

Galvanic Lead Corrosion in Potable Water: Mechanisms, Water Quality Impacts, and Practical Implications

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ABSTRACT

As stagnant water contacts copper pipe and lead solder (simulated soldered joints), a corrosion cell is formed between the metals in solder (Pb, Sn) and copper. If the resulting galvanic current exceeds about $2 \mu\text{A}/\text{cm}^2$, a highly corrosive microenvironment can form at the solder surface, with $\text{pH} < 2.5$ and chloride concentrations 11 times higher than bulk water levels. Waters with relatively high chloride tend to sustain high galvanic currents, preventing passivation of the solder surface and contributing to lead contamination of potable water. If the concentration of sulfate increased relative to chloride, galvanic currents and associated lead contamination could be greatly reduced, and solder surfaces were readily passivated.

Mechanistically, at the relatively high concentrations of lead and low pH values that might be present at lead surfaces, sulfate forms precipitates while chloride forms soluble complexes with lead. Considering net transport of anions in water, a chloride-to-sulfate mass ratio (CSMR) above 0.77 results in more chloride than sulfate transported to the lead anode surface, whereas the converse occurs below this CSMR. Bicarbonate can compete with chloride transport and buffer the pH, providing benefits to lead corrosion.

Although orthophosphate is often an effective corrosion inhibitor, tests revealed cases in which orthophosphate increased lead and tin release from simulated soldered joints in potable water. Phosphate tended to increase the current between lead-tin and copper when the water contained less than $10 \text{ mg/L SO}_4^{2-}$ or the percentage of the anodic current carried by SO_4^{2-} ions was less than 30%.

Additionally, nitrate in the potable water range of 0-10 mg/L N dramatically increased lead leaching from simulated soldered pipe joints. Chloramine decay and the associated conversion of ammonia to nitrate during nitrification could create much higher lead contamination of potable water from solder in some cases.

In practical bench-scale studies with water utilities, the CSMR was affected by the coagulant chemical, blending of desalinated seawater, anion exchange, and sodium chloride brine leaks from on-site hypochlorite generators. Consistent with prior experiences, increasing the CSMR in the range of 0.1 to 1.0 produced dramatic increases in lead leaching from lead-tin solder connected to copper.

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Finally, special thanks to my family and friends for their unrelenting support throughout the challenges and good times.

AUTHOR'S PREFACE

The work presented in Chapter 1 is the first to demonstrate large gradients in pH, chloride, sulfate, and lead arising at solder surfaces galvanically connected to copper. Specifically, this work found situations where persistent galvanic corrosion occurred due to very low pH and saline micro-layers at the lead solder surface. These conditions were observed for different water chemistries that simulated real-world problems encountered in practice using simulated lead soldered copper pipe joints under stagnant water conditions, similar to those found in home plumbing. Chapter 1 is published in *Environmental Science and Technology*.

Chapter 2 is the first to unambiguously illustrate that sulfate is beneficial in lead corrosion because it forms precipitates with lead, whereas chloride is detrimental by forming soluble complexes. This work also confirms the mechanistic basis of the chloride-to-sulfate mass ratio threshold, which was observed by others but not explained, by considering simplistic mass transport equations and evaluating the chemical impacts of chloride and sulfate ions on lead chemistry at lead anode surfaces. Furthermore, bicarbonate can compete with the transport of sulfate and chloride and can mitigate lead leaching by reducing the extent of the pH drop at lead anode surfaces. This chapter has been submitted to *CORROSION*.

Although orthophosphate is often an effective corrosion inhibitor, the work in Chapter 3 is the first to reveal significant adverse consequences of orthophosphate on galvanic corrosion of lead plumbing materials connected to copper pipes. Specifically, the adverse consequences tended to occur in water with lower sulfate, lower alkalinity, and higher chloride. In these circumstances, tin in solder was more affected than lead, suggesting that tin plays an important role in the effect of phosphate on solder corrosion. Chapter 3 has been submitted to *Corrosion Science*.

Work in Chapter 4 shows that increasing the nitrate concentration in the potable water range of 0-10 mg/L N dramatically increased lead release from solder. Nitrate also increased the galvanic corrosion rate, and the corrosive attack was non-uniform. This work also found that in practical situations where the nitrate concentration increases in distribution systems due to chloramines decay and nitrification, lead solder corrosion could accelerate dramatically. Chapter 4 has been submitted to *Corrosion Science*.

Chapter 5 describes a simple bench-scale test that water utilities can use to rapidly screen for significant changes in lead leaching from water treatment modifications, and demonstrates that a range of treatment changes can alter the chloride-to-sulfate mass ratio and subsequently increase the lead in water. The chapter has been accepted to *Journal American Water Works Association*.

The research work presented herein was a collaborative effort between Caroline Nguyen, Kendall Stone, Brandi Clark, and Marc Edwards. The dissertation author was the lead author for Chapters 1, 2, and 3. Drafts of Chapters 4 and 5 were co-authored by Kendall Stone and Caroline Nguyen, and the dissertation author revised those drafts and is lead author on the versions of the papers submitted to the journals. The draft for Chapter 5 was based on a published Water Research Foundation final report in which the dissertation author was the first author.

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CHAPTER 1: CORROSIVE MICROENVIRONMENTS AT LEAD SOLDER SURFACES ARISING FROM GALVANIC CORROSION WITH COPPER PIPE

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ABSTRACT. As stagnant water contacts copper pipe and lead solder (simulated soldered joints), a corrosion cell is formed between the metals in solder (Pb, Sn) and the copper. If the resulting galvanic current exceeds about $2 \mu\text{A}/\text{cm}^2$, a highly corrosive micro-environment can form at the solder surface, with $\text{pH} < 2.5$ and chloride concentrations at least 11 times higher than bulk water levels. Waters with relatively high chloride tend to sustain high galvanic currents, preventing passivation of the solder surface, and contributing to lead contamination of potable water supplies. The total mass of lead corroded was consistent with predictions based on the galvanic current, and lead leaching to water was correlated with galvanic current. If the concentration of sulfate in the water increased relative to chloride, galvanic currents and associated lead contamination could be greatly reduced, and solder surfaces were readily passivated.

KEYWORDS. Galvanic corrosion, current, solder, anode, pH, ion migration

INTRODUCTION

Seemingly innocuous changes in chemistry can sometimes dramatically increase the likelihood of lead contamination from lead pipes, soldered joints, and lead-bearing brass (1-5). In some

cases, the changes have resulted in exceedances of lead levels specified in the United States Environmental Protection Agency (US EPA) Lead and Copper Rule (LCR), elevated blood lead, and even lead poisoning (2, 6-8). One important subset of influential treatment changes, as highlighted by Edwards et al., involves dramatically increased lead release from lead solder:copper joints that are triggered by increases in the chloride-to-sulfate mass ratio (CSMR = mg/L chloride divided by mg/L sulfate) of the water supply (2). Some of the resulting problems with elevated lead occurred while utilities practiced optimized corrosion control using orthophosphate inhibitors (2).

The nature and importance of galvanic corrosion on contamination of water from lead plumbing was first detailed by Oliphant and Gregory (9, 10). These authors discovered that waters with a CSMR above about 0.6 had very high and persistent galvanic currents flowing between copper pipe and lead solder. The lead solder anode, sacrificed by the connection to the cathodic copper, was suspected to cause severe lead contamination of potable water (9, 10). If the CSMR of the water was lower, galvanic currents between lead solder and copper decreased markedly with time (9, 10), which is consistent with observations of Reiber et al. in continuous flow testing of waters to which sulfate was added (11, 12). Later practical data demonstrated very strong links between the reported 90th percentile lead at certain utilities and the CSMR (13), as well as elevated CSMR due to changing coagulant chemical from aluminum sulfate to either ferric chloride or polyaluminum chloride (2). Increased leaching and galvanic corrosion of lead solder at higher CSMR has also been unambiguously demonstrated at bench scale by Dudi et al. (14) and Edwards et al. (2). Practical case studies by Nguyen et al. found a correlation between the CSMR and lead release from galvanic solder in a range of waters (15).

Although the practical link between higher CSMR and higher lead leaching from solder is now well established in the literature, the precise mechanism(s) for the sustained attack due to chloride have never been elucidated. The goal of this work was to unambiguously identify the key steps by which galvanic corrosion currents can cause persistent dissolution of lead bearing materials connected to copper pipe. Conceptually, when lead is physically connected to copper, the lead surface is anodic and the rate of lead corrosion is accelerated. The free lead (Pb^{2+}) released to the water is a Lewis acid, which decreases pH upon removal of OH^- ions from the water via formation of soluble complexes or insoluble precipitates that contain OH^- (14). Specifically, release of 50 mg/L Pb(II) can reduce the pH from 8 to 5.8 in water with 20 mg/L alkalinity as CaCO_3 . However, if the same mass of tin, which is a stronger Lewis acid than lead, were released from 50:50 (by weight) Pb/Sn solder, the pH is predicted to decrease to 2.9-3.5. A higher alkalinity might tend to buffer the pH drop (14). Because the resulting low pH can hinder formation of passive films on the lead solder surfaces, it could contribute to self-perpetuation of the attack and associated water contamination.

Another factor affecting corrosion is the migration of anions such as chloride or sulfate to the lead anode surface, which is necessary to balance electroneutrality of the released Pb^{2+} or Sn^{2+} . The increased concentration of anions at anode surfaces versus the concentration in bulk water is well understood, and has even been considered as a means of removing anionic contaminants from soils via electromigration (16, 17). The net concentration of anions at anode surfaces can be predicted using a one dimensional model that accounts for anion migration and diffusion (18). Key results of this model illustrate two extremes in behavior that are relevant to the current application. Specifically, if the current density exceeds about $2 \mu\text{A}/\text{cm}^2$, net anion transport is towards the anode (anion migration toward the anode is much greater than diffusion of anions

away from the anode), resulting in accumulation of Cl^- or SO_4^{2-} at the anode surface relative to bulk water (16). In other words, when this threshold of current density is exceeded, the anion concentration factor (CF = anion concentration near the anode surface divided by the anion concentration in the bulk water) becomes very high. At another extreme, if the current density is very low, net transport of anions towards the anode is low relative to diffusion of anions away from the anode, reducing the net CF of anions near the anode surface. In the experimental data of Horng using a copper anode, sulfate was concentrated at the anode surface by a factor of 1.4 to 5 when the current density increased from $10 \mu\text{A}/\text{cm}^2$ to $25 \mu\text{A}/\text{cm}^2$ (16).

