons were exposed to nitrate (Figure 4.13). At this time, the mechanism of the nitrate corrosive attack is unknown, and additional research on this issue is underway.

In practice, nitrate can increase in a water supply via a variety of methods. In distribution systems where nitrification occurs, nitrate in the range of 1 mg/L can be formed from ammonia. Heavy use of nitrogen fertilizers has caused increasing amounts of nitrate to enter some water supplies via runoff (Schlesinger et al. 2006). Regardless of cause(s), higher levels of nitrate deserve increased scrutiny relative to lead leaching from old 50:50 Pb/Sn solder.
Figure 4.15 Effect of nitrate on lead leaching from coupons exposed to high alkalinity waters (log scale). The error bars represent the 95% confidence intervals.

Figure 4.16 Effect of increasing alkalinity from 25 mg/L to 50 mg/L as CaCO₃ on lead leaching at the end of the study. The error bars represent 95% confidence intervals.
Effect of CSMR after Long Stagnation Period

We were curious what would happen to lead levels in a sample exposed to various CSMR and inhibitor levels for a very long stagnation time. The passivated coupons in this study were last used in 2006 and were stored in their respective target waters for 2 years without further water changes (Edwards and Triantafyllidou 2007). At the end of the study in 2006, PACl was shown to be much worse than alum in terms of lead leaching for 48-hour stagnation events, except in the case where zinc orthophosphate was dosed. Orthophosphate addition reduced the lead levels (Figure 4.17).

When the study was resumed in 2008, the water that had stayed stagnant for 2 years was collected and analyzed for lead. The results indicated that all of the samples were contaminated with very high levels of lead regardless of CSMR (Figures 4.18 and 4.19). The only exception was alum-treated water with orthophosphate, which had very low lead (Figure 4.18).

Orthophosphate reduced the lead release for alum-treated water (p-value < 0.03) but did not reduce lead leaching from PACl-treated water (p-value = 0.35) when exposed to solder-copper coupons in stagnant water for 2 years. Although t-testing indicated that the conditions were not statistically different based on the replicate data, PACl dosed with orthophosphate did leach as much as 3 times more lead than PACl with no inhibitor.

Additionally, the replicate with the highest lead leaching that was exposed to alum treated water with no orthophosphate leached 12,000 ppb Pb to the water during the 2-year period of stagnation, which was twice the amount of lead from the worst coupon treated with PACl and no inhibitor. Overall, the alum and PACl conditions without orthophosphate were not statistically different, and the results suggest that the CSMR of the water had no effect on lead leaching for galvanic lead solder following a very long period of stagnation.


Figure 4.17 Lead release vs. corrosion control treatment for galvanic solder, in PACl-treated water and alum-treated water, averaged from Weeks 5 to 9 of the previous study (Edwards et al., 2007). The error bars denote 95% confidence intervals.
Figure 4.18 Lead concentrations in water after 2 years of stagnation for the passivated solder-copper coupons.

Figure 4.19 Lead concentrations in water after 2 years of stagnation for the passivated solder (no connection to copper).
Effect of CSMR on Passivated Coupons after Regular Water Changes

The tests described in Figure 4.18 were continued with regular water changes in order to see if trends of CSMR on lead leaching would be resumed. After several weeks of regular water changes and collecting water from the passivated coupons, the lead leaching gradually decreased to levels that were approximately 50% of the lead levels in the previous study three years ago (Figure 4.20 and Table 4.2). The coupons exposed to orthophosphate had the lowest lead levels. Furthermore, the only condition that was unchanged compared to the lead levels 3 years ago was the PACl treated water that contained no orthophosphate (Table 4.2).

When there was no orthophosphate in the water, the CSMR had a large impact on lead leaching. There was 4 times more lead in PACl-treated water, which had approximately 3,800 ppb Pb, than in alum-treated water, which had approximately 950 ppb Pb (Figure 4.20).

In contrast, orthophosphate was effective in reducing lead leaching from passivated solder-copper coupons (p-value < 0.01), and CSMR had no statistically significant effect on the passivated coupons when orthophosphate was present, which is contrary to results for new solder exposed to orthophosphate. For passivated solder galvanically connected to copper, the addition of orthophosphate dramatically decreased the lead leaching by 3.5 times for alum-treated water and 16 times for PACl treated water (Figure 4.20). Therefore, passivated solder-copper coupons exposed to orthophosphate were not affected by the CSMR.

![Figure 4.20 Lead release from coupons aged 2 years, and then exposed to alum or PACl coagulants with or without orthophosphate during Weeks 22 through 25. Error bars show the 95% confidence intervals.](image-url)
Table 4.2
Comparison of average lead released from the aged solder during the first study in 2006 (Edwards and Triantafyllidou 2007) and in this study in 2009. The 2009 values are based on averages of Weeks 22-25 of this study.

<table>
<thead>
<tr>
<th>Condition and Treatment Type</th>
<th>Lead Concentration (ppb Pb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2006</td>
</tr>
<tr>
<td><strong>Galvanic solder</strong></td>
<td></td>
</tr>
<tr>
<td>Alum, no inhibitor</td>
<td>1,460</td>
</tr>
<tr>
<td>Alum, orthophosphate</td>
<td>440</td>
</tr>
<tr>
<td>PACl, no inhibitor</td>
<td>2,930</td>
</tr>
<tr>
<td>PACl, orthophosphate</td>
<td>610</td>
</tr>
<tr>
<td><strong>Non-galvanic solder</strong></td>
<td></td>
</tr>
<tr>
<td>Alum, no inhibitor</td>
<td>270</td>
</tr>
<tr>
<td>PACl, no inhibitor</td>
<td>230</td>
</tr>
</tbody>
</table>

Effect of Galvanic Connection on Passivated Solder

Solder-copper coupons and solder (not connected to copper) that were used in the previous study in 2006 were stagnant in water for 2 years and then used in this study. The galvanic connection of passivated lead solder to copper markedly increased lead leaching compared to lead solder alone. For instance, by connecting the solder to copper, the lead leaching increased 9 times for alum treated water and 31 times for PACl treated water (Figure 4.21). Furthermore, when solder was alone in water, the coagulant type (and CSMR) did not have a significant effect on lead leaching at the 95% confidence level. Therefore, the results support previous theory that the effect of CSMR is dominated by galvanic corrosion (Edwards and Triantafyllidou 2007) and that the effects continue for years.

Figure 4.21 Lead release from passivated solder, which were passivated for 2 years, as a result of connection to copper during Weeks 23-25 of this study. Error bars show 95% confidence intervals.
FUTURE WORK

Alkalinity

To determine the effect of alkalinity on lead leaching in PACl-treated water without complications of nitrate, a new test with new coupons will be conducted. The evaluation is currently in-progress.

CONCLUSIONS

- For this water, higher CSMR and higher levels of nitrate in the water dramatically increased the lead release from solder galvanically connected to copper.

- In the simulation where the coagulant was switched from alum to PACl, it took approximately 2 weeks for the lead leaching to increase from new solder-copper coupons.

- After 2 years of stagnation, the only condition that had low lead leaching was the condition with orthophosphate and low CSMR water.

- Passivated coupons had reduced lead levels compared to results from 3 years ago, except for the condition with PACl and no orthophosphate, which sustained high levels of lead leaching.

- The results in this study in relation to effects of alkalinity were not conclusive; therefore, a range of alkalinites will be re-evaluated with new solder-copper coupons.
CHAPTER 5: CASE STUDY OF UTILITY G, NC (COAGULANTS)

Caroline Nguyen, Kendall Stone, and Marc Edwards

Keywords: Coagulants, ferric chloride, ferric sulfate, alum, ferric sulfate polymer blend, ferric sulfate / aluminum chlorohydrate blend

INTRODUCTION

Bench scale experiments were conducted for five weeks to study the effects of coagulant selection on lead leaching in water for Utility G in North Carolina. Within the last few years, Utility G has implemented four different coagulants with varying chloride and sulfate content, and high 90th percentile lead in the system has coincided with times when chloride-based coagulants were used. Therefore, five different types of coagulants (including one prospective coagulant) in treated waters were compared head-to-head in terms of lead leaching from brass (5% lead content) and 50:50 Pb/Sn solder galvanically connected to copper. These lead materials are assumed to be present in the distribution systems throughout the county at some level of occurrence. The goal was to determine whether the coagulants that contributed chloride to the water, definitively increased lead leaching, versus those that contribute sulfate to the water.

MATERIALS AND METHODS

Test Water

Utility G water was shipped to Virginia Tech approximately every other week. Collected water was separated and subjected to simulated drinking water treatment, which was otherwise identical except for the type of coagulant used. Treatment involved coagulation, filtration, phosphate corrosion inhibitor addition, disinfection with chloramines, and final pH adjustment. A summary of the treatment scenarios and water quality information is provided in Table 5.1. The alkalinity of the water was approximately 40 mg/L as CaCO₃.

Table 5.1
Chloride and Sulfate Concentrations after Indicated Water Treatment

<table>
<thead>
<tr>
<th>Coagulant Type</th>
<th>Chloride (mg/L Cl)</th>
<th>Sulfate (mg/L SO₄)</th>
<th>CSMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum sulfate (alum)</td>
<td>14</td>
<td>32</td>
<td>0.4</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>28</td>
<td>9</td>
<td>3.1</td>
</tr>
<tr>
<td>Ferric sulfate / aluminum chlorohydrate blend</td>
<td>18</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td>Ferric sulfate</td>
<td>13</td>
<td>30</td>
<td>0.4</td>
</tr>
<tr>
<td>Ferric sulfate polymer blend</td>
<td>14</td>
<td>32</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Coagulant type

The five types of coagulation treatment evaluated were: (1) aluminum sulfate, (2) ferric chloride, (3) a ferric sulfate / aluminum chlorohydrate blend, (4) ferric sulfate, and (5) a ferric sulfate polymer blend. Utility G has used the first four over the last couple of years, and the ferric sulfate polymer blend is a coagulant that is being considered for future use.

The ferric sulfate coagulant dose was provided by the utility, and mixing speeds and times (rapid mix for one minute, 20 rpm for 20 minutes, and settling for 30 minutes) were selected to simulate to the extent possible the full-scale treatment practice in jar tests. The coagulant doses for ferric chloride and aluminum sulfate were based on the total molar dose of ferric (mol/L Fe\(^{3+}\)) that the treatment plant used. For instance, if 1 mol/L Fe\(^{3+}\) was dosed at the plant, 1 mol/L Fe\(^{3+}\) was also used for the ferric chloride condition, and 1 mol/L Al\(^{3+}\) was dosed during coagulation for aluminum sulfate (alum). The doses of the ferric sulfate blends were based on the manufacturer’s recommendations. The final chloride and sulfate concentrations in the treated water are listed in Table 5.1 for each coagulant condition, and the removal of natural organic matter (NOM) from the water after coagulation/sedimentation and filtration is listed in Table 5.2 for each of the coagulants.

Corrosion Inhibitor, Disinfectant, and Target pH

The dose of orthophosphate for this study was 1 mg/L as P. The target free chlorine disinfectant dose was 2.5 mg/L Cl\(_2\). The pH was adjusted to the target value of pH 7.3 within 0.1 pH units with either 0.1 M NaOH or 0.1 M HNO\(_3\) prior to exposure to the test coupons.

Evaluated Lead Plumbing Materials

Two common lead bearing plumbing materials were evaluated for impacts on lead leaching. Brass and 50:50 Pb/Sn solder were exposed to the water conditions listed in Table 5.1. Three replicates were tested for each condition to examine statistical confidence of key trends. Water exposed to the lead materials was changed twice per week (Monday and Thursday) and was otherwise stagnant. All materials were kept at room temperature throughout the testing period.

Solder

Simulated lead-copper joints were prepared using a 1-inch in length copper coupling (½-inch diameter copper) with a 1-inch length of 50:50 Pb/Sn solder melted inside (Figure 5.1). The solder-copper couplings were exposed to 100 mL of all water conditions listed in Table 5.1.

Brass

Brass coupons (5% lead content) that were ½-inch in diameter were cut in 0.4-inch lengths and epoxied to the bottom of glass containers (Figure 5.2). The brass coupons were exposed to 50 mL of all water conditions listed in Table 5.1.
Table 5.2
Water Quality during Water Treatment for Utility G

<table>
<thead>
<tr>
<th>Coagulant Type</th>
<th>TOC * (mg/L C)</th>
<th>UV254 Absorbance ** (cm⁻¹)</th>
<th>Turbidity *** (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After Settling</td>
<td>After Filtration</td>
<td>After Settling</td>
</tr>
<tr>
<td>Aluminum sulfate (alu)</td>
<td>1.8</td>
<td>1.7</td>
<td>0.053</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>1.5</td>
<td>1.3</td>
<td>0.076</td>
</tr>
<tr>
<td>Ferric sulfate / aluminum chlorohydrate blend</td>
<td>2.8</td>
<td>1.9</td>
<td>0.112</td>
</tr>
<tr>
<td>Ferric sulfate</td>
<td>1.6</td>
<td>1.3</td>
<td>0.072</td>
</tr>
<tr>
<td>Ferric sulfate polymer blend</td>
<td>1.7</td>
<td>1.4</td>
<td>0.078</td>
</tr>
</tbody>
</table>

* Raw water = 2.88 mg/L total organic carbon.
** Raw water = 0.137 cm⁻¹.
*** Raw water = 13 NTU.

Measurements

Composite weekly samples were routinely collected for each water condition (i.e., two water changes collected for each weekly sample) and lead material. The samples were acidified with 2% HNO₃ for at least 24 hours to dissolve metals. The unfiltered composite samples were analyzed for metals with Induced Coupled Plasma Mass Spectrometry (ICP-MS). The results for brass in this report were from the entire study period since the lead remained relatively low and constant during the 5 weeks. Results for solder were from the last three weeks of the study since the lead levels changed dramatically with time.

Figure 5.1 Solder-copper coupon for Utility G
RESULTS AND DISCUSSION

Effect of CSMR

Water with low CSMR (i.e., treated with alum, ferric sulfate, or the ferric sulfate polymer blend) consistently had lower lead leaching from solder. Treating water with coagulants containing chloride (including the ferric sulfate aluminum chlorohydrate blend) resulted in the highest lead release from solder (Figure 5.3). Brass, which contained 5% lead, did not appear to be affected as strongly by the CSMR.