In general, the range of chloride and sulfate concentrations commonly encountered in potable water are not expected to influence lead solubility via formation of either soluble complexes or lead precipitates (19). However, if these ions were to become concentrated at the surface of the anode, significant impacts on lead solubility at the anode surface are predicted. Specifically, at high concentrations, chloride is predicted to form soluble complexes with lead and increase its solubility, whereas sulfate can form a relatively insoluble precipitate with lead and decrease its solubility (20, 21). Work by Guo with polarized lead electrodes suggested that insoluble metal salts, such as PbSO_4 or other salts containing multivalent anions, could passivate the scale from the active state even under highly acidic conditions (22, 23). However, in the presence of chloride, very rapid corrosion (metal polishing) could occur as soluble metal chloride complexes form (23), which occurs for iron if chloride exceeds about 8 M (24).

The experimental work that follows attempts to verify the expectations of very low pH and higher anion concentration in the solder anode microlayer, thereby providing fundamental mechanistic insights to explain practical observations of CSMR impacts on lead contamination of potable water from solder.

EXPERIMENTAL METHODS

Pipe Setup. The volume of water in the microlayer contacting solder in a real-world pipe joint is extremely small and the physical contact between the dissimilar metals prevents measurement of ambient galvanic currents. Therefore, a simulated pipe joint corrosion macrocell was designed and constructed to track changes in water chemistry that result from galvanic corrosion between copper pipe and lead solder during stagnation events (Figure 1-1). This type of apparatus was shown to semi-quantitatively track observed changes in lead leaching due to real-world pipe joints (2).

The macrocell in this work included a 1.9 cm diameter copper pipe (31 cm long) and a 1.3 cm diameter copper pipe (6.4 cm long), connected by clear Tygon tubing with a 2-mm gap

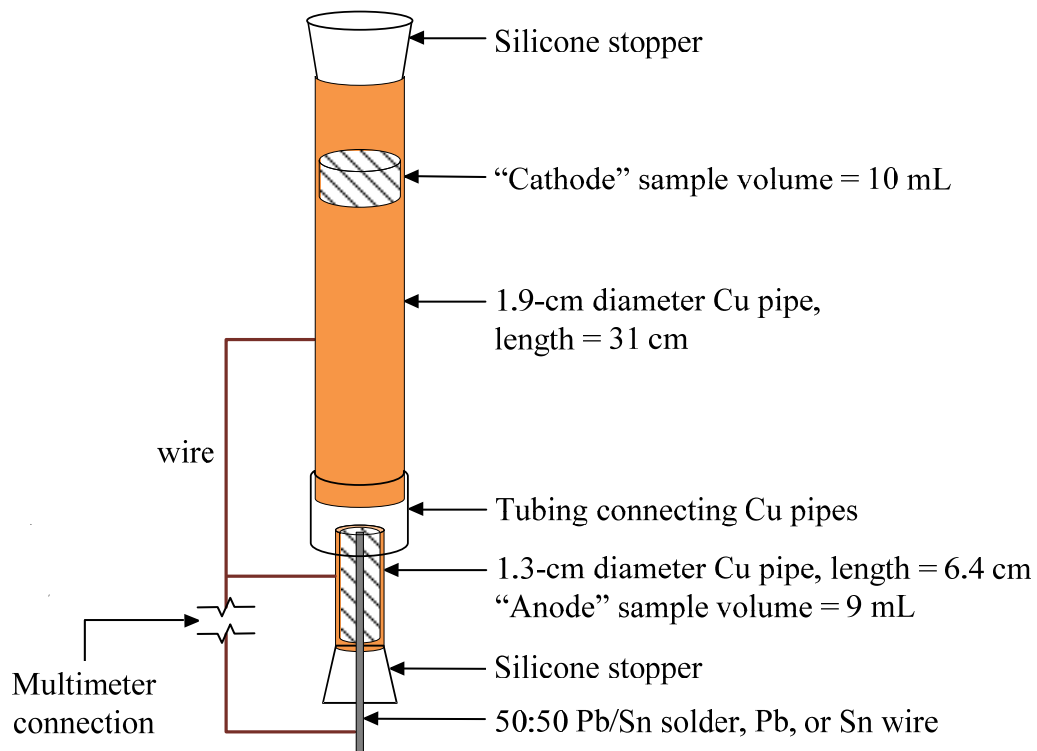


Figure 1-1. Schematic of copper joint macrocell used in case studies.

separation between the pipes. A 50:50 lead:tin, pure tin, or pure lead wire was inserted through the center of a silicone stopper, and then the stopper with wire was inserted into the 1.3 cm diameter copper pipe. The wetted surface area of lead solder (or pure lead or pure tin wire) was 6.2 cm^2 (Case Studies 1 and 3) or 5.2 cm^2 (Case Study 2). The smaller diameter (1.3 cm) copper pipe could be removed to isolate a volume of water near the surface of the anodic solder, suitable for measurement of Cl^- or SO_4^{2-} . The larger diameter (1.9 cm) pipe had the dual purpose of allowing extraction of water samples from various depths within the apparatus using a pipette inserted into the apparatus, and also providing a large copper-to-solder surface area of approximately 34:1 in Case Studies 1 and 3 and 41:1 in Case Study 2. To simulate the galvanic connection between copper pipes and lead solder in joints while having the ability to measure galvanic corrosion with an ammeter, each lead or tin bearing wire was externally connected to the copper pipes via copper wires. The apparatus was oriented vertically so that the solder, lead, and tin wires were at the bottom. Pure lead and tin wires were also evaluated in this study to identify tendencies specific to each metal present in 50:50 Pb/Sn solder.

Water Chemistry. The pipes were exposed to different water chemistries to simulate real-world problems observed in practice (Table 1-1). Raw water from the utility in Case Study 1 was received and treated at bench scale with the specified coagulants and disinfectants to simulate full-scale treatment (Table 1-1). In Case Study 2, treated water, but prior to disinfection, was received at Virginia Tech from Utility 2. Water for Case Study 3 was treated using reagent grade chemicals. The chloride and sulfate concentrations were selected to represent the range of chloride and sulfate concentrations quantified in potable water. The pH, inhibitor dose, and disinfectant concentrations were adjusted for all waters prior to exposure to the macrocells.

Details of the bench scale treatment for each case study are provided in the Supporting Information.

Experimental Protocol. The water in the pipes was changed three times per week using a “dump-and-fill” protocol (2). Each water condition was tested in triplicate. Water left stagnant in the pipes for two to three days was collected and analyzed for metals at the end of each week. Although the average stagnation time in buildings between flow events is on the order of 30 minutes, a longer stagnation time was selected in this study to represent that encountered during a typical weekend in many buildings such as schools.

Table 1-1. Bulk water chemistry of test waters.

| (Case Study #) Water Type | Cl ⁻ , mg/L Cl | SO ₄ ²⁻ , mg/L SO ₄ | CSMR* | Alkalinity, mg/L as CaCO ₃ | pH | Inhibitor (dose) | Disinfectant, mg/L as Cl ₂ |
|---|---------------------------------|--|---------|---|-----|---------------------------------------|--|
| (1) Alum-treated | 27 | 21 | 1.4 | 25 | 7.7 | | |
| (1) PACl-treated** | 32 | 6 | 5.3 | 25 | 7.7 | Ortho-phosphate | Various - free chlorine or chloramines |
| (1) PACl-treated**, simulated road salt runoff (+16 mg/L Cl) | 48 | 6 | 8.5 | 25 | 7.7 | (1 mg/L P) | (3.5 mg/L) |
| (2) Typical treated water subjected to corrosion control strategies | 4 and 14 | 3-12 | 3.0-4.7 | 8-58 | 7.3 | Ortho-phosphate (various: 0-1 mg/L P) | Free chlorine (2 mg/L) |
| (3) Low chloride and high sulfate | 22 | 121 | 0.2 | 10 | 8.3 | | |
| (3) High chloride and low sulfate | 129 | 8 | 16 | 10 | 8.3 | None | Chloramines (4 mg/L) |

* Chloride-to-sulfate mass ratio (CSMR) is given as mg/L Cl⁻ per mg/L SO₄²⁻.

** PACl – polyaluminum chloride.

A mass balance of lead released throughout the study was determined at the end of Case Study 2 for the pure lead wire apparatus. The scale of the lead wire was carefully abraded from the surface using a soft cloth. The lead wire, which remained inserted in the 1.3 cm diameter stopper, was weighed before and after removal of the scale, and the collected scale was dissolved with 2% nitric acid and analyzed to determine the fraction of lead in the scale. The internal surface of the upper copper pipe section (1.9 cm diameter) was soaked in pH 1.5 water (approximately 0.15% HNO₃) for 16 hours. Following stagnation, the water was removed from each pipe, acidified to a total of 2% nitric acid, and analyzed for lead and copper.

Analytical Methods. Total lead release was quantified by acidifying water samples with 2% nitric acid for at least 24 hours. Lead, chloride, and sulfate in the bulk water were measured using an inductively coupled plasma mass spectrometer (ICP-MS) in accordance with Standard Method 3125-B (25). Concentrations of chloride and sulfate were cross-checked using DIONEX DX-120 ion chromatography according to Standard Method 4110 (25). Chloride microelectrode measurements were made with an ion-selective microelectrode by Lazar for Case Studies 1 and 3. Chloride and sulfate concentrations used in the calculation of the concentration factors were determined from ICP analysis of “anode” and “cathode” water samples. “Anode” samples consisted of the 9-mL solution closest to the solder wire, and “cathode” samples comprised the 10-mL solution withdrawn from the apparatus top, farthest from the solder wire (Figure 1-1). The pH of the bulk water was measured before exposure to the macro-cells with an Accumet electrode in accordance with Standard Method 4500-H⁺ B (25). The pH of the anode (within 1 mm from the solder, Pb, or Sn surface) and cathode (in the bulk water in the 1.9-cm diameter copper pipe) was measured using a flat membrane microelectrode and a reference electrode from

Microelectrodes, Inc. Electrochemical measurements between the copper pipes and the solder, lead, or tin wires were conducted using RadioShack multimeters with 100 Ω resistance.

RESULTS AND DISCUSSION

Effect of Galvanic Corrosion on Lead Release. Galvanic current measured between the anode (solder, lead, or tin wire) and the cathode (copper pipe) is an indicator of galvanic corrosion (26). For this study, negative current values indicated that the lead-tin solder, lead, or tin wires were anodic (sacrificed) while the copper pipes were cathodic (protected). As the magnitude of the measured galvanic current increased, lead release to the water increased for solder wires across all three case studies and for pure lead wire investigated in the second case study (Figure 1-2). Lead release followed a roughly linear relationship with the galvanic current, consistent with expectations based on Faraday's law. This is also consistent with recent work by Sastri et al. who linked galvanic corrosion to lead leaching from solder in drinking water (27). In some cases lead concentrations reached more than 20,000 ppb in the macrocell anode compartment (results not shown).

For 50:50 Pb/Sn solder, the measured currents reflected not only the corrosion rate of lead but also that of tin. Solder alloy corrosion may proceed with preferential leaching of one metal versus the other, but if it is assumed that each metal corroded at the same rate, the lead released from 50:50 Pb/Sn solder to the water was approximately three times less than predicted by Faraday's law for the three case studies (Figure 1-2). Similarly, lead release to water from pure lead wire in Case Study 2 was about 4 times less compared to the predicted amount, assuming that 100% of the galvanic current was associated with the lead release. However, consistent with Oliphant's findings (10), the vast majority of this "missing" lead was found to be accumulated in

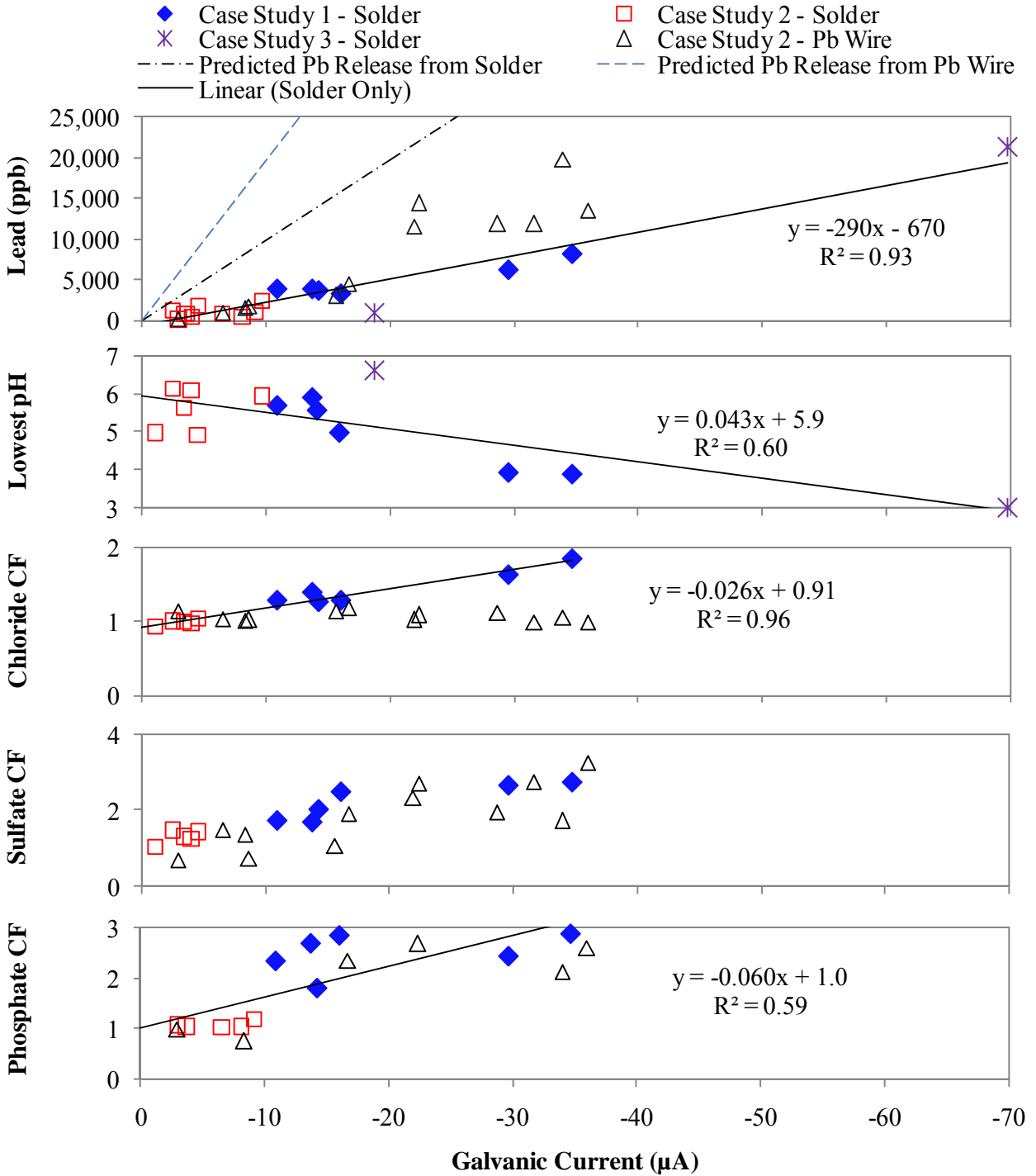


Figure 1-2. Lead release to bulk water, pH at solder surface, chloride concentration factor (CF), sulfate CF, and phosphate CF at the anode as a function of galvanic current. The blue diamonds, red squares, purple asterisks, and black triangles represent Case Study 1 solder, Case Study 2 solder, Case Study 3 solder, and Case Study 2 lead wire, respectively. The solid line, dash-dot line, and dashed line

represent the linear regression for solder, predicted oxidized lead from solder, and predicted oxidized lead from pure lead wire, respectively. Measurements were taken after two days of water stagnation. The CF is equal to the concentration at the anode divided by the concentration at the cathode. The lead measurements were taken from the entire volume in the apparatus, while the chloride and sulfate concentrations were determined from “anode” and “cathode” volumes (Figure 1-1). The pH was measured within 1 mm of the solder surface using a microelectrode. Case Study 2 solder data points include conditions with no phosphate, and the lead wire data are the waters with 4 and 14 mg/L Cl and alkalinity above 15 mg/L as CaCO₃.

lead scales on the lead anode and elsewhere in the apparatus, as confirmed by mass balances at the end of the experiment. Similar trends were observed for tin release from solder and tin wires.

The potential of the copper pipe was stable (± 0.1 V) as the CSMR was varied (results not shown), further confirming that the electrochemical factors propagating the attack at higher CSMR were occurring at the lead anode surfaces. The actual lead levels released to the water from the apparatus used in these case studies was much greater than is observed in practice, but is in close agreement to prior studies examining small volumes of water contacting typical lead solder joints in copper pipe (2).

Anion Migration. Anions such as chloride, sulfate, and phosphate must be drawn to the anode surface to counterbalance released Pb²⁺ and Sn²⁺ and maintain electroneutrality (Figure 1-3). The measured concentrations of these metals in the water near the anode were as high as 157,000 ppb Pb and 41,000 ppb Sn, and cations such as sodium (Na⁺) also migrated toward the cathode, which is the site of OH⁻ production (results not shown). Other work by Kim (17) and Horng (16) also measured chloride and sulfate migration to the anode. Concentration factors (CFs) were