Brass

Lead leaching from brass was similar for all of the tested water conditions (Figure 5.4). There were no significant differences among the test conditions based on statistical t-tests. For this utility, brass is not a problem in terms of lead leaching.

Solder

Consistent with theory and practical experience at this utility, lead leaching from 50:50 Pb/Sn solder galvanically connected to copper was affected by the CSMR of the water. The ranking from least to worst lead leaching was: (1) ferric sulfate, (2) alum or the ferric sulfate polymer blend, (3) ferric chloride or the chlorohydrate blend. Therefore, after exposure to solder, ferric sulfate-treated water resulted in the lowest lead leaching. The other sulfate-based coagulants (alum and the ferric sulfate polymer blend) also had significantly less lead released than the chloride-based coagulants (ferric chloride and ferric sulfate/aluminum chlorohydrate...
Figure 5.3 Lead leaching from solder as a function of the chloride-to-sulfate mass ratio (CSMR) for Utility G

Figure 5.4 Lead leaching from brass for each of the simulated coagulation conditions for Utility G. The error bars depict the 95% confidence intervals.
For example, water treated with the chlorohydrate blend coagulant was about 13 times more aggressive than the ferric sulfate-treated water and 5 times more aggressive than alum-treated water (Figure 5.5). Lead leaching from solder in this water is extraordinarily impacted by coagulation conditions, as manifested by changes in the CSMR.

If anything, the chlorohydrate blend actually caused more lead leaching than did the ferric chloride alone, although the difference was not significant at >95% confidence (Figure 5.5). This might be because this coagulant was not as effective at removing natural organic matter (1.9 vs. 1.3 mg/L as TOC). NOM is also known to increase lead leaching (Table 5.2). However, the TOC of the treated water did not correlate with the lead in the water when comparing all five coagulation conditions.

The ferric sulfate polymer blend is being considered due to the possibility of reducing caustic costs and the hypothesized ability to better control lead leaching with the addition of sulfate. However, the ferric sulfate polymer blend had 3 times higher lead than the current ferric sulfate coagulant and 50% more lead than alum. Therefore, the prospective ferric sulfate polymer blend is not recommended for future use as a coagulant.

![Figure 5.5 Lead leaching from galvanic solder for each of the simulated coagulation conditions for Utility G. The error bars show the 95% confidence intervals.](image-url)
CONCLUSIONS

- Consistent with past experience, the condition that offered the best lead corrosion control was water treated with ferric sulfate.

- The chloride-based coagulants (ferric chloride and aluminum chlorohydrate blend) had the highest lead levels.

- The proposed ferric sulfate polymer blend did not exhibit promise in mitigating lead leaching, and its use cannot be recommended in the future for this utility.
CHAPTER 6: CASE STUDY OF UTILITIES B AND E, NC  
(COAGULANTS)

Caroline Nguyen, Kendall Stone, and Marc Edwards

**Keywords:** Coagulants, anion exchange, corrosion inhibitors, alkalinity, lime, ferric chloride, ferric sulfate, orthophosphate, silicate polyphosphate

**INTRODUCTION**

Bench scale experiments were undertaken for six weeks to study the effects of coagulant selection, corrosion inhibitor type and dose, alkalinity, and lime on lead leaching in water for two neighboring cities in North Carolina. Six different types of coagulation (including ferric sulfate and ferric chloride) and three corrosion inhibitors (including a silicate polyphosphate blend and orthophosphate) in treated waters were compared head-to-head in terms of lead leaching from brass (5% lead content), 50:50 Pb/Sn solder galvanically connected to copper, and pure lead pipe. These three lead materials are assumed to be present in the distribution systems throughout the city at some level of occurrence.

**MATERIALS AND METHODS**

**Test Water**

Utility E’s raw water (Table 6.1) was shipped to Virginia Tech approximately every other week by the utility. Collected water was separated and subjected to simulated drinking water treatment, which was otherwise identical except for the type of coagulant or inhibitor used. Treatment involved coagulation, filtration, phosphate corrosion inhibitor addition (if specified), disinfection with chloramines, fluoride addition, and final pH adjustment. Utility E currently coagulates with ferric sulfate, doses a silicate polyphosphate blend corrosion inhibitor, and adjusts the final pH to around pH 8.0. Utility B coagulates with aluminum sulfate (alum), adds orthophosphate as a corrosion inhibitor, and adjusts the final pH to 7.6. A summary of the treatment scenarios and water quality information is provided in Table 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>13 mg/L $\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>Chloride</td>
<td>9 mg/L Cl</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.8 mg/L Si</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>35 mg/L as $\text{CaCO}_3$</td>
</tr>
</tbody>
</table>
Coagulant Type

The six types of coagulation treatment evaluated were: (1) 100% ferric sulfate, (2) 100% ferric chloride, (3) blend of ferric chloride and ferric sulfate to achieve a CSMR of 0.3, (4) blend of ferric chloride and ferric sulfate to achieve a CSMR of 1.0, (5) anion exchange followed by a low dose of ferric sulfate, and (6) anion exchange followed by a low dose of ferric chloride. The ferric sulfate coagulant dose was provided by Utility E, and mixing speeds and times (rapid mix for one minute, 20 rpm for 20 minutes, and settling for 30 minutes) were selected to simulate to the extent possible the full-scale treatment practice in jar tests. The coagulant dose for the ferric chloride condition and the ferric chloride/sulfate blends were based on the total ferric dose (mg/L Fe\(^{3+}\)) that the treatment plant used. In the anion exchange conditions, the raw water was mixed for 1 hour with chloride-based anion exchange resin to remove natural organic matter (NOM) in the water, and the supernatant was collected and mixed with a third of the full ferric sulfate or ferric chloride dose.

<table>
<thead>
<tr>
<th>Coagulant Type</th>
<th>Corrosion Inhibitor</th>
<th>Special Condition*</th>
<th>pH</th>
<th>CSMR</th>
</tr>
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<td>100% ferric sulfate</td>
<td>None</td>
<td>--</td>
<td>8.0</td>
<td>0.2</td>
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<tr>
<td></td>
<td>Orthophosphate</td>
<td>--</td>
<td>7.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Silicate polyphosphate</td>
<td>--</td>
<td>8.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>4X inhibitor dose</td>
<td></td>
<td>8.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Lime</td>
<td></td>
<td>8.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Higher alkalinity</td>
<td></td>
<td>8.0</td>
<td>0.2</td>
</tr>
<tr>
<td>100% ferric chloride</td>
<td>None</td>
<td>--</td>
<td>8.0</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Silicate polyphosphate</td>
<td>--</td>
<td>8.0</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>--</td>
<td>7.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Ferric blend – CSMR 0.3</td>
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<td>--</td>
<td>8.0</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Silicate polyphosphate</td>
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<td>8.0</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>--</td>
<td>7.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Ferric blend – CSMR 1.0</td>
<td>None</td>
<td>--</td>
<td>8.0</td>
<td>1.0</td>
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<tr>
<td></td>
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<td>1.0</td>
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<td></td>
<td>Orthophosphate</td>
<td>--</td>
<td>7.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Anion exchange, ferric sulfate</td>
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<td>--</td>
<td>8.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Silicate polyphosphate</td>
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<td>8.0</td>
<td>1.0</td>
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<tr>
<td></td>
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<td>Anion exchange, ferric chloride</td>
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<td>8.0</td>
<td>5.9</td>
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<tr>
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<td>Silicate polyphosphate</td>
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<td>5.9</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>--</td>
<td>7.6</td>
<td>5.8</td>
</tr>
</tbody>
</table>

* if applicable
Corrosion Inhibitor and Target pH

Three corrosion inhibitors were evaluated for each of the six coagulation conditions: (1) no inhibitor at pH 8.0, (2) silicate polyphosphate blend at pH 8.0, and (3) orthophosphate at pH 7.6. The current dose of silicate polyphosphate used by Utility E and for this study was 0.74 mg/L SiO₂ and 0.28 mg/L phosphate. Additionally, the silicate polyphosphate inhibitor was tested at four times the current dose for ferric sulfate-treated water at pH 8.0. The no inhibitor condition and the silicate polyphosphate conditions were tested at Utility E’s pH of 8.0. Utility B currently uses Orthophosphate for corrosion control; therefore, the target pH of 7.6 was selected to simulate the Utility B finished water. The dose of orthophosphate for this study was 1 mg/L as P. The pH was adjusted to the target value within 0.1 pH units with either 0.1 M NaOH or 0.1 M HNO₃ prior to exposure to the test coupons.

Alkalinity and Lime

The effects of higher alkalinity and lime were investigated for Utility E’s current treatment with ferric sulfate coagulation and silicate polyphosphate corrosion inhibitor at and pH 8.0. A higher silicate polyphosphate level of four times the current inhibitor dose was also investigated for ferric sulfate-treated water. The higher alkalinity water was adjusted to 50 mg/L as CaCO₃ using sodium bicarbonate. Lime with 0.1% calcium hydroxide (CAL FLO slurry) was used in lieu of sodium hydroxide to increase the pH to 8.0.

Chloramines and Fluoride

The target chloramines disinfectant dose was 3.5 mg/L Cl₂, and the fluoride concentration was 0.9 mg/L F⁻. The ratio of chlorine-to-ammonia for the chloramines was 4:1 mg Cl₂:mg N. Fluoride was added from hydrofluorosilicic acid.

Evaluated Lead Plumbing Materials

Three common lead bearing plumbing materials were evaluated for impacts on lead leaching. Brass, 50:50 Pb/Sn solder, and pure lead pipe were all exposed to water conditions listed in Table 6.2. Three replicates were tested for each condition to examine statistical confidence of key trends. Water exposed to the lead materials was changed twice per week (Monday and Thursday) and was otherwise stagnant. All materials were kept at room temperature throughout the testing period.

Solder

Simulated lead-copper joints were prepared using a 1-inch in length copper coupling (½-inch diameter copper) with a 1-inch length of 50:50 Pb/Sn solder melted inside (Figure 6.1). The solder-copper couplings were exposed to 100 mL of all water conditions listed in Table 6.2.
Brass

Brass coupons (5% lead content) that were ½-inch in diameter were cut in 0.4-inch lengths and epoxied to the bottom of glass containers (Figure 6.2). The brass coupons were exposed to 50 mL of all water conditions listed in Table 6.2.

Lead pipe

New pure lead pipes, which were ½-inch in diameter and cut into 1-foot segments, were evaluated in this study (Figure 6.3). While one end of each pipe was sealed with a chemically inert silicone stopper, parafilm covered the other side to minimize abrasion of the lead material while emptying and filling the pipes during water changes. Only two water conditions were tested in lead pipes to evaluate the effects of lime for pH adjustment compared to caustic, which is currently by Utility E. Both evaluated waters were coagulated with 100% ferric sulfate and dosed with Utility E’s current silicate polyphosphate dose.
Measurements

Composite weekly samples were routinely collected for each water condition (i.e., two water changes collected for each weekly sample) and lead material. The samples were acidified with 2% HNO₃ for at least 24 hours to dissolve metals. The unfiltered composite samples were analyzed for metals with Induced Coupled Plasma Mass Spectrometry (ICP-MS). At the end of the first six weeks, intensive sampling was conducted to establish statistical confidence intervals. In the intensive sampling event, water was collected for each test coupon after each water change for three consecutive water changes. Data in this report is from the period of intensive sampling.

RESULTS AND DISCUSSION

Effect of CSMR

Water with low CSMR (i.e., treated with 100% ferric sulfate or a blend to produce a CSMR of 0.3) consistently had lower lead leaching from solder and brass. The anion exchange treated waters and 100% ferric chloride coagulated water were among the highest in lead. Lead was shown to have a roughly positive correlation with CSMR (Figure 6.4).
Figure 6.4 Lead leaching from solder as a function of the chloride-to-sulfate mass ratio (CSMR) for Utilities B and E.

**Brass**

The ranking of least to most aggressive water conditions in terms of lead leaching from brass was: (1) CSMR 0.3, (2) ferric sulfate, CSMR 1.0, and anion exchange with ferric sulfate, and (3) ferric chloride and anion exchange with ferric chloride (Figure 6.5). For example, the ferric chloride treated water had about 2.5 times more lead than the water treated with ferric sulfate. Water conditions that share a ranking level were shown to have no statistically significant difference based on t-tests.

**Solder**

The ranking of least to most aggressive water coagulation conditions in terms of lead leaching from 50:50 Pb/Sn solder galvanically connected to copper was: (1) ferric sulfate, (2) blend with final CSMR of 0.3, (3) blend with CSMR 1.0, ferric chloride, and anion exchange with ferric sulfate, and (4) anion exchange with ferric chloride (Figure 6.6). The ferric chloride treated water was about 6.5 times more aggressive than water coagulated with ferric sulfate for lead from solder. Lead leaching from solder in this water is extraordinarily impacted by coagulation conditions, as manifested by changes in the CSMR.
Figure 6.5 Lead leaching from brass for each of the simulated coagulation conditions for Utilities B and E. The error bars depict the 95% confidence intervals.

Figure 6.6 Lead leaching from galvanic solder for each of the simulated coagulation conditions for Utilities B and E. The error bars show the 95% confidence intervals.
Effect of Corrosion Inhibitors

**Brass**

Orthophosphate was the most effective corrosion control of lead from brass (p-value < 0.04). Adding no inhibitor to the water resulted in approximately 4 times more lead than did orthophosphate, and 2 times more lead than silicate polyphosphate (Figure 6.7).

**Solder**

Orthophosphate dramatically decreased lead from solder when excluding the condition with anion exchange followed by ferric chloride coagulation. Other studies performed at Virginia Tech also found that orthophosphate can actually increase the lead leaching in waters with high amounts of chloride. For this study, dosing orthophosphate almost doubled the amount of lead measured in water for the highest CSMR condition (anion exchange followed by ferric chloride coagulation; resulting CSMR of 5.9). Excluding the highest CSMR condition, water with no inhibitor had 1.7 times more lead than water with Utility E’s current dose of silicate polyphosphate (Figure 6.8). Furthermore, the condition with no inhibitor or the condition of silicate polyphosphate inhibitor had about 20 times and 12 times more lead, respectively, than water with orthophosphate.