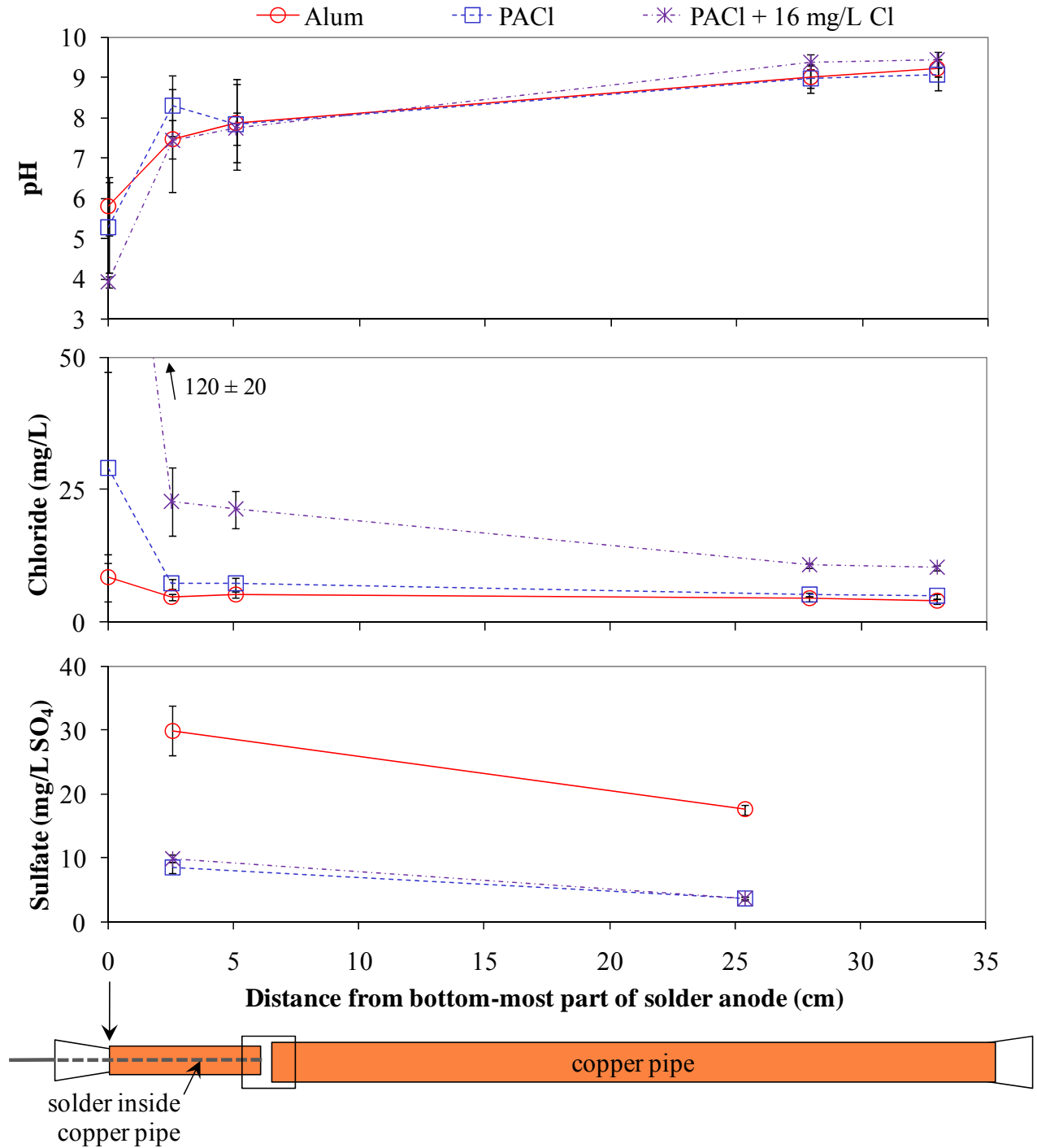


Figure 1-3. pH, chloride concentration, and sulfate concentration as a function of distance from the bottom-most part of the solder anode for Utility 1. The pH and the chloride concentrations were measured using a microelectrode. Sulfate was measured by withdrawing samples from the apparatus. The location of the anode was between 0 and 6.4 cm on the x-axis, and distances greater than 6.4 cm on the x-

axis was considered the cathodic region. Error bars represent 95% confidence intervals over triplicate measurements.

used to compare anion accumulation at the anode versus the cathode in this work and in Horng's work. The CFs in this study were calculated by dividing the concentration in the 9 mL of solution closest to the anode by the concentration near the cathode. As the galvanic corrosion rate increased, the sulfate, phosphate, and chloride CFs increased as electromigration became dominant over ion diffusion (Figure 1-2). For instance, sulfate was concentrated at the anode surface by a factor of 1.5 when the current density was approximately $-1.2 \mu\text{A}/\text{cm}^2$. When the current density quadrupled to $-4.8 \mu\text{A}/\text{cm}^2$, 2.7 times more sulfate was measured in the anode compartment than in the cathodic area of the pipe. Similar trends were observed in Horng's work, although the extent of ion migration was less than that measured in this work. Specifically, a current density of $-10 \mu\text{A}/\text{cm}^2$ resulted in a sulfate concentration factor of 1.4 at the anode, and the concentration factor increased to 5 when the current density increased to $-25 \mu\text{A}/\text{cm}^2$ (16). The most prominent difference between the two studies is the presence of a cathodic copper surface immediately adjacent to the anode in this work, which would tend to decrease the CF versus the microlayer at anode surfaces in practice, since this portion of the copper surface in the apparatus carried about 50% of the cathodic current.

In situations with very low galvanic currents, lead concentrations were not as strongly impacted by the levels of chloride and sulfate in the water in this study (ex., Case Study 2; Figure 1-4), consistent with expectations outlined earlier. Although CFs greater than one for sulfate and chloride in Case Study 3 were not detected with the macrocell measurement technique as was observed in the other two case studies, a chloride concentration factor of 4 was detected using a

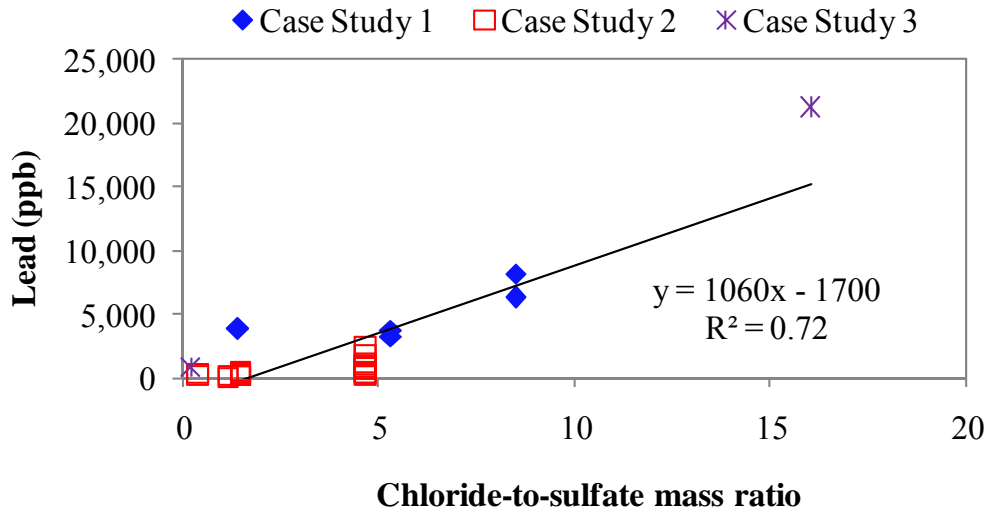


Figure 1-4. Lead release from 50:50 Pb/Sn solder as a function of the chloride-to-sulfate mass ratio (CSMR) for the case studies. Data from Case Study 2 in the plot represent a range of alkalinity (8-58 mg/L as CaCO_3) with and without orthophosphate. Water in Case Study 1 was dosed with orthophosphate, and treated water in Case Study 3 contained no phosphate.

microelectrode brought to within 1 mm of the anode surface. Hence, the actual CFs in the microlayer at the lead anode surface are likely much larger than reported herein based on collection of the relatively large water volumes (≈ 9 mL) near the anode surface. As expected based on the higher ionic transport numbers of sulfate versus chloride (28, 29), sulfate had a CF higher than for chloride at a given current density (Figure 1-2).

Pure lead and pure tin wires were also evaluated in Case Study 2. For reasons that are not fully understood, in one water tested, only sulfate and phosphate accumulated at the pure lead anode surface, and chloride did not (Figure 1-2). For example, the sulfate concentration factor ranged from 0.7 to 3.3 for some water conditions, but there was not a strong trend between the concentration factor and the galvanic current density, which ranged from -0.6 to $-6.9 \mu\text{A}/\text{cm}^2$.

For pure tin wire in Case Study 2, there was little concentration of the anions because the current density was nearly always below $2 \mu\text{A}/\text{cm}^2$.

pH at Anodic Solder Surface. As the galvanic corrosion rate increased, the pH decreased at the anodic solder surface due to the Lewis acidity of lead and tin (Figure 1-2). At the solder surface after a two-day stagnation period, pH was as low as 3.7 for Case Study 1 and 2.5 for Case Study 3. Some measurements indicated that the pH dropped as much as 2 pH units within 1 hour of stagnation, demonstrating that days of stagnation are not required to observe significant galvanic effects. Even when the galvanic corrosion activity was relatively low as in Case Study 2, the pH still dropped from pH 7.3 in the bulk water to as low as pH 3.8 at the solder surface. The very low pH values measured for solder and tin wire were in the range of those predicted by solubility models (30), considering the Lewis acidity of the detected lead and tin concentrations. Consistent with expectations and prior research (31), the pH increased with distance from the anode due to the net OH^- production at the cathode (Figure 1-3).

Predicted Effect of pH and Anion Migration on Lead Leaching. To illustrate the effects of chloride and sulfate on lead solubility at the surface of lead anodes, modeling with MINEQL⁺ was conducted. For example, if 50 mg/L Pb(II) were released to the microlayer of water with 8 mg/L alkalinity as CaCO_3 and the sulfate concentration at equilibrium was 240 mg/L (2.5 mM SO_4^{2-}), 95% of the released lead is predicted to form larnakite ($\text{PbSO}_4 \cdot \text{PbO}$) and cerrusite (PbCO_3) solid precipitates at pH 6.5 (Figure 1-5). These solids could coat the anode surface and reduce the rate of corrosive galvanic attack. The 240 mg/L SO_4^{2-} in the microlayer near the lead surface could also be obtained by a 10X concentration of 24 mg/L SO_4^{2-} (0.25 mM) from the bulk water due to electromigration. In contrast, if chloride were present at the similar molar concentration mentioned for sulfate in the preceding example, the solubility of lead at the anode

would be increased by 37% to 3.7 mg/L soluble Pb due to the formation of soluble PbCl^+ complexes (Figure 1-5).

The relative effect of chloride and sulfate on soluble lead at the solder surface would be much more dramatic at lower pH values, or with greater concentration factors arising from higher galvanic current densities. For example, if 240 mg/L SO_4^{2-} and 50 mg/L Pb(II) were added to water at pH 4, only 3.7 mg/L Pb is predicted to remain soluble while 93% of the lead would precipitate as PbSO_4 which could coat the anode and reduce the corrosion rate (Figure 1-5). Conversely, chloride, if present in the microlayer near the anode surface at the same molar concentration as sulfate in this example, would yield 100% soluble lead at the same pH (77% free Pb^{2+} , 15% PbHCO_3^+ , 8% PbCl^+). This explains the benefits of sulfate and the detrimental effect of chloride in preventing lead contamination of potable water in lead solder:copper joints (Figure 1-4).

In the present study, all of the lead would be leached from the solder wires in Case Study 2 after the experiment continued 5-630 years, based on the galvanic currents from Week 15 of the study. In practice, the quality of soldering workmanship varies from home to home, as exposed solder at a given pipe joint can range from a nearly negligible mass to well over 10 grams (32). Thus, the self-perpetuating corrosion can be very serious in some situations and can require adjustment of the CSMR back to lower ranges to reduce lead leaching to below the USEPA LCR action level of 15 ppb (2).

Implications for Drinking Water Systems. Galvanic reactions can drive corrosion of lead metal at copper joints and contribute to exceedance of the USEPA LCR (2, 15). Furthermore, in waters supporting relatively high galvanic currents, higher chloride and lower sulfate can worsen corrosion of lead solder, which is believed to be the dominant source of lead in water in many

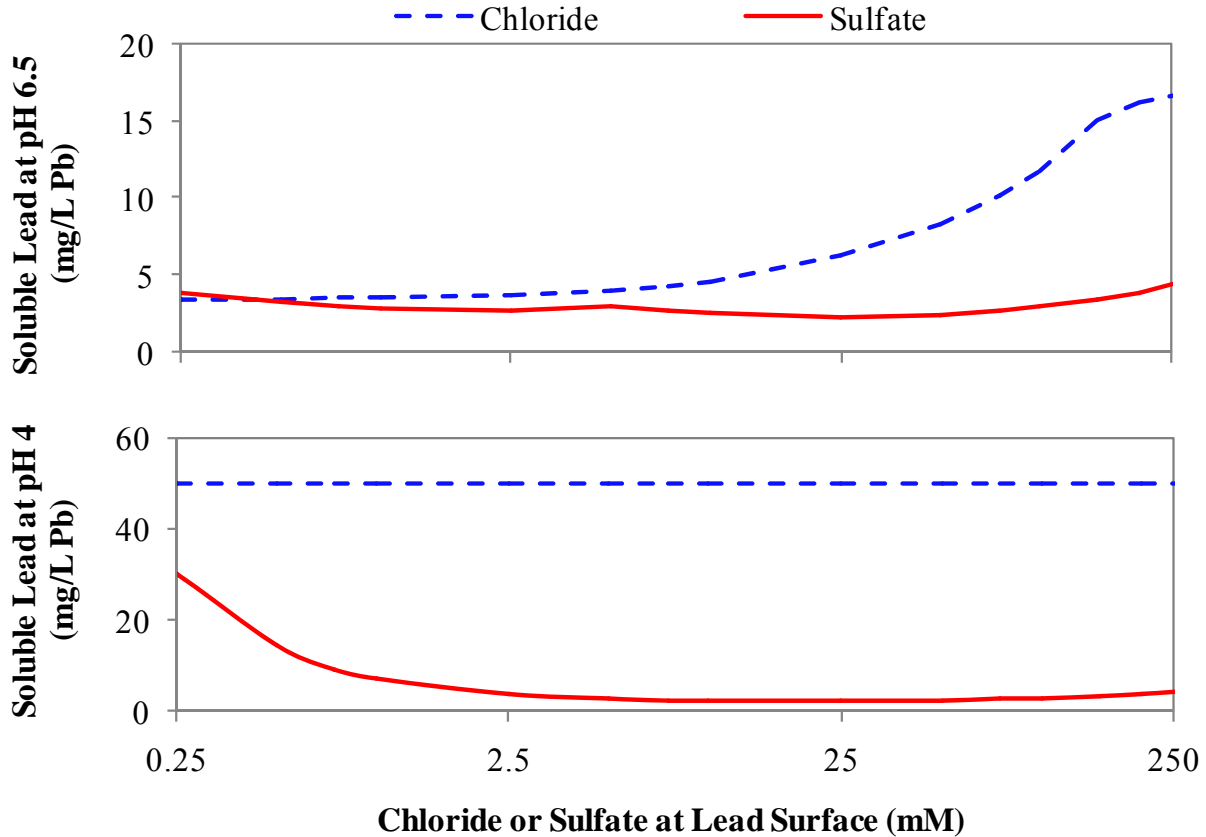


Figure 1-5. Equilibrium soluble lead concentrations at pH 6.5 (top) and pH 4.0 (bottom) at a lead surface if 50 mg/L Pb(II) is released to water with 8 mg/L alkalinity as CaCO₃. Sulfate and chloride concentrations at the lead surface can be greater than in bulk water due to electromigration. In water with sulfate, larnakite (PbSO₄:PbO), anglesite (PbSO₄), and cerrusite (PbCO₃) solids are predicted to form at pH 6.5, and PbSO₄ solids are predicted to begin forming at 0.1 mM SO₄ at pH 4.0. If chloride were dominant in the water and at the lead anode, PbCO₃ and Pb(OH)₂ solids would form at pH 6.5, and no precipitates are predicted to form at pH 4.0.

situations (11). The detriments of chloride are attributed to its migration to the anode surface and formation of soluble PbCl⁺ complexes, whereas the benefits of sulfate may be attributed to formation of relatively insoluble PbSO₄ (or similar) solids. This work is the first to demonstrate the very large gradation in pH, chloride, sulfate, and lead that can be produced via galvanic

corrosion of lead solder:copper joints under stagnant water conditions, which can often exceed 48 hours duration over weekends in building plumbing systems. Recently, similar conclusions about low local pH, high chloride, high sulfate, and very high lead in micro-environments near surfaces of lead anodes were drawn by Desantis et al., based on independent mineralogical examination of lead:copper pipe connections from extracted service line samples (20). In sum, these microlayer effects can explain a subset of persistent lead corrosion problems in some buildings and from lead:copper service line joints at some water utilities (2). Additional work is needed to better understand situations in which persistent galvanic currents occur, and how they can be practically mitigated through control of water chemistry.

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SUPPORTING INFORMATION AVAILABLE. Additional descriptions, figures, and tables regarding the bench scale water treatment, tin release, predicted pH, chloride concentrations in Case Study 3, potential measurements, and mass balance of oxidized lead are included in Appendix A.

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CHAPTER 2: ROLE OF CHLORIDE, SULFATE, AND ALKALINITY ON GALVANIC LEAD CORROSION

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ABSTRACT

The effects of chloride, sulfate and alkalinity on galvanic corrosion were investigated with beaker tests, lead wire electrochemical tests, and lead solder galvanic cells. At relatively high concentrations of lead and low pH values that might be present at the lead anode surface, sulfate forms precipitates with lead while chloride forms soluble complexes, explaining the detriments of chloride and benefits of sulfate during galvanic corrosion in prior research. Considering net transport of anions in water, a chloride-to-sulfate mass ratio (CSMR) above 0.77 yields more chloride than sulfate transported to the lead anode surface, whereas the converse occurs below this level of CSMR. Bicarbonate can compete with chloride and sulfate transport and also buffer pH at the anode surface, providing benefits to lead corrosion.

KEY WORDS. Alkalinity, pH, chloride, sulfate, galvanic corrosion, lead, solder

INTRODUCTION

Galvanic Corrosion

Lead contamination of potable water due to galvanic attack of lead solder was first demonstrated by Oliphant¹ and Gregory², who discovered high and persistent galvanic currents

between copper pipe and lead solder when the chloride-to-sulfate mass ratio (CSMR, or mg/L chloride $[Cl^-]$ divided by mg/L sulfate $[SO_4^{2-}]$) of the water was above about 0.6, and public health concerns might arise from the acceleration of lead corrosion. If the CSMR of the water was low, galvanic currents between lead solder and copper decreased markedly with time^{1, 2}, consistent with observations of Reiber et al. when sulfate-amended water was tested during continuous flow^{3, 4}. Later practical data linked high 90th percentile lead at certain utilities to higher CSMR⁵, and other work demonstrated that certain changes in coagulant chemicals, such as ferric chloride or polyaluminum chloride instead of aluminum sulfate, could increase the CSMR of the water and trigger lead problems⁶.

Increased lead leaching and galvanic corrosion of lead solder at higher CSMR was also recently demonstrated at bench-scale for a wide-range of relatively low alkalinity water⁶⁻⁸. The on-set of galvanic corrosion dropped the pH at the lead solder anode to as low as pH 2.5, and at least 10 times more lead, chloride, and sulfate accumulated at the anode surface relative to the bulk water⁹. Similar conclusions were drawn by Desantis et al.¹⁰, who found that lead sulfate, lead carbonate, copper sulfate, and copper carbonate formed on the surface of lead pipes connected to copper joints.

Alkalinity and pH

Buffering, as controlled by the interplay of pH and alkalinity, is predicted to reduce the extent of the pH drop at the lead anode surfaces during galvanic corrosion⁷, and also contributes to the formation of protective and low solubility pipe scale^{11, 12}. Higher pH values generally decrease lead solubility¹²⁻¹⁴, and increasing the pH and/or alkalinity in some cases reduced lead concentrations in water when lead solder corrosion was believed to be problematic¹⁵⁻¹⁷. Others

have found that increasing alkalinity sometimes worsened lead leaching from brass¹⁸ and from lead (Pb)-tin (Sn) solder coated on copper in a water at pH 7.5 containing orthophosphate¹⁹. In other work, the dissolution of lead dioxide (PbO₂) solids was accelerated with greater concentrations of dissolved inorganic carbon (DIC), perhaps due to formation of soluble lead carbonate complexes²⁰, which is analogous to increased iron corrosion due to carbonate complexes²¹. In summary, there is reason to believe that alkalinity would generally have multiple benefits to lead corrosion control, and it is predicted that the benefits might be particularly important in mitigating persistent leaching of lead solder galvanically connected to copper.