![Figure 6.7 Effect of corrosion inhibitors on lead leaching from brass for Utilities B and E. The error bars show the 95% confidence intervals.](image-url)
CHAPTER 6: CASE STUDY OF UTILITIES B AND E, NC (COAGULANTS) | 93

Figure 6.8 Effect of corrosion inhibitors on lead leaching from solder for Utilities B and E. The error bars show the 95% confidence intervals.

**Effect of Lime**

The use of lime instead of caustic to increase pH resulted in no difference in lead leaching for solder: copper galvanic connections, lead pipe, and brass. Although lead leaching from brass initially increased by about 3.7 times from 15±2 ppb to 54±32 ppb with the use of lime (Figure 6.9), further testing for the utility suggested that brass is actually not affected by lime.

**Lead Corrosion in Water Coagulated with Ferric Sulfate**

**Brass**

Orthophosphate, a typical dose of silicate polyphosphate, and higher alkalinity of 50 mg/L as CaCO₃ produced the lowest levels of lead from brass (Figure 6.10). The worst conditions were water with no inhibitor, lime with silicate polyphosphate, and quadruple the current silicate polyphosphate dose. Approximately three times more lead was released from the more aggressive conditions than the less aggressive conditions.

**Solder**

The ranking from best to worst lead leaching for solder exposure was: (1) orthophosphate, (2) higher alkalinity, (3) 4 X silicate polyphosphate dose, (4) lime with silicate polyphosphate, (5) current dose of silicate polyphosphate, and (6) no inhibitor. Adding orthophosphate resulted in a 98% decrease in lead compared to when no inhibitor was added.
Figure 6.9. Comparison of lime and caustic for pH adjustment. The error bars show the 95% confidence intervals.

Figure 6.10 Lead from brass for water coagulated with 100% ferric sulfate. The error bars show the 95% confidence intervals.
(Figure 6.11). Although the increase in silicate polyphosphate dose resulted in a proportional decrease in lead leaching to water, the lead leaching did not decrease to the levels of orthophosphate. By increasing the alkalinity in water coagulated with ferric sulfate, lead leaching from solder was reduced compared to when silicate polyphosphate was added alone; however, the reduction was not to the same extent as reduction due to orthophosphate.

**CONCLUSIONS**

- The condition that offered the best lead corrosion control was water coagulated with ferric sulfate and dosed with 1 mg/L PO$_4$-P.

- Anion exchange using a chloride-based resin increases chloride in drinking water.

- Lead leaching from solder-copper couples increased with higher CSMR.

- Orthophosphate was effective in reducing lead leaching from brass and solder-copper coupons. However, orthophosphate dosed in the highest CSMR condition (CSMR of 5.8) doubled the amount of lead released to the water.

- Lime, which has become a more economical alternative to caustic for many utilities, did not appear to impact the levels of lead.

**Figure 6.11 Lead from solder for water coagulated with 100% ferric sulfate.** The error bars show the 95% confidence intervals.
Keywords: Coagulants, alum, ferric sulfate, polyaluminum chloride, polyphosphate

INTRODUCTION

Utility D in Nova Scotia has collaborated with Dalhousie University to execute a long-term water quality research program to ensure safe, high quality water is delivered to its consumers through the development of effective treatment solutions for their facilities. As part of this research program, Dalhousie University is currently investigating coagulation and flocculation processes at the utility to optimize NOM removal to mitigate the formation of disinfection by-products (DBPs). This includes the evaluation of alternative coagulants to achieve such goals and, subsequently, the evaluation of potential “unintended consequences” of such chemical changeovers on finished water quality and distribution systems with respect to metal release occurrences. It is essential that the research results achieve a balance between coagulation optimization techniques to meet pending treatment objectives and the role of lead leaching associated with each.

The Utility D treatment plant is a direct filtration plant that treats surface water characterized by low alkalinity, turbidity, and organic matter. In general, the data relating CSMR and lead leaching in systems with water sources characterized by low alkalinity and turbidity is limited and more research is required to validate the effects of CSMR. Coagulant changeover cases suggest that a high chloride (Cl\(^{-}\)) to sulfate (SO\(_4^{2-}\)) mass ratio (CSMR) governs lead leaching incidences in distribution systems (Dodrill and Edwards 1995; Dudi 2004; Edwards and Triantafyllidou 2007). When chloride and sulfate co-exist in a distribution system, the concentration of sulfate must be sufficient to overcome the counteractive effects of chloride (Edwards and Triantafyllidou 2007). Common coagulants are typically chloride and sulfate based (i.e.; aluminum sulfate, ferric chloride, polyaluminum chloride, ferric sulfate, etc), therefore, changes in the coagulant at water treatment plant can significantly alter the ratio of chloride and sulfate concentrations in the finished water. The critical CSMR level cited from multiple bench scale and full-scale studies that governs the effects of lead leaching is 0.5 mg of chloride per mg of sulfate (Dodrill and Edwards 1995; Dudi, 2004; Edwards and Triantafyllidou 2007). Above this level, galvanic corrosion of lead pipe is increased, and below this threshold, lead leaching is mitigated.

Bench scale experiments were conducted to evaluate the effects of coagulant changeovers and the CSMR changes induced by such changeovers on both lead and copper leaching in the distribution system. The coagulants evaluated include aluminum sulfate (alum), ferric sulfate, and polyaluminum chloride (PACl). The two lead bearing plumbing materials studied were lead:tin solder and harvested lead pipe, both in connection with copper pipe.
MATERIALS AND METHODS

The experimental design and procedure was based on lead leaching studies in plumbing materials resulting from coagulant changeovers being lead by Edwards and co-workers (e.g., Nguyen et al. 2008).

Apparatus

Bench scale pipe set-ups were designed to compare the leaching effects of lead:tin solder and harvested lead pipe, both in connection with copper pipe through two pipe set-ups:

Pipe Set-up 1

- Pb pipe – Pb/Sn solder – Cu pipe
- extracted lead pipe with a pre-existing pipe scale connected to copper using a simulated 40:60 lead:tin solder joint

Pipe Set-up 2

- Cu pipe – Pb/Sn solder – Cu pipe
- copper to copper pipe connection using a simulated 40:60 lead:tin solder joint

Pipe Set-up 1 was composed of a 12.25” length of extracted ¾” lead pipe connected to a 2.5” length of ½” copper pipe using clear tubing and leaving an approximately 2-mm gap between the two pipes (Figure 7.1). The pipe sizes and experimental set-up were chosen to induce the worst-case scenario with respect to high corrosion and lead leaching conditions and to allow for micro-electrode measurements within the pipes (Nguyen et al. 2008). To simulate a soldered joint, solder wire was inserted through the ½” copper pipe until it reached the interface of the two pipes (Figures 7.1 and 7.2). The solder and pipes were electrically connected using copper wires and clips to simulate a galvanic connection. The pipes were capped using silicone stoppers throughout the experiment. Pipe Set-up 2 was erected in the same manner, except the simulated solder joint was connected to two copper pipes.

Test Water

The test water was treated to simulate, within reason, all conditions in the current full-scale treatment process (i.e.; chemical dosages, detention times, mixing regimes, etc.). All water conditions were subjected to identical treatment processes, with the only differences being the coagulant type, dosage and coagulation pH used. The coagulants evaluated included alum, ferric sulfate and PACl. Coagulant dosages were calculated as an equivalent metal molar ratio based on the 8 mg/L alum dosage currently employed in the full-scale treatment plant. Optimal coagulation pHs were determine through jar testing for each coagulant used.
Figure 7.1 Picture of 4 of 12 pipe setups: a) Pb pipe – Pb/Sn solder – Cu pipe; b) Cu pipe – Pb/Sn solder – Cu pipe

Figure 7.2 Picture of simulated 40:60 Pb/Sn soldered joint for Utility D.
Pre-oxidized water was drawn from the full-scale plant and was subsequently coagulated, filtered through a 1.5 µm filter paper, and dosed with the following chemicals for final treatment: 1) polyphosphate corrosion inhibitor/iron and manganese sequestering agent addition of 1.65 mg/L (0.5 mg/L as phosphate), 2) disinfectant addition of 1.3 mg/L chlorine, and 3) final pH adjustment using sodium hydroxide to 7.4. Treated water for each condition was made in batches as required but was only treated as far as the direct filtration stage. The finished water chemicals were added immediately before the water change occurred. Since this study involved changing the coagulant type, dosage, and coagulation pH, the finished water alkalinity and organic content were different between the three water conditions. Table 7.1 presents the raw water and treated water quality characteristics for each water condition tested. Clearly, the condition with the ferric sulfate is an outlier relative to coagulant performance, since it had twice the alkalinity and more TOC relative to the other coagulant conditions.

Based on the hypothesis that the CSMR is the controlling factor with respect to lead release, it is theorized that the ferric sulfate (CSMR of 0.91) and alum (CSMR of 0.93) water conditions would have similar levels of lead leaching, since their CSMR levels are approximately the same. The PACl (CSMR of 2.1) treated water was expected to correlate with a higher lead release, since the CSMR is more than double that of the other two treated water conditions. However, because the CSMRs of the waters were relatively high (>0.58), other factors such as TOC and alkalinity may have a larger role in lead release.

**Protocol**

For the testing, the two pipe set-ups were exposed to the 3 water conditions. Each test was performed in duplicate; therefore, 12 tests were conducted in total. Exposure of the finished water to each pipe condition was via a static “dump-and-fill” protocol three times per week. The water changes occurred on Monday (M), Wednesday (W) and Friday (F), therefore yielding two stagnation periods of 48 hours (M-W, W-F) and one stagnation time of 72 hours (F-M). Over

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw Water</th>
<th>PACl</th>
<th>Alum</th>
<th>Ferric Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulant Dosage (mg/L)</td>
<td>---</td>
<td>1.5</td>
<td>8.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Coagulation pH(^1)</td>
<td>---</td>
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<td>5.0</td>
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<tr>
<td>Alkalinity (mg/L as CaCO(_3))</td>
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<td>16.3 ± 1.6</td>
<td>16.8 ± 2.8</td>
<td>32.6 ± 7.4</td>
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<tr>
<td>TOC (mg/L)</td>
<td>2.89 ± 0.13</td>
<td>1.86 ± 0.57</td>
<td>1.88 ± 0.10</td>
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<tr>
<td>DOC (mg/L)</td>
<td>2.82 ± 0.13</td>
<td>1.86 ± 0.55</td>
<td>1.81 ± 0.24</td>
<td>2.13 ± 0.41</td>
</tr>
<tr>
<td>CSMR</td>
<td>1.49</td>
<td>2.06 ± 0.25</td>
<td>0.93 ± 0.10</td>
<td>0.91 ± 0.10</td>
</tr>
</tbody>
</table>

\(^1\)Finished water pH is 7.4.
the 27-week duration of the experiment, the samples obtained after each water change were tested for total metals content (lead, copper, and tin) using an atomic absorption graphite furnace (PerkinElmer Analyst 200), and an anion analysis was performed using ion chromatography to monitor chloride, sulfate, and phosphate levels. After week 17, samples were filtered through 0.45 µm pore size filters and analyzed for dissolved metals. The TOC, UV254, turbidity, pH, and alkalinity of each batch of treated water were monitored.

Measurements of chloride and pH were attempted at the lead and copper material surface using micro-probe technologies to track further mechanisms of corrosive attack. However, the measurements had a negative effect on the experimental results, and these effects are described in the results section.

RESULTS AND DISCUSSION

For all water conditions, the total lead entering the pipe set-ups was not detectable. Figures 7.3 and 7.5 present the total lead released from each of the pipe-set-ups throughout the 27 weeks of this study. Figures 7.4 and 7.6 present the dissolved lead released from each of the pipe-set-ups from weeks 17 to 27 of this study. The conditioning or acclimation period for both pipe-set-ups was between 5 and 6 weeks.

The total lead spikes observed throughout the first 6 weeks for the extracted lead pipes (Figure 7.3) can be attributed to lead particles sloughing off the extracted pipe during this initial acclimation phase and sitting at the bottom of the pipe set-up during stagnation and causing increased lead concentrations in the sampled water. Additionally, lead spikes were observed in both pipe-setups in Week 11 following micro-electrode measurements (Figure 7.3 and 7.5). In order to gain more insight into the localized effects at the solder surface and pipe interface, chloride and pH micro-electrodes were placed inside the test pipes before the water was changed at the end of Week 10, which disturbed the surfaces within the pipes and increased lead levels the following week. These lead spikes were caused by the electrodes scraping the lead pipe walls and disturbing the lead:tin solder. The increased lead release effects were significantly worse in the extracted lead pipe set-up, due to additional lead particles sloughing off the mature pipe scale inside of the pipe. Thus, no further microelectrode measurements were collected for the remainder of the study. Following this disturbance, the lead release data returned after one or two weeks to the apparent trends that was surfacing prior to the use of the microelectrodes.

Generally, lead leaching was very high in this study, which was expected since all of the CSMR values exceeded the threshold value of 0.5 for all water conditions tested (Edwards and Triantafyllidou 2007). Additionally, the geometry and physical experimental set-up were designed to maximize the worst-case conditions that contribute to lead corrosion (Nguyen et al. 2008). However, there was significantly more lead leached due to the presence of the combination of extracted lead and lead:tin solder, as opposed to the presence of lead:tin solder alone. Additionally, the polyphosphate inhibitor did not protect the lead bearing materials from corrosion.

It was expected that the ferric sulfate and alum water conditions would lead to similar levels of lead leaching, since their CSMR levels were approximately the same, and that the PACl treated water would correlate with a higher lead release, since the CSMR levels were more than double that of the other two water conditions. The trends reported from this study did not support this hypothesis. However, the results are consistent with other findings in the project in
that other factors are important when the CSMR is greater than 0.5. Unlike the other case studies in this Water Research Foundation project, the coagulation pH, TOC, and alkalinity were different among the water conditions. Therefore, TOC and alkalinity could affect the lead leaching to a greater extent than the CSMR.

**Pipe Set-up 1: Pb pipe – Pb/Sn solder – Cu pipe**

The ferric sulfate water was the most corrosive condition for the extracted lead pipe set-up, whereas, the alum and PACI treated waters behaved similarly despite the large CSMR differences between the two water conditions (Figures 7.3). For all conditions, the lead levels continued to decrease over time; however, more dramatic decreases were observed for the alum and PACI conditions, particularly in the first half of this study. The dissolved lead trends observed throughout the last 10 weeks of the study were significantly less than the total lead concentrations; however, similar trends were observed with respect to CSMR (Figure 7.4). This indicates that the majority of the lead released was in a particulate form. The high levels of particulate lead could be attributed to plumbing scales being broken down on the extracted lead pipe despite the corrosion inhibitor presence. For this reason, the dissolved lead trends were much less variable than total lead trends. The peak observed in weeks 24 through 25 for the alum water condition was likely a result of the lead solder being exposed to the atmosphere for maintenance of the simulate solder connection (Figure 7.3). A small portion of the solder was replaced with new material to repair the solder joint.