Alkalinity, Chloride, and Sulfate Effects on Galvanic Corrosion: Conceptual Modeling

Lead and tin are Lewis acids that decrease the pH with the removal of hydroxide (OH⁻) ions from the water through formation of soluble complexes or insoluble precipitates containing OH⁻. For example, adding 70 mg/L Pb(II) to water with an alkalinity of 20 mg/L as calcium carbonate (CaCO₃) can reduce the pH from 8 to approximately 6 at equilibrium (Figure 2-1a). Moreover, the same concentration of Sn(II) or Sn(IV), which is found in 50:50 Pb/Sn solder, drops the pH to 3 (Figure 2-1a). These high levels of lead and tin can be found in the microlayer at the surface of lead-tin solder undergoing galvanic corrosion⁹. Increasing the alkalinity buffers the pH drop as lead carbonate solids form, and the soluble lead decreases from a combined effect of higher pH and higher DIC (Figure 2-1b). For example, if the alkalinity was increased from 20 to 200 mg/L as CaCO₃ and 50 mg/L Pb(II) was added to water, the pH would only decrease to 7.4 instead of 5.7. Likewise, the soluble lead at equilibrium would decrease from 15 mg/L Pb to 0.3 mg/L Pb due to the increase in 180 mg/L as CaCO₃.

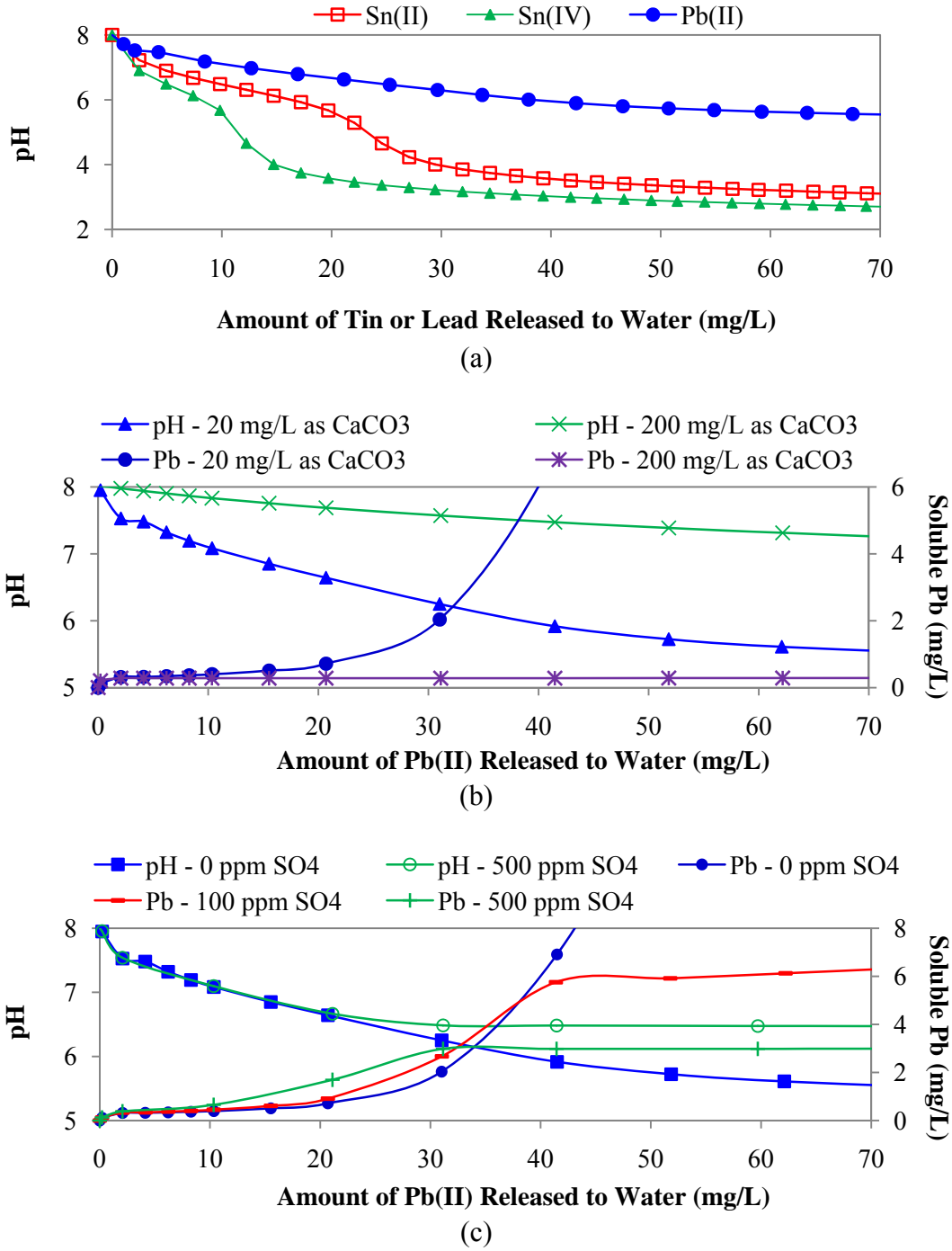


Figure 2-1. Equilibrium pH and soluble lead as a function of lead or tin released to the water in the following conditions: (a) 20 mg/L alkalinity as CaCO₃, (b) 20 or 200 mg/L alkalinity as CaCO₃ with no sulfate and chloride, and (c) 0-500 mg/L SO₄²⁻ with 20 mg/L alkalinity as CaCO₃. All water had an initial pH of 8.0, and equilibrium modeling was conducted with MINEQL+²⁷.

If the alkalinity and the amount of carbonate in the water are low, sulfate can form a protective layer and also buffer the pH drop associated with the Lewis acid (Pb^{2+}) addition by precipitating lead (Figure 2-1c). Specifically, increasing the sulfate concentration from 0 to 500 mg/L SO_4^{2-} in water with 20 mg/L as CaCO_3 would reduce the pH drop from the addition 50 mg/L Pb(II) by 0.8 pH units. Similarly, the soluble lead concentration would decrease from 15 mg/L Pb to 3 mg/L Pb at equilibrium by the addition of 500 mg/L SO_4^{2-} . In contrast, chloride is not expected to precipitate lead but will complex lead and increase its solubility⁹. Based on these simple models, alkalinity and sulfate are expected to be beneficial in passivating lead-bearing plumbing materials while chloride is not.

Ionic Transport

The transport and prevalence of ions, such as sulfate and carbonate, at the surface of corroding lead-bearing materials is important in the passivation of the lead materials. The percentage of the anodic corrosion current that is carried by transport of certain ions (e.g., Cl^- ; Equation [2-1]) is a function of the molar concentrations of significant anions in water and the terminal velocity (also limiting equivalent ionic conductance) of each ion^{5, 22}. In typical potable water at pH 7.2, the dibasic phosphate (HPO_4^{2-}) concentration is half of the total phosphate concentration.

$$\% \text{ Current Carried by } \text{Cl}^- = \frac{[\text{Cl}^-]}{[\text{Cl}^-] + [\text{SO}_4^{2-}] \times 2.09 + [\text{HCO}_3^-] \times 0.58 + [\text{OH}^-] \times 2.59 + [\text{HPO}_4^{2-}] \times 0.86} \quad (2-1)$$

By equating the above equation for Cl^- to that for SO_4^{2-} for a condition when Cl^- and SO_4^{2-} are transported at equal rates to the lead anode surface, a critical CSMR of 0.77 is determined:

$$\text{CSMR Threshold} = \frac{\text{Molecular Weight of Cl}^-}{(\text{Molecular Weight of SO}_4^{2-}) / 2.09} = 0.77 \quad (2-2)$$

When the CSMR is greater than 0.77, which may be considered a threshold, adverse Cl^- ions concentrate more at the lead surface than beneficial SO_4^{2-} ions, potentially sustaining galvanic corrosion. In contrast, when the CSMR is below 0.77, the transport and concentration of beneficial sulfate to the lead anode surface exceeds that of chloride. This simplistically calculated threshold is in reasonable agreement with the empirically derived threshold of 0.5-0.6 established by Oliphant¹ and Edwards et al.⁵ (Figure 2-2).

Also based on Equation (2-1), bicarbonate ions (HCO_3^-) would carry more of the current when the alkalinity is higher. For example, if the chloride and sulfate concentrations were 17 mg/L Cl^- and 22 mg/L SO_4^{2-} , respectively, more HCO_3^- would be transported than chloride or sulfate when the alkalinity was 40 mg/L as CaCO_3 or greater. For greater chloride and sulfate concentrations than in the previous example, more alkalinity would be needed for HCO_3^- ions to

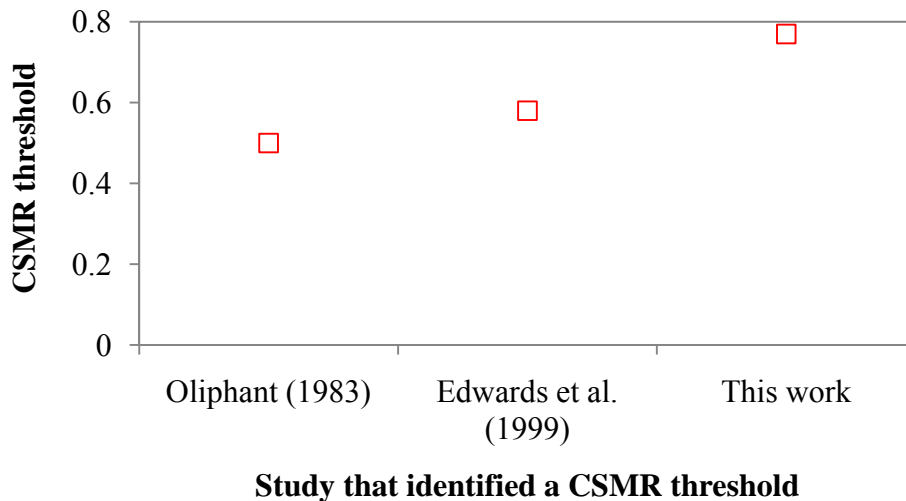


Figure 2-2. The chloride-to-sulfate mass ratio (CSMR) threshold above which lead problems would tend to occur, as identified in this and other work.

carry the same amount of current as chloride and sulfate ions. For a range of waters from utility case studies²³, higher percent current carried by Cl^- tended to increase lead release from solder, while a larger percentage of the current carried by SO_4^{2-} or HCO_3^- resulted in lower lead concentrations in water (results not shown).