![Figure 7.3](image_url)  
**Figure 7.3** Total lead concentrations throughout the 27 weeks of the study for the Pb pipe – Pb/Sn solder – Cu pipe scenario. Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons in this figure.
Figure 7.4 Dissolved lead concentrations throughout Weeks 17 to 27 of the study for the Pb pipe – Pb/Sn solder – Cu pipe scenario. Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons in this figure.

Figure 7.5 Total lead concentrations throughout the 27 weeks of the study for the Cu pipe – Pb/Sn solder – Cu pipe scenario. Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons in this figure.
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Pipe Set-up 2: Cu pipe – Pb/Sn solder – Cu pipe

Over the duration of the study, the considerable variability in total lead release was such that no considerable difference could be seen among the water conditions for the pipe set-up containing lead:tin solder as the only lead bearing material (Figure 7.5). For all conditions, the lead levels continued to decrease over time. However, much more dramatic decreases were observed for the solder only pipe scenario in comparison to the extracted lead pipe condition. The dissolved lead concentrations observed throughout the last 10 weeks of the study were significantly less than the total lead concentrations, indicating that a majority of the lead being release was in a particulate form (Figure 7.6). However, the amount of particulate lead being released was much less than that released from the extracted lead pipe condition. As was true for the extracted lead condition, the dissolved lead trends were less variable than the total lead trends. Additionally, the total lead variability was less apparent in the solder only condition than the extracted lead pipe condition. Over a longer study duration (and perhaps if the pipes had not been disturbed in week 10), it is possible that all water conditions could have much lower total and dissolved lead levels for this pipe condition.

Direct comparisons of the average total lead release in both plumbing scenarios for Weeks 14 through 27 of this study are presented in Figure 7.7 and Table 7.2. For the extracted lead pipe scenario, the ferric sulfate condition released an average of approximately 1.5 to 2.5 times more lead than the PACl and alum conditions. The differences in average total lead concentrations for the alum and PACl conditions for the extracted lead pipe scenario was not considered significantly different, and the 90% confidence intervals of the water conditions overlapped.

Figure 7.6 Dissolved lead concentrations throughout Weeks 17 to 27 of the study for the Pb pipe – Pb/Sn solder – Cu pipe scenario. Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons in this figure.
Figure 7.7 Average lead release data for each water condition during Weeks 14 through 27 of the Utility D study. Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons. The error bars indicate the 90% confidence interval.

Table 7.2
Average lead release for each water condition during Weeks 14 through 27 of the Utility D study (±90% confidence interval). Data from the three samples per week and duplicate pipes were averaged to obtain the comparisons in this figure.

<table>
<thead>
<tr>
<th>Water Condition</th>
<th>Lead (µg/L)</th>
<th>Pb pipe</th>
<th>Pb/Sn Solder</th>
<th>Cu pipe</th>
<th>Pb/Sn Solder</th>
<th>Cu pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Sulfate</td>
<td>1080 ± 204</td>
<td>40 ± 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PACI</td>
<td>607 ± 114</td>
<td>40 ± 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alum</td>
<td>447 ± 84</td>
<td>68 ± 13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Despite the CSMR differences, there was no considerable difference in average lead concentrations between each water condition for the solder only pipe scenario; however, the lead released from the alum condition was slightly higher and significantly different at the 90% confidence interval. On average, the extracted lead pipe condition resulted in lead concentrations 6.5 times more than the lead/tin solder to copper condition for alum, 15 times more for PACl and 27 times for the ferric sulfate treated water. The lead release was expected to be higher in the extracted lead pipes because there were two sources of lead (lead pipe and solder) in the apparatus versus one source for the second pipe setup (solder).

CONCLUSIONS

- The extracted lead pipes connected to lead:tin solder and copper pipes maintained significantly higher lead concentrations for each water condition compared to when lead:tin solder was the only source of lead. This is consistent with expectations given that there were multiple lead materials in the lead pipe apparatus.
- Ferric sulfate released the most lead for the extracted lead pipe scenario, whereas the PACl and alum lead trends were not significantly different from each other.
- The lead release from the scenarios where solder was the only lead source was not significantly different for the three water conditions tested.
- All of the water conditions had CSMRs greater than the threshold of 0.5. Consistent with other findings when the CSMR of the raw water was high, no definitive trends were observed relating CSMR to lead leaching concentrations:
  - The highest CSMR condition (PACl with a CSMR of 2) did not yield the highest lead concentrations.
  - The replicate CSMR conditions (alum and ferric sulfate with CSMRs of 0.9) did not yield similar lead levels.
- CSMR was not the only factor contributing to lead release:
  - Alkalinity and TOC appear to be the other contributing factors (Table 7.1).
  - Lead release trends associated with alkalinity changes have been observed in data from other participating utilities.
  - There is evidence that NOM has adverse effects on lead release (Korshin et al. 2005).
CHAPTER 8: CASE STUDY OF UTILITY K, CA (DESALINATION)

Kendall Stone, Caroline Nguyen, and Marc Edwards

Keywords: desalination, nanofiltration

INTRODUCTION

Utility K plans to blend desalinated water with treated groundwater, which among other impacts will increase the chloride-to-sulfate mass ratio (CSMR) of the water. Prior research has indicated that this can cause serious lead leaching problems from lead solder:copper joints and brass under at least some circumstances. Virginia Tech examined the effects of a range of desalinated water and groundwater blends on the corrosion of lead-bearing plumbing materials including solder and brass. Six water conditions were evaluated through bench scale tests to determine the effects of blending desalinated water.

MATERIALS AND METHODS

Test Water

Utility K shipped samples of groundwater and nanofilter-treated water to Virginia Tech. The alkalinity of the nanofiltered water was adjusted to 40 mg/L as CaCO$_3$ by adding NaHCO$_3$ prior to blending with groundwater. Distribution water (groundwater) and nanofiltered water were blended at four different ratios (Table 8.1). The 100% distribution water represents the current water in the system.

In order to provide mechanistic insights to changes in corrosivity due to variable chloride and sulfate in the blends, two additional tests were conducted. For one sample of distributed water, chloride (30 mg/L Cl$^-$ from CaCl$_2$) was added to match the chloride level that was present in the 25% distributed and 75% nanofiltered (NF) blend. Likewise, for one sample of 25% distributed and 75% NF water, sulfate (50 mg/L SO$_4^{2-}$ from CaSO$_4$) was added to match the sulfate level present in the 100% distributed water. For all waters, the pH was adjusted with either 0.1 M NaOH or 0.1 M HNO$_3$ to a target value of pH 8.2 ± 0.1, and the target monochloramine concentration was 2.5 mg/L Cl$_2$ with a chlorine-to-nitrogen ratio of 5:1 by weight.

Protocol

Simulated lead-copper joints were prepared using a 1-inch in length copper coupling (½-inch diameter copper) with a 1-inch length of 50:50 Pb/Sn solder melted inside (Figure 8.1). Brass coupons (5% lead content) that were ½-inch in diameter were cut in 0.4-inch lengths and epoxied to glass containers (Figure 8.2). The solder-copper couplings were exposed to 100 mL of the six water conditions listed in Table 8.1, and the brass coupons were exposed to 50 mL of each condition. Three replicates were tested for each condition. The water was changed twice per week (Monday and Thursday), and composite weekly samples were collected for each water condition at the end of each week and analyzed for metals.
Table 8.1

<table>
<thead>
<tr>
<th>Water Blend</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Chloride (mg/L Cl)</th>
<th>Sulfate (mg/L SO₄)</th>
<th>CSMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Distribution</td>
<td>125</td>
<td>54</td>
<td>68</td>
<td>0.8</td>
</tr>
<tr>
<td>75% Distribution, 25% NF</td>
<td>100</td>
<td>64</td>
<td>52</td>
<td>1.2</td>
</tr>
<tr>
<td>50% Distribution, 50% NF</td>
<td>80</td>
<td>72</td>
<td>36</td>
<td>2.0</td>
</tr>
<tr>
<td>25% Distribution, 75% NF</td>
<td>65</td>
<td>81</td>
<td>21</td>
<td>3.9</td>
</tr>
<tr>
<td>100% Distribution + Cl</td>
<td>125</td>
<td>76</td>
<td>69</td>
<td>1.1</td>
</tr>
<tr>
<td>25% Distribution, 75% NF + SO₄</td>
<td>65</td>
<td>75</td>
<td>70</td>
<td>1.1</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Lead Release from Brass

Release of lead from the brass dropped somewhat over the six-week testing period in most waters (Figure 8.3) but not as rapidly as has been observed in other waters. Although there were no dramatic differences in trends for the lead levels in brass amongst the different waters, the amount of lead released from the small brass coupons were significant and above the EPA action level of 15 ppb (Figure 8.4). Given that the relatively small volume to surface area for the experimental apparatus versus that present in some faucets, the results are deemed significant relative to the lead and copper rule even considering the atypically long detention time of 3.5 days.
Figure 8.2 Brass coupon (5% lead content) in glass for Utility K.

Figure 8.3 Lead release from brass for Utility K water over six weeks.
Zinc Release from Brass

Zinc release from brass can be important in determining the longevity of brass products as well as lead leaching. In this case, zinc is also affected by chloride and sulfate since the 75% nanofiltered water had the highest zinc release and the 0% nanofiltered water had the lowest zinc release (Figures 8.5 and 8.6). By adding additional chloride to the distribution water, the zinc was increased approximately 50%, and the addition of sulfate to the nanofiltered water resulted in a 20% decrease in zinc (Figure 8.6). Thus, dezincification may be slightly impacted by the higher CSMR of the nanofiltered water. Definitive trends will be established in the next few weeks.

Lead Release from Solder

Blending desalinated water with the current distribution water clearly increased lead release from lead solder that is galvanically connected to copper (Figures 8.7 and 8.8). The current distribution water with no desalinated water generated the least amount of lead, while the 75% nanofiltered water sustained lead levels more than 40 times higher than the current distribution water. Even a blend with 25% nanofiltered water increased the amount of lead by 18 times (Figure 8.8).

The increased corrosivity of the nanofiltered water is consistent with expectations based on the high CSMR and the lower alkalinity of the water compared to the groundwater (Table 8.1). Clearly, chloride and sulfate are factors in lead corrosion for the lead solder galvanically coupled to the copper. For example, when the current distribution water was dosed with chloride to equal the chloride concentration in the 75% nanofiltered water, the lead concentration was increased 2.5 times. When the 75% nanofiltered water was dosed with sulfate to match the current distribution water, the lead released was decreased 2.6 times (Figure 8.9). It is also
Figure 8.5 The release of zinc from brass over five weeks for Utility K water.

Figure 8.6 The release of zinc from brass during the fifth week of the Utility K study.
Figure 8.7 Lead release from 50:50 Pb/Sn solder galvanically connected to copper over six weeks when exposed to Utility K water.

Figure 8.8 Lead release from 50:50 Pb/Sn solder during the sixth week of the Utility K study.
possible that the higher alkalinity in the distribution water buffers pH between the lead solder anode and copper cathode, further contributing to the dramatic difference between the blend and the current water.

**CONCLUSIONS**

- Blending the desalinated water with the current distributed groundwater dramatically increased the lead levels in Utility K water when exposed to lead solder.

- Lead leaching from brass coupons was not as significantly impacted.

- Amongst the factors that might be tested to mitigate lead solder corrosion in the blends, dosing of orthophosphate, zinc orthophosphate, higher alkalinity, and higher pH are all viable possibilities. It is recommended that additional work be conducted to identify mitigation strategies.
CHAPTER 9: CASE STUDY OF UTILITY F, ME (ARSENIC TREATMENT)

Caroline Nguyen, Kendall Stone, and Marc Edwards

Keywords: anion exchange, arsenic treatment, pH

INTRODUCTION

Extremely high levels of lead were measured at the tap in a community in Maine following installation of anion exchange to remove arsenic from the water. In arsenic treatment via anion exchange, sulfate is removed and replaced with chloride by the resin. As a result, the chloride-to-sulfate mass ratio (CSMR) increases, which is sometimes implicated to higher lead leaching from copper:lead solder galvanic couples (Edwards and Triantafyllidou 2007). One case of lead poisoning was reported in this community after implementing arsenic treatment, and lead levels were documented in the thousands of ppb.

Complicating the interpretation of the data, the anion exchange treatment also reduced the pH of the distributed water to about pH 5.5 for several months due to very frequent regeneration of the exchange resin. The pH was stabilized later at pH 7.8 by stripping CO₂ from the water. In practice, the lead problems were triggered by a number of factors including very low alkalinity, low pH, and higher CSMR.

The objectives of this bench scale study were to (1) evaluate the effect of sulfate removal and chloride addition in arsenic treatment on lead leaching from solder, (2) determine the impact of low pH on lead release from simulated solder-copper pipes, and (3) simulate the period when CO₂ stripping was implemented to increase the pH. Based on conventional wisdom and as occurred in practice, lead leaching was expected to decrease as the pH was increased. By simulating the pH increase at bench scale, the time required before achieving the benefits of higher pH could be approximated. This was not tracked in practice for the case study but could provide valuable information to consumers about the lead reduction time that could be expected. To achieve these objectives, the drinking water was treated with anion exchange to simulate arsenic (and sulfate) removal that triggered the real-world lead problem, and the water was exposed to copper:lead solder couples in bench tests.

MATERIALS AND METHODS

Test Water

Fifteen gallons of water were collected at a point prior to treatment in the community in Maine. Five gallons of this water were subjected to no anion exchange treatment or other further treatment, other than adjusting the pH to 7.0. The remaining ten gallons of water were treated by anion exchange and then adjusted to pH of 7.0 or 5.5 using 0.1 M NaOH for base addition or CO₂ for acid addition. After pH adjustment the water was not treated further, similar to what had occurred in practice. Thus, three water conditions were tested in this study (Table 9.1):

1) control with no arsenic treatment and pH 7.0,
2) water treated with anion exchange, and pH adjusted to 7.0, and
3) water treated with anion exchange, and pH adjusted to 5.5.
Simulated Arsenic Treatment

To simulate arsenic treatment without a column, a chloride-based anion exchange resin was mixed with the water from Utility F, ME (at a ratio of 1.7 mL resin per 1 L of treated water) at 100 rpm for 30 minutes. After settling for 30 minutes, the treated supernatant was used to prepare the two anion exchange water conditions in Table 9.1.

Bio-Rad AG 1-X8 resin (50-100 mesh size) in the chloride form was used for this study. Prior to use, the resin was rinsed thoroughly with deionized water several times to remove excess chloride.

Using this simple anion exchange method, less arsenic and sulfate were removed from the water when compared with anion exchange via a column in practice. As a result, the CSMR after treatment would not be as high as it may be in practice. Thus, any changes observed in this experiment due to the higher CSMR, would likely underestimate the actual impacts if the water had been treated using a column.

Protocol

Copper couplings 1-inch in length and ½-inch in diameter were soldered with 1-inch lengths of 50:50 Pb/Sn solder (Figure 9.1). The coupons were exposed to 100 mL of each of the water conditions listed in Table 9.1. Three replicates were tested for each condition. The water was changed twice per week (Monday and Thursday), and composite weekly samples were collected for each water condition at the end of each week and analyzed for metals. The study was conducted over a 6-week period.

After the initial 6-week study, the pH was increased from pH 5.5 to 7.0 for the arsenic removal condition at low pH to simulate what occurred in practice after the installation an air stripper to increase the pH. The purpose of simulating this at the bench scale was to determine the length of time before the lead release decreased significantly. It was expected that it could be several days or even a couple of weeks after the pH change for lower lead levels to be reached.

Table 9.1
Water quality after indicated water treatment for Utility F

<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>[As] (µg/L As)</th>
<th>[Cl(^-)] (mg/L Cl(^-))</th>
<th>[SO_4^{2-}] (mg/L SO_4^{2-})</th>
<th>CSMR</th>
<th>Alkalinity (mg/L as CaCO_3)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distribution water</td>
<td>4.5</td>
<td>4.4</td>
<td>4.1</td>
<td>1.1</td>
<td>22</td>
<td>7.0</td>
</tr>
<tr>
<td>Distribution water treated with anion exchange</td>
<td>1.8</td>
<td>13.2</td>
<td>1.7</td>
<td>7.8</td>
<td>12</td>
<td>7.0</td>
</tr>
<tr>
<td>Distribution water treated with anion exchange and pH reduced</td>
<td>1.8</td>
<td>13.2</td>
<td>1.7</td>
<td>7.8</td>
<td>12</td>
<td>5.5</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Effect of Anion Exchange

The most dramatic increase in lead release was observed in water subjected to anion exchange treatment, which had a CSMR of 7.8 at pH 7.0. Treating the water with anion exchange increased lead release an average of 47 times over the 6-week study period from 40 ppb to 1,830 ppb (Figure 9.2). The very high corrosivity of the anion exchange-treated water is attributed to the increase in CSMR, as well as the decrease in alkalinity from 22 mg/L to 12 mg/L as CaCO$_3$, and the results are therefore consistent with practical observations at this site. That is, installation of the arsenic treatment triggered a massive lead contamination event due to lead solder. The marked difference between the anion exchange treatment and no treatment was obvious throughout the study (Figure 9.3).

Effect of Low pH

A smaller but still significant increase in lead release was observed for the anion exchange-treated water at pH 5.5 versus the treated water at pH 7.0. The pH difference of 1.5 units resulted in 2.6 times higher lead leaching at the lower pH condition versus the condition with the same CSMR but pH 7.0 (Figure 9.2). At pH 7, the lead release was 1,800 ppb, while the lead in water was 4,800 for pH 5.5. The results are consistent with theory because lead is more soluble at lower pH.

Recovery Time after Increasing pH from 5.5 to 7

An attempt was made after the first six weeks of the study to determine how quickly the lead leaching would reach a steady state if the pH was increased to 7.0. The lead release decreased dramatically when the pH was increased from pH 5.5 to pH 7. Three weeks after the pH increase, the lead release from the coupons that were changed from pH 5.5 to pH 7 was not significantly different from the amount of lead released from the coupons that were exposed to pH 7 for the entire duration of the study (Figure 9.4).
Figure 9.2 Average lead release for each of the three water treatments of Utility F water during the first six weeks of the study. Error bars represent 95% confidence intervals.

Figure 9.3 Lead release in ppb over the first 6 weeks of the study for Utility F.
CONCLUSIONS

- Anion exchange treatment and resulting higher CSMR caused a dramatic increase in lead release in this water.
- Anion exchange treated water at pH 5.5 had higher lead release compared to water at pH 7.0, but the pH had a lesser effect on lead leaching compared to anion exchange treatment in the bench scale tests.
- After about 3 weeks, increasing the pH from 5.5 to 7 returned the lead levels to that observed for the water continuously held at pH 7.0
CHAPTER 10: CASE STUDY OF UTILITY J, TN (REMEDIAL STRATEGIES)

Caroline Nguyen, Kendall Stone, and Marc Edwards

Keywords: alkalinity, orthophosphate, polyphosphate, zinc phosphate

INTRODUCTION

Since 2006, Utility J in Tennessee has exceeded the Lead and Copper Rule (LCR) with 90th percentile lead as high as 110 ppb Pb in 2006. Before 2006, utility distributed water at pH 8.7 and had no reported problems with lead. Beginning in 2006, the utility distributed water at pH 7.3 and adding a polyphosphate/orthophosphate blend for corrosion control. Shortly after this change, Utility J began to exceed the LCR (Figure 10.1). Virginia Tech was asked to investigate methods to mitigate the lead problem at Utility J. Virginia Tech was also asked to explore the hypothesis that the lower distribution pH may be contributing to higher lead levels. Nine water conditions were evaluated to determine the effects of various corrosion inhibitors, pH, chloride, sulfate, and alkalinity on the resulting lead released from lead solder galvanically connected to copper pipes. Lead solder is a common culprit of lead in drinking water and is believed to be a dominant source in Utility J.

On the basis of previous studies that pointed to the role of high chloride as a possible contributor to lead in water (Edwards and Triantafyllidou 2007), Utility J determined that chloride levels in their finished water (about 10 ppm and as high as 15 ppm) were much higher than in their raw water (about 2 ppm). This sample result was surprising given that the utility does not use any coagulant such as ferric chloride. Utility personnel traced the higher chloride to a leaky valve in their brine solution that is used to produce free chlorine disinfectant. This leaking valve was fixed as of 2/15/2008, after which time chloride levels in the finished water returned to very low levels.

This utility is not alone, as many utilities across the United States that use on-site hypochlorite generators have measured higher levels of chloride in their waters compared to the use of other chlorine sources, but not necessarily because of brine leaks. In the chlorine generation process, more chloride is produced per unit of free chlorine for on-site hypochlorite generators compared to chlorine gas, and more utilities are switching from chlorine gas to hypochlorite generators because of homeland security concerns. The amount of chloride produced per unit of chlorine disinfectant can be calculated for each chlorine source using the chemical reactions that occur while generating chlorine (Table 10.1). For example, one mole of chlorine gas dissolved in water forms 1 mole of free chlorine (HOCl) and 1 mole of HCl, which dissociates into H+ and Cl- in water.

Chlorine gas has the lowest Cl- to Cl2 ratio compared to other chlorine sources because every 1 mg/L Cl2 of dosed from chlorine gas would have approximately 0.5 mg/L Cl- in the treated water (Table 10.1). In comparison, manufactured hypochlorite solution could have between 0.5 and 0.7 mg/L Cl- per mg/L Cl2, where fresh solution ideally contains 0.5 mg/L Cl- per mg/L Cl2. In practice, on-site hypochlorite generators produce even more Cl- per Cl2, ranging from 0.75 to 2. When monochloramine is used as the disinfectant, the total chlorine residual can be as much as 10 times more than when free chlorine is used. Therefore, the
The magnitude of chloride in the water is higher with chloramines, even though the ratio of Cl\textsuperscript{−} to Cl\textsubscript{2} remains the same. Furthermore, as the chlorine/chloramine disinfectant from any source inherently decays to Cl\textsuperscript{−} via autodecomposition reactions (Table 10.1), the amount of Cl\textsuperscript{−} per unit Cl\textsubscript{2} residual eventually rises to infinity.

The objective of the case study for Utility J was to evaluate corrosion remedial strategies, with slightly elevated chloride in their water due to on-site hypochlorite generation.

### Table 10.1
**Chloride from Disinfection**

<table>
<thead>
<tr>
<th>Method of Chlorination</th>
<th>Sources of Cl\textsuperscript{−} or Cl\textsubscript{2} Reactions *</th>
<th>Typical mg Cl\textsuperscript{−} Produced per mg Cl\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>( \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} ) ( \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{Cl}^- )</td>
<td>0.5</td>
</tr>
<tr>
<td>Hypochlorite Solution</td>
<td>( \text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} ) (generation) ( \text{3 OCl}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- ) (auto-decomposition) ( \text{2 OCl}^- \rightarrow \text{O}_2 + 2\text{Cl}^- ) (decomposition, catalyzed by metals)</td>
<td>0.5-0.7</td>
</tr>
<tr>
<td>Hypochlorite Generator (On-site)</td>
<td>( 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{NaOH} ) ( \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} )</td>
<td>0.75-2 **</td>
</tr>
<tr>
<td>Chloramine</td>
<td>Same reactions as above, depending on chlorine source; however, more Cl\textsubscript{2} is typically added (10X more than free chlorine)</td>
<td>0.5-2, depending on chlorine source</td>
</tr>
</tbody>
</table>

* AWWA 2006 ** MIOX

---

**Figure 10.1** Historical 90\textsuperscript{th} percentile lead release data for Utility J. Dotted line indicates the lead action level of 15 ppb.
MATERIALS AND METHODS

Test Water

Test water was obtained at Virginia Tech by shipments of Utility J treated water from the UV channel of the treatment plant. Collected water was separated into aliquots and subjected to various treatments (Table 10.2). Chemicals added to the water included orthophosphate corrosion inhibitor with or without zinc, polyphosphate/orthophosphate blend, bicarbonate, sulfate, disinfection with free chlorine, and acid or base for final pH adjustment. All waters (unless specified) were dosed with 3 mg/L Cl to simulate a portion of the chloride that entered the water due to the hypochlorite generator.

The pH was adjusted with either 0.1 M NaOH or 0.1 M HNO₃ to the target value of pH 7.3 or 8.7. All water was also dosed with free chlorine at a concentration of 2 mg/L Cl₂. Utility J provided the poly-orthophosphate blend corrosion inhibitor, which is currently used by the utility. Orthophosphate was dosed from sodium phosphate (Na₂HPO₄), and zinc was added as zinc sulfate (ZnSO₄). Alkalinity was adjusted with sodium bicarbonate (NaHCO₃). Chloride and sulfate were added from sodium chloride (NaCl) and sodium sulfate (Na₂SO₄).

Table 10.2

<table>
<thead>
<tr>
<th>Water Type</th>
<th>pH</th>
<th>Conductivity (μS)</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Chloride (mg/L Cl)</th>
<th>Sulfate (mg/L SO₄)</th>
<th>Silica (mg/L Si)</th>
<th>Phosphate (mg/L P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 8.7</td>
<td>8.7</td>
<td>48</td>
<td>8</td>
<td>10.0</td>
<td>2.4</td>
<td>2.1</td>
<td>0.0</td>
</tr>
<tr>
<td>pH 7.3</td>
<td>7.3</td>
<td>190</td>
<td>8</td>
<td>10.0</td>
<td>1.7</td>
<td>2.3</td>
<td>0.0</td>
</tr>
<tr>
<td>pH 7.3, 20 mg/L as CaCO₃</td>
<td>7.3</td>
<td>49</td>
<td>20</td>
<td>7.5</td>
<td>2.6</td>
<td>2.3</td>
<td>0.0</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L PO₄ as P, 20 mg/L as CaCO₃</td>
<td>7.3</td>
<td>55</td>
<td>20</td>
<td>7.5</td>
<td>2.4</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L PO₄ as P</td>
<td>7.3</td>
<td>55</td>
<td>8</td>
<td>8.0</td>
<td>2.4</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L PO₄ as P, 100 μg/L Zn</td>
<td>7.3</td>
<td>70</td>
<td>8</td>
<td>7.6</td>
<td>2.7</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L PO₄ as P, 300 μg/L Zn</td>
<td>7.3</td>
<td>76</td>
<td>8</td>
<td>7.5</td>
<td>3.1</td>
<td>2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>pH 7.3, poly-orthophosphate inhibitor</td>
<td>7.3</td>
<td>54</td>
<td>8</td>
<td>7.5</td>
<td>2.0</td>
<td>2.3</td>
<td>0.2</td>
</tr>
<tr>
<td>pH 7.3, 15 mg/L Cl, 45 mg/L SO₄</td>
<td>7.3</td>
<td>53</td>
<td>8</td>
<td>19.2</td>
<td>55.1</td>
<td>2.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Protocol

A 1” length of 50:50 Pb/Sn solder was melted within a 1” length of ½” diameter copper couplings (Figure 10.2). The solder-copper couplings were exposed to 100 mL of the nine water conditions listed in Table 10.2. Three replicates were performed for each water condition. The water was changed twice per week (Tuesday and Friday), and composite weekly samples were collected for each water condition at the end of each week and analyzed for lead. Therefore, the lead values were a composite average of a 3.5-day (Tuesday through Friday) and 4-day (Friday through Tuesday) stagnation.

RESULTS AND DISCUSSION

Effect of Phosphate Inhibitors

The addition of 1 mg/L orthophosphate as P to the Utility J water produced water with the lowest lead levels compared to other treatments evaluated in this study (Figure 10.3 and Table 10.3). By switching from the current corrosion inhibitor, which is a poly-orthophosphate blend, to orthophosphate the lead concentration could be reduced by about 75%. Waters with orthophosphate consistently had lower lead levels than the other conditions after the third week of the study (Figure 10.4). The addition of zinc as a corrosion inhibitor did not provide a greater benefit than when orthophosphate alone was added after the first few weeks, although the zinc seemed to have a short-term benefit during the first month of the study (Figure 10.4).
**Figure 10.3** Average lead released for each water condition during the eighth week of the Utility J study. The error bars represent 90% confidence intervals based on data from the replicates.