The goal of this work is to unambiguously confirm the mechanistic basis of the chloride-to-sulfate mass ratio, by tracking reaction rates at a lead anode surface. The beneficial role of alkalinity is explored as part of that evaluation.

EXPERIMENTAL PROCEDURES

Apparatus

Gamry Electrochemical Test. The effects of chloride, sulfate, alkalinity, and water conductivity on the anodic reaction rates were evaluated using direct current potentiostatic corrosion tests with a Gamry Instruments electrochemical data analysis system. A lead wire with a wetted surface area of 240 mm^2 was used as the working electrode (anode), and a platinum wire (175 mm^2 area) was used as the counter electrode (cathode). The lead wire was polarized $+0.10 \text{ V}$ relative to the silver/silver chloride (Ag/AgCl) reference electrode, and the galvanic current and lead concentration in water were measured over time.

Simulated Soldered Copper Joints Using End Caps. Simulated joints were prepared by assembling a 24-mm diameter copper end cap and a 51-mm length of 19-mm diameter Type M copper pipe (Figure 2-3). A 152-mm length of 3-mm diameter 50:50 Pb-Sn solder was then melted to form a layer of solder at the bottom of the inner surface of the end cap. The galvanic lead soldered copper end caps were placed into glass containers and exposed to approximately

500 mL of each test water in triplicate. The headspace was minimized by filling the glass containers to capacity to limit dissolution of CO₂ from the air during stagnation. The water was changed using a dump-and-fill protocol twice per week⁶, and weekly composite samples were collected for each water condition at the end of each week. At Week 5, an “anode” sample was taken by carefully removing the soldered end cap from the glass vial and collected the ≈4 mL volume of water inside the end cap to be analyzed for metals (Pb, Sn) and chloride.

Galvanic Lead Solder Coupons. The 50:50 Pb-Sn soldered copper coupons for utility case studies were prepared as described elsewhere⁸. A 25.4-mm length of 3-mm diameter 50:50 Pb-Sn solder was placed on the inner edge of a 25.4-mm length of 12.7-mm diameter copper coupling. The galvanic lead solder-copper coupons were exposed to 100 mL of each test water in triplicate. The water was changed using a static “dump-and-fill” protocol⁶ twice per week (Monday/Thursday or Tuesday/Friday), and weekly composite samples were collected for each water condition at the end of each week. The stagnation time was selected to represent long stagnation times that can occur during weekends in building plumbing and that allow the

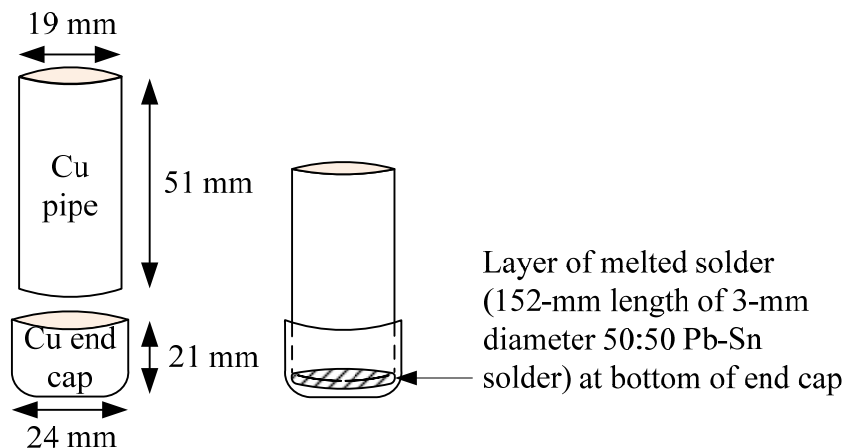


Figure 2-3. Schematic of the soldered end cap that was placed in a 500-mL glass container.

formation of microclimates that are detrimental to lead corrosion⁹. Each utility study lasted for at least 12 weeks.

Water Chemistry

All chemicals in this work were added as reagent grade salts to distilled and deionized water, except in the utility case studies, where water from the utility treatment plants were shipped to Virginia Tech.

Verification of Lead Solubility & Complexation. All solutions were prepared by dissolving 0.48 mM lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in distilled and deionized water and adjusting to a target pH of 3, 4, or 5 using nitric acid (HNO_3). The sulfate concentrations ranged from 0 to 2.1 mM (203 mg/L) SO_4^{2-} by adding sodium sulfate (Na_2SO_4). In the chloride complexation experiment, 0 to 8 mM Cl^- was added as sodium chloride (NaCl). Constant ionic strength of 0.01 M was maintained in each sulfate or chloride solution by adding sodium nitrate (NaNO_3). The final pH was adjusted to 3.00, 4.00, or 5.00 ± 0.05 using HNO_3 or sodium hydroxide (NaOH).

After 24 hours, unfiltered samples and samples filtered through 0.45 μm pore size nylon filters were collected for each sulfate solution. For the chloride solutions, the free Pb^{2+} concentration was measured, and filtered and unfiltered samples were collected to determine the total and soluble lead concentrations.

Gamry Electrochemical Tests with Cl^- , SO_4^{2-} , Alkalinity, and Conductivity. To evaluate the effects of chloride and sulfate on galvanic current, 0 to 1,000 mg/L Cl^- or SO_4^{2-} from NaCl or Na_2SO_4 were added to water (Table 2-1). The test waters were dosed with sodium bicarbonate

(Na_2HCO_3) to reach an alkalinity of 15 mg/L as CaCO_3 and were adjusted to pH 7 ± 0.1 prior to the start of the test.

A similar test to evaluate alkalinity and conductivity was conducted for 0 to 120 mg/L alkalinity as CaCO_3 (9-273 μS) and equivalent levels of conductivity (9-325 μS) by adding sodium perchlorate (NaClO_4) to pH 7.5 ± 0.1 water. The test waters contained 2 mg/L Cl and no sulfate.

Table 2-1. Water chemistry of test waters.

| (Case Study #) Water Type | Cl ⁻ , mg/L | SO ₄ ²⁻ , mg/L SO ₄ | CSMR ^(a) | Alkalinity, mg/L as CaCO ₃ | pH | Corrosion Inhibitor (dose) | Disinfectant (mg/L as Cl ₂) | Test Apparatus |
|--|----------------------------------|--|---------------------|---|---------------|---|--|---------------------------|
| Sulfate solubility study | 0 | 0-203 | - | 0 | 3, 4, or 5 | None | None | Beaker |
| Chloride complexation study | 0-284 | 0 | - | 0 | 3, 4, or 5 | None | None | Beaker |
| Electrochemical test (Cl ⁻ & SO ₄ ²⁻) | 0-1,000 | 0-1,000 | - | 15 | 7.0 | None | None | Gamry system |
| Electrochemical test (bicarbonate) | 2 | 0 | - | 0-120 | 7.5 | None | None | Gamry system |
| Electrochemical test (perchlorate/ conductivity) | 2 | 0 | - | 0 | 7.5 | None | None | Gamry system |
| Alkalinity test | 10 and 2 (after Week 5) | 0 | | 0-120 | 7.5 or 8.5 | None | None | Soldered Cu end caps |
| Utility A | 38 | 15 | 2.5 | 25-100 | 7.7 | Ortho- phosphate (1 mg/L P) | Chloramines (3.5 mg/L Cl ₂) ^(c) | Lead solder coupons |
| Utility B - Treated water subjected to corrosion control strategies | 8 (typ.) ^(b) or 17 | 2 | 4 (typ.) or 8.5 | 8 (typ.) or 20 | 7.3 | Ortho- phosphate (0 or 1 mg/L P) | Free chlorine (2 mg/L) | Lead solder coupons |
| Utility C – Lower alkalinity | 74 | 44 | 1.7 | 80 | 8.2 | none | Chloramines (2.5 mg/L Cl ₂) ^(d) | Lead solder coupons |
| Utility C – Higher alkalinity | 72 | 40 | 1.8 | 110 | | | | |

^(a) chloride-to-sulfate mass ratio (CSMR) provided as mg/L Cl⁻ per mg/L SO₄²⁻.

^(b) typical (typ.)

^(c) chloramines dose of 4:1 mg Cl₂/mg NH₃-N

^(d) chloramines dose of 5:1 mg Cl₂/mg NH₃-N

Simulated Joints Using End Caps. Water was prepared with 0-120 mg/L alkalinity as CaCO_3 , and chloride was added at a concentration of 10 mg/L Cl^- for the first 6 weeks and reduced to 2 mg/L Cl^- for Weeks 7 through 9 (Table 2-1). The final pH was adjusted to pH 7.5 or 8.5 (± 0.1) by dosing NaOH or carbon dioxide (CO_2).

Effect of Alkalinity: Utility Case Studies. Utilities A, B, and C water were evaluated with 50:50 Pb-Sn soldered copper coupons. Typical water from Utility A had a CSMR of 2.5 and an alkalinity of 25 mg/L as CaCO_3 . Supplemental alkalinities between 5 and 75 mg/L as CaCO_3 were evaluated in the study (Table 2-1). The typical water from Utility B had an alkalinity of 8 mg/L as CaCO_3 and a CSMR of about 4 (Table 2-1). To simulate a brine leak that occurred from the on-site hypochlorite disinfectant generator at Utility B, 9 mg/L Cl^- was added to the water after Week 17 of the study, increasing the CSMR to 8.5. In addition to a higher concentration of chloride, orthophosphate at a dose of 1 mg/L P and 20 mg/L alkalinity as CaCO_3 were also evaluated. Utility C water was a mixture of 50% groundwater and 50% desalinated water, which was obtained from a multi-stage nanofiltration process at the treatment plant and was amended with 40 mg/L alkalinity as CaCO_3 . The final blended water had a CSMR of 1.7 and an alkalinity of 80 mg/L as CaCO_3 . An aliquot of the water was dosed with NaHCO_3 to increase the alkalinity to 110 mg/L as CaCO_3 .