**Effect of pH**

Contrary to the initial hypothesis, which was that the high lead may have been triggered by changing the corrosion control strategy from a pH of 8.7 without inhibitor to pH 7.3 with phosphate inhibitor, lead leaching at pH 8.7 was not lower than at pH 7.3 with inhibitor. It is therefore considered likely that the high lead was triggered by a leak of chloride from the valve starting sometime before July 2006.

**Table 10.3**

Average lead values for the eighth week of the Utility J study (±95% confidence interval).

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Average Lead (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 8.7</td>
<td>287 ±120</td>
</tr>
<tr>
<td>pH 7.3</td>
<td>134 ±50</td>
</tr>
<tr>
<td>pH 7.3, 20 mg/L as CaCO₃</td>
<td>609 ±210</td>
</tr>
<tr>
<td>pH 7.3, 20 mg/L as CaCO₃, 1 mg/L P</td>
<td>2,657 ±720</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L P</td>
<td>57 ±10</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L P, 100 μg/L Zn (or 0.1 Zn:P)</td>
<td>81 ±20</td>
</tr>
<tr>
<td>pH 7.3, 1 mg/L P, 300 μg/L Zn (or 0.3 Zn:P)</td>
<td>85 ±60</td>
</tr>
<tr>
<td>pH 7.3, 2 mg/L poly-orthophosphate</td>
<td>261 ±130</td>
</tr>
<tr>
<td>pH 7.3, 15 mg/L Cl, 45 mg/L SO₄</td>
<td>499 ±60</td>
</tr>
</tbody>
</table>
Effect of Alkalinity

It was also surprising that contrary to current expectations, increasing the alkalinity slightly from around 10 mg/L as CaCO$_3$ to 20 mg/L as CaCO$_3$ appeared to dramatically worsen the lead released from the solder-copper couplings. Clearly, addition of alkalinity will not solve lead problems at Utility J and would actually make the situation worse. These results are very interesting, and future intensive additional experiments will be conducted to gain mechanistic insights. It is possible that higher alkalinity does not always reduce the magnitude of this problem.

pH Microelectrode Measurements

The galvanic interaction between the copper-solder couplings causes a dramatic local drop in pH of water next to the solder surface (Figure 10.5), as measured with a microelectrode. This drop is caused by the galvanic current between lead and the copper, and is a large contributor to the high levels of lead in this system. However, unlike prior results, there is no correlation between the pH measured at the lead surface and the amount of lead leached to the water (Figure 10.6). In this particular water, which has extremely low conductivity (Table 10.2), it is believed that the total amount of salt in the water may play a decisive role in controlling lead release.
Figure 10.5 Local pH measurements taken during the 14th week of the study for Utility J. The blue bars represent the pH in the water above the copper-solder coupling. The yellow bars represent the pH at the copper surface inside the coupling. The red bars represent the pH at the solder surface inside the coupling. The error bars represent the 90% confidence interval based on data collected from the triplicates.

Figure 10.6 Lead release plotted against pH at the solder surface for Utility J water.
CONCLUSIONS

- Changing the pH from 8.7 to 7.3 did not have an effect on lead release.

- Galvanic interactions between copper and solder, indicated by a local pH drop at the solder surface, caused a leaching of lead into the water.

- The lead release was lessened by the addition of orthophosphate corrosion inhibitor.

- Addition of alkalinity had no positive effect on lead release. Addition of zinc had no additional benefit.

- There was no correlation between pH at the solder surface and lead release.

The recommendation is that Utility J immediately should begin dosing orthophosphate at a dose of 1 mg/L P (3 mg/L PO₄). After a few months dosing this would likely bring the utility into compliance with the LCR (now that higher Cl⁻ in the water is no longer a problem), and the utility could then consider decreasing the orthophosphate dose to the more typical level of 0.33 mg/L P (1 mg/L PO₄) to reduce costs.
INTRODUCTION

The objective of this part of the research was to evaluate the effects of high and low chloride-to-sulfate mass ratio (CSMR) on release of lead from a variety of lead plumbing materials found in distribution and premise piping (i.e., lead pipe, brass pipe, lead solder joints) utilizing a recirculating pipe loop apparatus. The water used for these experiments contained phosphate at approximately 1 mg/L and the pH was adjusted to 7.0-7.5. These conditions were selected to simulate optimal corrosion control treatment using phosphates, to evaluate the impact of changes in CSMR on lead release under these conditions. Both single metal and dual metal pipe loops containing leaded materials were evaluated. During the testing the occurrence of particulate lead in the reservoirs and the potential for sorption of lead onto the reservoirs used in the testing apparatus were evaluated.

MATERIALS AND METHODS

Pipe Loop Setup and Materials

Pipe loop testing was conducted at the HDR Applied Research and Technology Center (ARTC) facility in Redmond, WA. The testing involved the use of lead pipe segments recovered from a local service area in Washington, simulated lead solder joints (fabricated at Virginia Tech), bronze piping (containing 7% lead by weight), and new copper tubing. Pipe loops were constructed using these plumbing materials to study the effects of changes in the CSMR of the influent water on lead release from the metal pipe loop sections. The pipe loop set-up consisted of both single and dual-metal pipe loop sections. Each loop was designed to recirculate target water quality conditions, and a timer was installed on each loop to control on/off cycling of the water flow.

The pipe loops were assembled in March 2008, and testing was conducted from April 21, 2008 through September 4, 2008. A schematic of the recirculating pipe loop setup at the ARTC facility is shown in Figure 11.1, with photographs of the individual pipe loop sections shown in Figures 11.2 through 11.8. As shown in Figure 11.1, the pipe loops were categorized as:

- Series (setup) A – single metal series
- Series (setup) B – galvanic series (dual metals)

The lead materials tested in the pipe loops included lead pipe, bronze pipe, and simulated lead solder joints. Lead and bronze pipe sections used in these pipe loops were previously used in a separate Water Research Foundation study, Project 3107 (Boyd et al. 2010), and modified for this study, Project 4088.
Pipe Materials

**Lead Pipe.** Lead pipe sections consisted of lead goosenecks recovered from the existing distribution system of Utility H, WA and were $\frac{3}{4}$" in diameter. The inside surfaces of some of these lead pipe segments had been reamed prior to use in the previous Foundation project (newer passivated lead pipe), while others had not (older passivated lead pipe). Therefore, the older passivated pipes had variable histories of scale exposure to differing water qualities over time in the distribution system as well as the varying water quality conditions of exposure under the previous Foundation project testing conditions (changes in chlorine, chloramines, pH, alkalinity, PO$_4$ concentration). The newer passivated pipes had been reamed prior to use in the WaterRF Project 3107, and therefore the internal surface of the pipes had been exposed to the varying water quality testing conditions for the previous study.

**Bronze Pipe.** Bronze pipe (containing 7% lead) (passivated bronze) was originally purchased from Spectrum Machine, Inc., Streetsboro, Ohio. They were used as part of a previous Foundation study (Boyd et al. 2010) and then retrofitted into the pipe loop design for this study. The bronze pipe contained 7% Pb (C93200 tube, $\frac{3}{4}$” ID), which was used as a surrogate for standard brass typically used in distribution and premise piping containing up to 8% Pb, as brass pipe containing 8% Pb was not commercially available.

**Copper Pipe.** New, $\frac{3}{4}$” diameter type M copper pipe was purchased from a local supplier. The copper pipes were used in the dual metal loops and connected to the lead-bearing pipes.

**Simulated Lead Solder Joints.** Virginia Tech provided simulated lead soldered joints. Two sampling ports $\frac{1}{2}$” in diameter were drilled in 3” long new copper pipe sections. The copper pipe sections were then dipped into liquid non-corrosive flux and into molten 50:50 lead:tin solder. The solder formed a continuous coating in the inner and outer surfaces of each copper section so that no copper was showing.

Description of Loops

The Series A single-metal pipe loops were labeled Loops 1 and 2 (Figures 11.2 and 11.3). Each of these loops consisted of one 12” length of a specific lead bearing pipe material, either newer passivated lead (Loop 1) or passivated bronze (Loop 2) which served as the source of lead release. For the Series B, dual-metal pipe loops, Loops 3 through 5 consisted of one 12” length of lead bearing material (older passivated lead pipe, newer passivated lead pipe, passivated bronze pipe) and 36” of new copper pipe (Figures 11.4, 11.5, and 11.6). This configuration provided approximately three times the surface area of copper to lead bearing material.

Loop 6 contained two 3” long simulated lead solder joints and 12” sections of copper pipe between each simulated joint, or a total of 36” of copper pipe (Figure 11.7). Loop 7 (Figures 11.1 and 11.8) contained only simulated lead solder joints. The plumbing materials used for each of the loops are summarized in Table 11.1. Thin, non-metallic spacers were placed between each of the pipe-to-pipe connections in the Series B, dual-metal pipe loops. For Loops 3, 4 and 5 a PVC spacer was used, and for Loops 6 and 7, fiber spacers were used. The spacers allow the galvanic current (that normally flows from one pipe section to another) to be quantified with an ammeter.
Set-up A – single metal series

Loop 1
Newer passivated lead

Loop 2
Passivated bronze

Set-up B – galvanic series

Loop 3
New copper/older passivated lead

Loop 4
New copper/Newer passivated lead

Loop 5
New copper/Passivated bronze

Loop 6
New copper/Simulated lead soldered joints

Loop 7
Simulated lead soldered joints (no copper)

---

LEGEND

- Reservoir
- Peristaltic Pump
- Flow Meter

Pipe Materials
- Newer passivated lead pipe
- New copper pipe
- Passivated bronze pipe
- Older passivated lead pipe

Figure 11.1 Pipe Loop Setup
Each pipe loop was equipped with a dedicated March magnetic impeller drive recirculating pump, PVC flow-control valve, King acrylic body (stainless steel flow indicator) flow meter, and a 20-L fluorinated polyethylene lined Nalgene water reservoir. Separate components (metal and non-metal) in the pipe loop setups were all connected using flexible tubing (Tygon SE200 for reservoir to pump, Tygon 2075 for all other connections). Flexible tubing was compressed around the exterior of the joints using stainless steel pipe clamps. A constant volumetric flow rate of 0.5 gpm was maintained throughout the course of the investigation, except during stagnation events as discussed in later text.

Prior to the start of the study, the reservoirs and tubing were cleaned (without metal sections attached) by adding nitric acid (Integra Scientific N767.10.40P (68-70%)) to each reservoir to create a 2% solution based on existing volume of water already in each reservoir (no additional water was added). This 2% nitric acid solution was recirculated through each loop including the reservoir and tubing for 2 days. After cleaning, the apparatus was neutralized by recirculating 10 mM sodium bicarbonate solution through the reservoir and tubing for 3 hours. After careful rinsing the metal sections were then incorporated into each loop.

Small ports were made by drilling 9/16” holes (1/2” holes for simulated lead solder sections) at intervals along the length of the metal pipe sections and simulated lead soldered joints for Loops 4 through 7 to allow for measurements inside the metal pipe sections (ex., pH). For Loops 4 and 5, these ports were centered at 1”, 2”, and 4” from the connection point between the two dissimilar metals. For Loops 6 and 7, the ports were drilled into the simulated lead soldered joints at locations ¾” from each end. Loop 6 also had 9/16” holes drilled, which were centered at 1” from each end of the copper pipe located on the inflow side. When not in use, ports were sealed (plugged) with FDA approved high purity silicone stoppers (Cole Parmer #R62994). Figure 11.1 displays the approximate locations of these ports.

Test Water

Local tap water was supplied by Utility H for all testing (Table 11.2), and the water was flushed for 3-5 minutes prior to filling the 200 L reservoir that was used to store water for the testing. The water chemistry in the 200-L reservoir was adjusted to provide the target chloride/

<table>
<thead>
<tr>
<th>Pipe Loop Designation</th>
<th>Pipe Material</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Newer passivated lead pipe</td>
<td>12”</td>
</tr>
<tr>
<td>2</td>
<td>Passivated bronze pipe</td>
<td>12”</td>
</tr>
<tr>
<td>3</td>
<td>Older passivated lead pipe</td>
<td>12”</td>
</tr>
<tr>
<td></td>
<td>Copper pipe</td>
<td>36”</td>
</tr>
<tr>
<td>4</td>
<td>Newer passivated lead pipe</td>
<td>12”</td>
</tr>
<tr>
<td></td>
<td>Copper pipe</td>
<td>36”</td>
</tr>
<tr>
<td>5</td>
<td>Passivated bronze pipe</td>
<td>12”</td>
</tr>
<tr>
<td></td>
<td>Copper pipe</td>
<td>36”</td>
</tr>
<tr>
<td>6</td>
<td>Simulated lead solder joints</td>
<td>3” (2 joints total)</td>
</tr>
<tr>
<td></td>
<td>Copper pipe</td>
<td>3 – 12” lengths (36” total)</td>
</tr>
<tr>
<td>7</td>
<td>Simulated lead solder joints</td>
<td>3” (2 joints total)</td>
</tr>
</tbody>
</table>
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Figure 11.2 Loop 1 – Newer Passivated Lead Pipe

Figure 11.3 Loop 2 - Passivated Bronze Pipe

Figure 11.4 Loop 3 - New Copper Pipe Connected to Older Passivated Lead Pipe

Figure 11.5 Loop 4 - New Copper Pipe Connected to Newer Passivated Lead Pipe

Figure 11.6 Loop 5 - New Copper Pipe and Passivated Bronze Pipe

Figure 11.7 Loop 6 - New Copper Pipe and Simulated Lead Solder Joint

Figure 11.8 Loop 7 - Simulated Lead Solder Joint Without Connection to Copper Pipe
Table 11.2
Background Water Quality for Utility H

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH range</td>
<td>8.27 – 8.72</td>
</tr>
<tr>
<td>Alkalinity, total (mg/L as CaCO₃)</td>
<td>19</td>
</tr>
<tr>
<td>Hardness (mg/L as CaCO₃)</td>
<td>28</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>0.9</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>41</td>
</tr>
<tr>
<td>Specific conductance (μmhos/cm)</td>
<td>64.4</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>3</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorine residual (mg/L as Cl₂)</td>
<td>0.86</td>
</tr>
<tr>
<td>Phosphate, soluble reactive (μg/L)</td>
<td>3</td>
</tr>
</tbody>
</table>

Sulfate ratio, disinfectant residual, pH, phosphate, and alkalinity levels required for each test condition. The adjusted test water was prepared once per week and then transferred into a separate recirculating test water reservoir for each loop.

Water quality parameters (pH, temperature, total chlorine) were measured approximately 5-7 times per week and adjusted further in each of the recirculating pipe loops as needed to maintain the targeted water quality conditions. The chloride-to-sulfate ratio of the water was adjusted by addition of NaCl at the beginning of the week. Chloride and sulfate were also monitored and NaCl was added in an effort to maintain the target chloride-to-sulfate ratio for each batch of water. Phosphate levels were adjusted to approximately 1.0 mg/L PO₄ and were not adjusted for each batch of water. Resultant phosphate levels were measured at the end of each test period prior to the water change. Detailed measurements of pH, alkalinity, chlorine, and chloride-to-sulfate mass ratio are included in Appendix B (Figures B.1 through B.4).

Table 11.3 lists the operational water quality parameters that were monitored during the course of the study. Typically, pH trended higher in each loop over time, and was adjusted to a pH between 7.0 and 7.5 with the addition of 1.0 N HCl.

Table 11.3
Operational Water Quality Parameter Measurements

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>Frequency Measured</th>
<th>Method Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH and Temperature</td>
<td>5-7 times per week</td>
<td>pH sensor electrode in conjunction with an electronic IQ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Scientific IQ150 pH/mV/temperature meter</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>5-7 times per week</td>
<td>Hach DR/4000 spectrophotometer Hach Method 8167 for total-chlorine, utilizing DPD.</td>
</tr>
<tr>
<td>Total Alkalinity</td>
<td>Weekly</td>
<td>Hach Method: Digital titration of H₂SO₄ to a pH end point of 4.9</td>
</tr>
<tr>
<td>Chloride</td>
<td>Weekly*</td>
<td>Hach Method 8206: Mercuric Thiocyanate Method 8113. using Hach DR 2800</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Weekly*</td>
<td>Hach Method 8051: Spectrophotometry at 450nm with SulfāVer Powder Pillows</td>
</tr>
<tr>
<td>Phosphate</td>
<td>Weekly</td>
<td>Hach DR/4000 spectrophotometer Hach Method 8048</td>
</tr>
</tbody>
</table>

*at a minimum
Testing began in the HDR ARTC facility on April 21, 2008. Six test sequences were conducted (Table 11.4). All seven pipe loops were operated simultaneously during each of the six test sequences. For each test sequence, pH, alkalinity, phosphate, and total chlorine levels were maintained as displayed in Table 11.5. The only water quality parameters that were altered for the various test sequences were chloride and sulfate levels to achieve either a high (~8-12) or low (~1-2) CSMR. Water was adjusted in the 200-L tank and then transferred to the 20-L reservoirs for each loop. The CSMR was adjusted to the specific target conditions for each test, and different flow regimes were established (continuous flow versus different stagnation periods). The contents of the 20-L recirculating pipe-loop reservoir were replenished with freshly prepared treated water on a weekly basis.

Test 1 characterized metals release for the pipe materials under a CSMR of approximately 1 - 2 (low CSMR) under continuous flow conditions. For Test 2, the CSMR was maintained at this low chloride/sulfate ratio and flow was adjusted so that water was stagnant with the exception of a 5-minute flow period every 8 hours (long stagnation period). For Test 3, the CSMR was adjusted to approximately 8-10 (high CSMR), and the flow was adjusted so that water was flowing with the exception of a 5-minute stagnation period every 8 hours (short

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Chloride/Sulfate Ratio</th>
<th>Flow/Stagnation Conditions</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low chloride/sulfate</td>
<td>Continuous Flow</td>
<td>April 30, 2008</td>
<td>May 14, 2008</td>
</tr>
<tr>
<td></td>
<td>ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Low chloride/sulfate</td>
<td>Long Stagnation</td>
<td>May 14, 2008</td>
<td>May 28, 2008</td>
</tr>
<tr>
<td></td>
<td>ratio</td>
<td>(5 minute flow every 8 hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>High chloride/sulfate</td>
<td>Short Stagnation</td>
<td>May 28, 2008</td>
<td>July 23, 2008</td>
</tr>
<tr>
<td></td>
<td>ratio</td>
<td>(5 minute stagnation every 8 hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ratio</td>
<td>(5 minute flow every 8 hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ratio</td>
<td>(5 minute flow every 8 hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ratio</td>
<td>(5 minute flow every 8 hours)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reservoirs were acid cleaned prior to these tests.
Table 11.5

Target Water Quality Conditions for Each Test Sequence

<table>
<thead>
<tr>
<th>Test No.</th>
<th>pH</th>
<th>Alkalinity, mg/L as CaCO₃</th>
<th>Total Chlorine (chloramines), mg/L</th>
<th>Phosphate, mg/L as PO₄</th>
<th>CSMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.0 – 7.5</td>
<td>20</td>
<td>3.5</td>
<td>1.0</td>
<td>1-2</td>
</tr>
<tr>
<td>2</td>
<td>7.0 – 7.5</td>
<td>20</td>
<td>3.5</td>
<td>1.0</td>
<td>1-2</td>
</tr>
<tr>
<td>3</td>
<td>7.0 – 7.5</td>
<td>20</td>
<td>3.5</td>
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</tr>
<tr>
<td>4</td>
<td>7.0 – 7.5</td>
<td>20</td>
<td>3.5</td>
<td>1.0</td>
<td>8-10</td>
</tr>
<tr>
<td>5</td>
<td>7.0 – 7.5</td>
<td>20</td>
<td>3.5</td>
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<td>8-10</td>
</tr>
<tr>
<td>6</td>
<td>7.0 – 7.5</td>
<td>20</td>
<td>3.5</td>
<td>1.0</td>
<td>1-2</td>
</tr>
</tbody>
</table>

stagnation period). Test 3 was conducted for eight weeks, in order to establish stability in the pipe sections under high CSMR conditions. The original test plan called for a long stagnation period for Test 3 (5 minute flow period every 8 hours); however, an error in the written testing plan resulted in the short stagnation period being implemented. Preliminary data evaluation conducted at the end of Test 3 raised questions about 1) possible lead sorption onto the 20-L Nalgene reservoirs, which could impact lead levels measured from the loops during recirculating flow conditions, and 2) particulate lead potentially developing in the reservoirs. A series of special samples were collected at the end of Test 3 to evaluate these issues, and a revised testing protocol was developed for the end of Test 4 and for Tests 5 and 6 to evaluate the effects of CSMR, the occurrence of particulate lead in the reservoirs, and the potential for sorption of lead onto the Nalgene reservoirs.

For Test 4, the chloride-to-sulfate ratio was maintained at approximately 8-10 (high CSMR), and the flow was adjusted so that water was stagnant with the exception of a 5-minute flow period every 8 hours (long stagnation period). Test 4 continued for approximately 2 weeks, after which the reservoirs were disconnected from the metal pipe loop sections. The reservoirs were cleaned by adding nitric acid to obtain a 2% nitric acid solution in each reservoir, which was maintained for 24 hours. After 24 hours, a sample was collected from each reservoir, after which the reservoirs were thoroughly rinsed with distilled water prior to the start of Test 5.

The water condition evaluated in Test 5 was the same as in Test 4 with a CSMR of 10 (high CSMR) and a 5-minute flow period every 8 hours (long stagnation period); however, the reservoir had been acid-cleaned prior to the start of Test 5. Flowing reservoir and stagnant pipe samples were taken under these conditions for approximately one week. At the end of Test 5, flowing samples were collected from the top of each reservoir, the reservoirs were disconnected from each loop, and an additional sample was collected from the middle of each reservoir after the water inside had been mixed. Each of the reservoirs was again cleaned using nitric acid, and rinsed with distilled water as described above, prior to the start of Test 6. The final test condition, Test 6, consisted of a CSMR of approximately 1-2 (low CSMR) with a 5-minute flow period every 8 hours (long stagnation period). This test condition was continued for one week.
Lead and Electrical Sampling Protocols

Metals Levels

Four sampling protocols were used to determine metals leaching from the pipe loops: 1) stagnation samples from the metal pipe loop sections, 2) flowing samples from the recirculating reservoirs, 3) standing samples from the recirculating reservoirs, and 4) standing, acidified samples from the recirculating reservoirs. Each of these protocols is described in more detail below. Grab samples collected for lead concentrations were acidified (100 \( \mu \text{L} \) concentrated nitric acid in 15 mL of sample) with nitric acid and shipped to VT for analysis. The samples were measured for lead and other metals using ICP-MS in accordance with Standard Method 3125.

**Stagnation Samples from the Metal Pipe Loop Sections.** Grab samples were collected directly from the metal pipe loop sections at the end of the stagnation period, with the exception of Test 1 when samples were collected during continuous flow conditions. Prior to sampling, while the pumps were off, the inflow and outflow flexible tubing was pinched closed using surgical clamps. The pipe sections were tilted slightly up towards the outflow port (outflow slightly higher) so when the silicone stopper in the end of the influent pipe cap assembly was removed, water could flow passively into a collection beaker. The entire volume of water in the pipe was collected. Subsamples from the beaker were poured into 15-ml sample vials, and the remaining sample was returned to the 20-L reservoir.

Samples were collected after the specified stagnation period for each test and analyzed for total lead levels. Stagnation samples were collected at three different times during the testing sequence:

a) After the final stagnation period each week, prior to the water change (final weekly stagnation sample). Metals level results from these samples represent the lead release measured from the final stagnation period for the week. These samples were collected for Tests 1 through 6.

b) After the first stagnation period following a water change (initial stagnation sample). These samples were collected during Tests 4, 5, and 6. Metals level results from these samples represent lead release from the first stagnation period after the water was changed.

c) After the second and subsequent stagnation periods for each week (intermediate stagnation samples), but before the final stagnation sample for the week. These samples were collected during Tests 4, 5, and 6. Results from these samples indicate how lead release after stagnation changed over the course of the week, between the initial stagnation sample and the final weekly stagnation sample. These intermediate stagnation samples were collected for Tests 4, 5, and 6.

**Flowing Reservoir Samples.** Grab samples were collected from the recirculating reservoirs during flowing water conditions to determine lead levels in the recirculated water and to compare results to lead levels measured from standing reservoir samples (described below) to evaluate the occurrence of particulate lead in the re-circulating pipe loop apparatus.
**Mixed Reservoir Samples.** Grab samples were collected from the recirculating reservoirs during non-flowing conditions and prior to the water change. These samples were collected at the end of Tests 3, 4, 5, and 6, and in the middle of Test 4. Each reservoir was disconnected from the loop, the contents were thoroughly mixed, and a grab sample was collected directly from the reservoir.

**Standing Acidified Reservoir Samples.** At the end of Tests 4, 5, and 6, the reservoirs for each pipe loop were disconnected and acid cleaned with a 2% nitric acid solution. Prior to collecting the sample, the contents of the reservoirs were stirred to suspend any particulate matter that may have settled to the bottom of the reservoir. Samples of the acidified contents were analyzed for total lead to evaluate the potential for adsorption of lead onto the Nalgene containers that were used for the recirculating reservoirs for each loop.

**Electric Current and Potential Measurements**

An ammeter was used to measure voltage and current between adjoining dissimilar metals in Loops 3 through 6, and between adjoining similar metals in Loop 7 to evaluate changes in these measurements under different testing conditions. These measurements were taken using a RadioShack 46-Range Digital Multimeter (#22-812) with an electrode attached (with a non-metallic spring clamp) to the exterior surface of the pipe materials. Measurements were made along the surface of the pipe and were collected a minimum of once a week at the end of a stagnation period.

**RESULTS AND DISCUSSION**

**Sorption of Lead on Reservoirs**

Concern about the impact of sorption of lead onto the Nalgene containers used for the recirculating reservoirs in this study might have on interpretation of lead release results prompted the acid cleaning and subsequent collection of acidified water samples from each of the reservoirs at the end of Tests 4, 5, and 6. Lead sorption was determined by evaluating lead levels measured from pipe loop reservoir samples before and after acidification at the end of Tests 4, 5, and 6 (Figure 11.9). In addition, a determination of particulate lead accumulation in the reservoirs was completed by evaluating lead levels from flowing reservoir samples, mixed reservoir samples and acidified reservoir samples (Figure 11.9).

The flowing and mixed reservoir samples had similar lead levels, indicating that either there were minimal amounts of particulate lead present, or they were not captured in the sampling protocol. However, high lead levels were measured from the acidified reservoirs at the end of Test 4, indicating that lead had been adsorbed and accumulated onto the plastic container walls throughout the course of the pipe loop study (Tests 1 through 4), and/or there may have been particulate lead present in the reservoirs that was solubilized upon acidification. This loss of lead in the recirculating loops may or may not have altered the trends seen in the lead levels measured under different water quality conditions. However, the rate of uptake and release of lead from the material used in the Nalgene reservoirs (fluorinated polyethylene) is unknown, as is the presence of particulate lead, so these phenomena confounded the interpretation of lead release data from the pipe loops, particularly for Test 3 and 4 water quality conditions.
Figure 11.9 Total Lead Levels Measured in Flowing, Mixed, and Acidified Reservoirs
Figure 11.10 displays the results of total and dissolved lead levels measured on mixed reservoir samples during Tests 5 and 6 for each pipe loop. Loop 6 (simulated lead solder and new copper pipe) had the biggest differences between total and dissolved lead measurements (i.e. higher percentages of particulate lead) when compared to the other loops, indicating the presence of particulate lead. In general, dissolved lead ranged from 38% to 89% of the total lead measured from these mixed reservoir samples.

**Galvanic Current**

**Effect of CSMR**

The galvanic current measurements are not impacted by issues related to metal sorption in the reservoir. The galvanic current was measured at the end of the stagnation period in the recirculating pipe loops. Throughout the testing period, the high CSMR water had higher currents, or higher galvanic activity, than low CSMR water (Figure 11.11). Based on this study, the high CSMR conditions had an average of two times higher galvanic corrosion of lead than the low CSMR conditions for each of the pipe materials evaluated in this study (p-value < 0.01). In this study, the notation of positive current indicates that the lead material was being sacrificed.

![Figure 11.10 Total and Filtered Lead from Mixed Reservoir Samples in the Last Two Testing Sequences](image)
The magnitude of the current was impacted by the flow frequency to a small extent (i.e., stagnation times). For example, for the high CSMR water tests, the magnitudes of the currents were similar between the period with only 5-minute stagnation and the period with 8 hours of stagnation (Figure 11.11). The galvanic currents were measured at the end of water stagnation periods.

**Comparison of Lead Materials**

The loop where copper and older passivated lead was connected exhibited the highest current densities at the 99% confidence level based on paired t-testing (Figure 11.12). The loops with the next highest currents from high to low were newer passivated lead connected to copper, simulated lead solder and copper, and passivated bronze and copper. Each loop was significantly different from the other loops, with the exception of the newer lead connected to copper and the simulated lead solder connected to copper. Those two loops had similar current densities throughout the study.

Contrary to expectations, the highest currents measured (or greatest galvanic corrosion activity) in this study were for the copper pipes coupled with old lead pipes (Figures 11.11 and 11.12). It was previously believed that the passivated or old lead pipes would have an established scale layer that would protect the lead from corrosion. The cause for this discrepancy is not understood. It is deemed possible that the passivating layer, which formed on the newer lead pipe surfaces in the 1+ year of exposure in the prior study using these samples, was more protective than the scale on the pipe surfaces that had not been cleaned.
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

When connected with an external wire to simulate what occurs when the two metals are connected, a strong current was detected. A fairly high corrosion rate for lead in potable water would be 0.1 μA/cm². The acceleration of lead corrosion due to the galvanic current between the older passivated lead and copper was on the order of 0.2 μA/cm² in the water with high CSMR and less than 0.1 μA/cm² in low CSMR water. Thus, the galvanic current between the copper pipe and the lead pipe is quite significant.

Lead Release from Stagnant Pipes

Effect of CSMR

To compare lead release among the loops, lead concentrations measured from the final weekly stagnation sample collected for each loop for Tests 5 (high CSMR) and 6 (low CSMR) were normalized by calculating the total mass of lead released per lead material surface area. To obtain these values, the lead concentrations were divided by the volume of water exposed to the pipes and divided by the surface area of the lead material. Table 11.6 displays the surface area of lead in contact with water for each loop that contained lead bearing material (lead pipe, bronze pipe, simulated lead solder). Loops 1, 3, and 4 had the same surface area of exposed lead, as all three loops incorporated a 12” length of lead pipe. Loops 2 and 5 had the same exposed surface area based on the 12” length of bronze pipe, which had a slightly smaller inner diameter than the lead pipe. Loops 6 and 7 had a much smaller area of lead exposed, as both loops incorporated two – 3” lengths of copper pipe that had been dipped in lead solder to simulate a lead solder joint.

The calculated mass of lead released per lead surface area after 8 hours of stagnation may be elevated because the samples were collected at the end of the week. By the end of the week, lead had already been released from the plumbing materials into the water and was being
recirculated throughout the week. However, the values provide a rough estimate of the impacts of stagnation, CSMR, galvanic connection, and plumbing material on lead leaching.

Higher CSMR appeared to exacerbate lead leaching from galvanic connections of newer lead, bronze, and lead solder to copper pipe (Figure 11.13). Additionally, lead solder with no connection to copper had elevated levels of lead in high CSMR water. Based on the current density data in Figure 11.12, high CSMR water would be expected to increase lead release for the passivated lead pipe compared to low CSMR water. However, the lead release data from the stagnant pipes did not confirm this effect.

**Effect of Galvanic Connection to Copper Pipe**

Additionally, in all cases, the galvanic connection of the lead pipe material to copper increased lead leaching compared to when there was no connection to copper (Figure 11.13). For example, galvanic corrosion of lead more than tripled from approximately 0.06 μg/cm² to 0.22 μg/cm² when newer lead pipe was connected to copper pipe for high CSMR water. Similar results were observed for low CSMR for newer passivated lead, but the increase was slightly lower at 1.5 times higher with the galvanic connection. When bronze pipe was connected to copper pipe, lead release increased between 6 and 30 times for low and high CSMR waters, respectively. Similarly, simulated lead solder connected to copper increased lead leaching approximately 7 times compared to simulated lead solder alone.

**Table 11.6**

<table>
<thead>
<tr>
<th>Pipe Loop Designation</th>
<th>Pipe Material</th>
<th>Surface Area of Lead Bearing Material Exposed (cm²)</th>
<th>Volume of Water Exposed to Pipes (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Newer passivated lead pipe</td>
<td>201.0</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>Passivated bronze pipe</td>
<td>172.3</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Older passivated lead pipe/Copper pipe</td>
<td>201.0</td>
<td>348</td>
</tr>
<tr>
<td>4</td>
<td>Newer passivated lead pipe/Copper pipe</td>
<td>201.0</td>
<td>348</td>
</tr>
<tr>
<td>5</td>
<td>Passivated bronze pipe/Copper pipe</td>
<td>172.3</td>
<td>341</td>
</tr>
<tr>
<td>6</td>
<td>Simulated lead solder joints/Copper pipe</td>
<td>95.7</td>
<td>304</td>
</tr>
<tr>
<td>7</td>
<td>Simulated lead solder joints</td>
<td>95.7</td>
<td>43</td>
</tr>
</tbody>
</table>
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Figure 11.13 Mass of lead released per surface area of lead material in low and high CSMR waters

Lead Levels in Acidified Reservoirs

Effect of CSMR

Results obtained for Tests 5 and 6 may represent the best comparison of lead levels and lead release from the various lead bearing materials under high and low CSMR conditions, since the acid cleaning of the reservoirs prior to the start of each of these tests allowed for an equivalent baseline starting point with respect to lead levels. High CSMR water was more aggressive than low CSMR water at the 95% confidence level, based on grouping all data into low and high CSMR (Figure 11.14). The increase in lead release due to CSMR is consistent with the galvanic current data; however, the magnitude increase in the lead levels was not as high as would be expected based on the galvanic current data. It is possible that lead particulate release and build-up or breakdown of the mass of lead in the existing scale on the reservoir, even with low CSMR water, contributes to the discrepancies between the lead levels and the galvanic currents.

Comparison of Galvanic Connection and Lead Materials

Comparing lead release per unit surface area for each lead bearing material for Tests 5 and 6, the newer passivated lead with no copper loop and the simulated solder connected to copper loop had the highest lead levels for both high and low CSMR waters (Figure 11.14). Contrary to expectations, the connection of copper pipe to the newer lead pipe decreased lead released to the water. It was deemed hypothetically possible that the connection of the lead pipe to copper could help stabilize pre-existing Pb(IV) scale on this pipe sample. Alternatively, recent work has shown that after longer-term exposure lead leaching data begins to agree with expectations based on trends in galvanic current (Nguyen et al. 2009). Additional work on this issue is needed.
CHAPTER 11: UTILITY H, WA (PIPE LOOP STUDY)

Consistent with theory, higher lead release was observed for bronze pipe connected to copper and solder connected to copper compared to the single metal loops for each metal. For example, connecting bronze pipe to copper pipe increased the lead in water by approximately 4 times for both CSMR levels. In high CSMR water, the lead release was increased from 0.08 to 0.32 µg/L/cm², while the lead release increased from 0.06 to 0.23 µg/L/cm² in low CSMR water. Similarly, the lead leaching was increased by 3 times for the simulated solder connected to copper compared to simulated lead solder alone, increasing lead release from 0.42 to 1.3 µg/L/cm² in high CSMR water and from 0.34 and 0.99 µg/L/cm² in low CSMR water.

CONCLUSIONS

Summary of Pipe Loop Testing Materials and Methods

- A pipe loop testing apparatus was developed to examine the effects of changing chloride to sulfate mass ratio (CSMR) on lead release from lead and bronze materials.
- The pipe loop testing apparatus was designed to test components in a “single-metal” and a “dual metal” (Figure 11.1) pipe loop configuration. In both configurations, the apparatus was operated in a re-circulating mode. The “dual metal” pipe loop configurations for Loops 3 through 6 were designed to provide ~three times the surface area of copper to lead bearing material.
- Three testing methods were integrated into the pipe loop apparatus to meet the testing objectives: (1) evaluation of lead release from various lead source materials under different CSMRs, (2) measurement of pH levels of water in the pipe sections, in the vicinity of the dissimilar pipe juncture to determine if there were any pH gradients in the vicinity of the connection between dissimilar metals, and if so, if the gradient was impacted by different CSMR conditions, and (3) measurement of current and voltage between dissimilar pipe sections to determine if these measurements were impacted by different CSMR conditions. Lead concentrations were measured by collecting...
grab samples 1) of water that had been allowed to stagnate in the metal pipe sections (stagnation samples from loops) and 2) of water from the re-circulating reservoirs.

- The pipe loop testing apparatus was assembled and operated at the HDR ARTC testing facility in Redmond, Wash. Tap water supplied to the ARTC testing facility was adjusted to pH 7.0-7.5 and phosphate of 1.0 mg/L. These conditions were selected to represent typical water quality conditions for use of phosphate for corrosion control. The chloride sulfate mass ratio of the water was altered for the various test conditions from ~2.0 (low) to ~10 (high by addition of NaCl in an effort to maintain the target chloride to sulfate ratio for each batch of water).

- For the final two test sequences (Test 5 and Test 6), the reservoirs were acid washed in order to assess the potential for sorption of lead onto the Nalgene reservoirs.

**Effects of CSMR and Galvanic Connection on Lead Release**

- Higher CSMR increased galvanic corrosion of lead:copper couples in dual metal loops.
- Connection of lead plumbing materials to copper pipe generally increased lead leaching, based on lead levels in stagnant pipes for most materials tested.
- Based on the acidified reservoir data, the connection of newer lead pipe to copper reduced the lead in water, compared to newer lead pipe not connected to copper.
- The current density data indicated that the corrosion rate for older lead pipe connected to copper was the highest of all the loops.
- The simulated lead solder/copper loop consistently had the greatest lead release under high CSMR. Even though the galvanic currents for the simulated solder were not the highest in this study, the release of particulate lead from the solder may explain the discrepancy between current and lead data.
- Simulated lead solder joints connected to copper pipe exhibited the largest difference between total and dissolved lead concentrations measured from the re-circulating reservoirs after the water had been mixed, indicating a higher percentage of particulate lead may have been released from this lead bearing material when compared to newer or older passivated lead pipe and bronze pipe.

**Sorption of Lead and Occurrence of Particulate Lead**

- Sorption of lead onto the material used for the re-circulating reservoirs was demonstrated by measuring lead levels from samples collected from the reservoirs after acidification. This sorption may or may not have altered trends seen in lead levels under different CSMRs.
- Lead release was lower during high CSMR and longer stagnation periods (8 hrs) (Test 4) when compared to high CSMR and short stagnation periods (Test 3), indicating that perhaps more lead was lost to sorption onto the Nalgene containers and/or other non-metals components of the pipe loops during the longer stagnation period during Test 4, and/or the rate of lead release was lower during this test. Alternatively, there may have been inherent variability in the lead data and/or the
impacts of sorption onto the Nalgene containers which would make it difficult to distinguish differences in lead release between the loops for these two test conditions.

- High levels of particulate lead did not occur during the study, with the exception of the simulated lead solder material. More particulate lead may be released from lead solder used to join copper pipes than from passivated lead pipes.

**Recommendations for Future Research**

This study provided initial evaluations of changes in CSMR on lead release from several different lead bearing materials. To expand on the results obtained, several issues have been identified that should be explored further:

- More research is needed to examine the inter-relationships of other water qualities (e.g., different pH, alkalinity, chlorine/chloramine, with and without phosphate, etc.) and the effects of changes in CSMR.
- The loop experiments carried out in this study involved relatively short periods of exposure to the different CSMR conditions. It may be appropriate to carry out these types of experiments under much longer periods of exposures to each water quality condition.
- More research is necessary to determine changes in interior scales formed under different CSMR conditions, and the characteristics of those scales with respect to lead uptake and release.
- An evaluation of the most appropriate materials to be used in dump and fill, re-circulating, and flow through experiments designed to assess lead release should be completed. Results from this study indicated that appreciable sorption onto the fluorinated polyethylene material used in the re-circulating reservoirs occurred, and clouded the interpretation of the data collected. In this study, results from Tests 5 and 6 were more reliable than results from Tests 1 through 4. An understanding of which materials are least likely to sorb lead and/or development of operations and sampling protocols to minimize the impact of this phenomenon should be explored.
- On the basis of these results, clear conclusions about the effects of Pb:Cu galvanic connections on leaching of lead from pure lead pipe are not possible. Additional research is needed to clarify this issue.
APPENDIX A: PICTURES FROM FAILED SOLDER IN UTILITY I STUDY
Figure A.1 Site of corrosive attack at silicone stopper/solder interface. The visual attack was not atypical for all of the water conditions. The solder pictured here was exposed to alum-treated water with chloramine.
Figure A.2 Top (a) and side (b) views of the solder that failed at the end of the experiment. The solder was exposed to alum-treated water with free chlorine and high alkalinity. Despite the solder failure, the water condition was the least aggressive in terms of lead release. Due to variability in corrosion, triplicates were used. The red arrows indicate the location of the solder failure.
APPENDIX B: OPERATIONAL AND FIELD WATER QUALITY PARAMETER MEASUREMENTS
Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

Figure B.1 pH as a function of time for Utility H pipe loop study.

Figure B.2 Alkalinity of water over time for Utility H pipe loop study.
APPENDIX B: OPERATIONAL AND FIELD WATER QUALITY PARAMETER MEASUREMENTS

Figure B.3 Total chlorine residual as a function of time for Utility H pipe loop.

Figure B.4 Chloride-to-sulfate mass ratio of the water in Utility H case study.
REFERENCES


# ABBREVIATIONS

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<th>Abbreviation</th>
<th>Description</th>
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<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>d</td>
<td>day</td>
</tr>
<tr>
<td>EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>°F</td>
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</tr>
<tr>
<td>gpm</td>
<td>gallons per minute</td>
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<tr>
<td>N</td>
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<td>natural organic matter</td>
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Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water

PAC  Project Advisory Committee
pp.  pages
ppb  parts per billion
ppm  parts per million
PVC  polyvinyl chloride
rpm  revolutions per minute
s    second
TOC  total organic carbon
wk   week
WQTC Water Quality Technology Conference
yr   year