The final test waters were adjusted to match the pH, disinfectant dose, and corrosion inhibitor used at the treatment plant (Table 2-1). The final pH (7.7, 7.3, and 8.2 ± 0.1 for Utilities A, B, and C, respectively) and disinfectant concentrations (3.5 mg/L chloramines as Cl_2 , 2 mg/L free chlorine as Cl_2 , and 2.5 mg/L chloramines as Cl_2 for Utilities A, B, and C, respectively)

were the same within each case study. A 4:1 mg Cl₂/mg ammonia as nitrogen (NH₃-N) ratio was for Utility A, whereas a ratio of 5:1 mg Cl₂/mg NH₃-N was used for Utility C.

Analytical Methods

Concentrations of metals (e.g., Pb, Sn) and anions (e.g., Cl, SO₄²⁻) were quantified by acidifying collected water samples with 2% nitric acid for at least 24 hours and analyzing with an inductively coupled plasma mass spectrometer (ICP-MS) in accordance with Standard Method 3125-B²⁴⁻²⁶. Concentrations of chloride and sulfate were cross-checked using DIONEX DX-120 ion chromatography according to Standard Method 4110²⁴. Free Pb was measured using a Pb²⁺ ion specific electrode (ISE) manufactured by Cole Parmer, Inc. The pH in the bulk water was measured with an Accumet electrode in accordance with Standard Method 4500-H⁺ B²⁴. Electrochemical measurements were conducted using a Gamry Instruments system.

RESULTS AND DISCUSSION

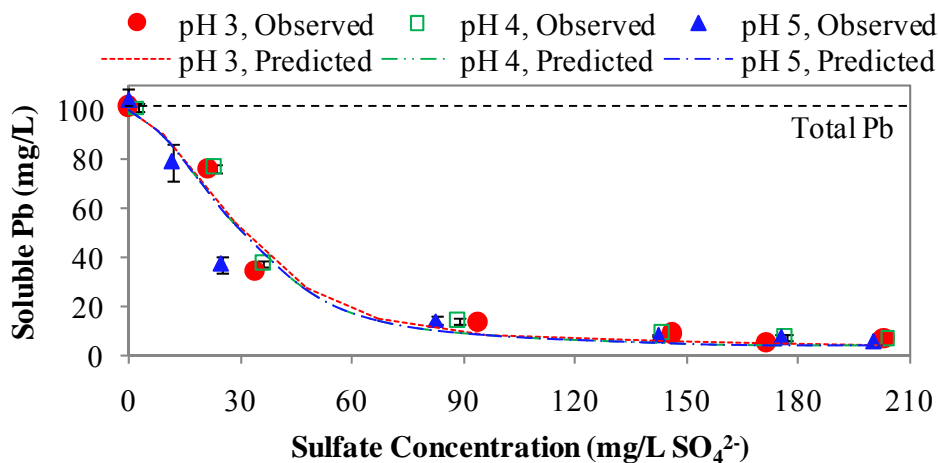
After verifying herein the predicted impacts of Cl⁻ and SO₄²⁻ on lead solubility at relatively low pH values found at surfaces of lead anodes⁹, the impacts of these anions and alkalinity on lead anode electrochemical reaction rates were defined. A final set of experiments verified the effects of these anions on lead corrosion in simulated lead solder plumbing joints.

Lead Sulfate Solubility and Chloride Complexation

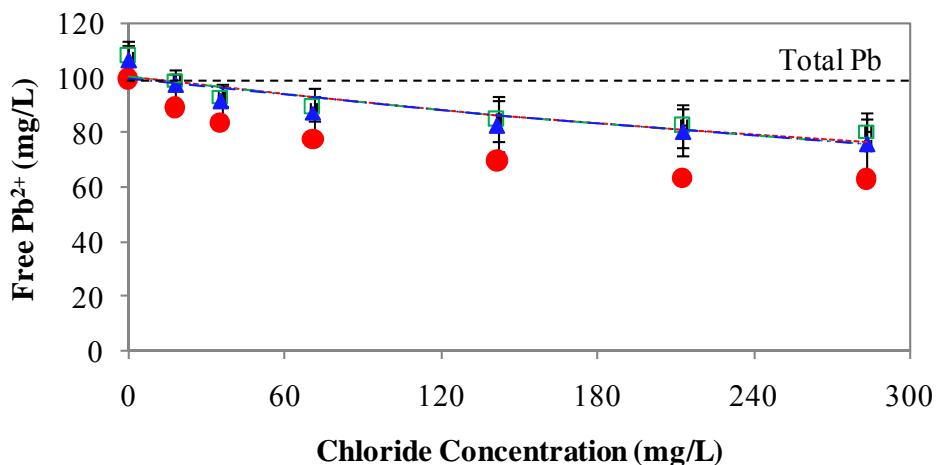
Solubility models predicting chemistry for the unusual conditions of low pH and concentrated sulfate or chloride at lead surfaces were tested.

Consistent with existing solubility models, adding 0 to 210 mg/L SO₄²⁻ (0-4 mM) sulfate at pH 3, 4, and 5 decreased soluble lead for water containing 100 mg/L total Pb (Figure 2-4a).

For example, 90 mg/L SO_4^{2-} precipitated about 60% of the lead. Concurrently, a visible precipitate formed, which had a Pb: SO_4 ratio of 0.93 ± 0.09 consistent with formation of PbSO_4 as per equilibrium modeling²⁷. Furthermore, based on soluble lead and sulfate data from the experiment, the optimized solubility product constant (K_{sp}) for lead sulfate was 1.54×10^{-8} , which



(a)



(b)

Figure 2-4. Effect of (a) sulfate addition on soluble lead and (b) chloride addition on free lead. All waters contained a total of 100 mg/L Pb. Predicted values were calculated from MINEQL⁺. Error bars indicate 95% confidence intervals.

is in very good agreement with previously determined values of 1.52×10^{-8} and 2.53×10^{-8} at 25°C ²⁸⁻³⁰. Under conditions favoring lead sulfate formation, lead solubility was not a function of pH over the range of 3 to 5 (Figure 2-4a).

No detectable precipitate (or decrease in soluble lead) occurred when the concentration of chloride increased from 0 to 280 mg/L in solutions with 100 mg/L Pb at pH 3, 4, and 5. However, the free lead decreased as chloride readily formed soluble complexes with Pb(II) (Figure 2-4b). An optimized formation constant of 59.5 for PbCl^+ was calculated by combining the data for pH 3, 4, and 5 and assuming that the PbCl^+ concentration was equal to the difference between the soluble and free lead concentrations. This value is very consistent with other work, which found that the complexation constant of PbCl^+ was 63 at 25°C ³¹.

In conclusion, greater electromigration of chloride versus sulfate towards lead anode surfaces would prevent formation of passive films, whereas greater electromigration of sulfate versus chloride could tend to form PbSO_4 passive films even at very low pH values. The next section examined this issue by tracking lead anode reaction kinetics in the presence of sulfate, chloride and bicarbonate.

Electrochemical Tests to Examine Effects of Chloride, Sulfate, Conductivity, and Alkalinity

Chloride and Sulfate. Previous work illustrated that higher sulfate concentrations relative to chloride in water can reduce galvanic corrosion of lead solder^{1, 2, 9}, and this hypothesis was confirmed in this study by tracking reaction kinetics of pure lead anodes. Specifically, the anodic current density between a corroding lead wire anode and a platinum cathode was about 1.3 A/m^2 for water with 10 mg/L Cl (Figure 2-5). Increasing the chloride concentration 10 times to 100 mg/L Cl⁻ elevated the galvanic current 5 times (Figure 2-5). In contrast, the galvanic

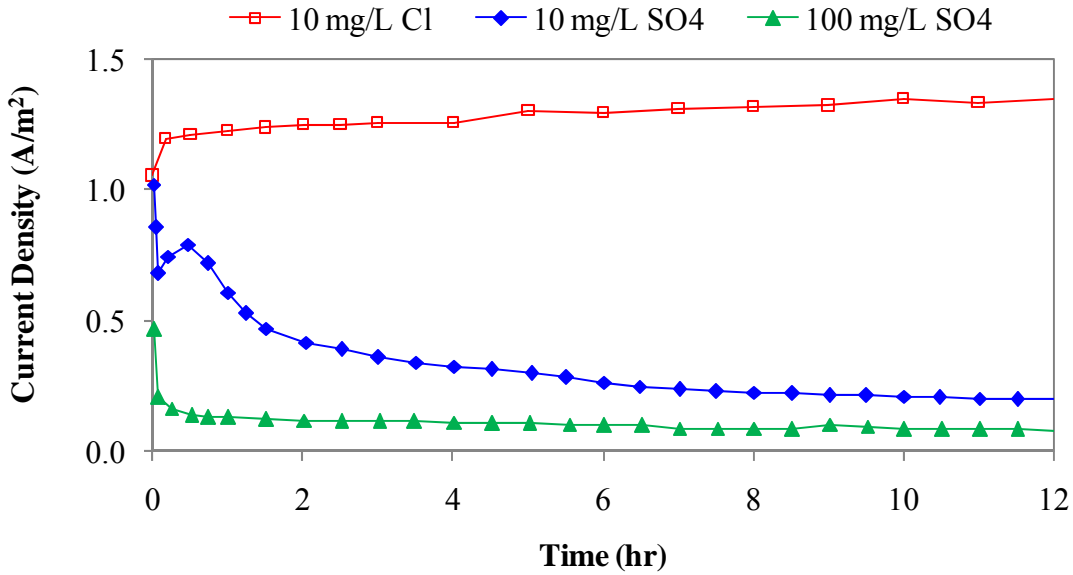


Figure 2-5. Effect of chloride (10 mg/L) and sulfate (10 and 100 mg/L SO₄²⁻) on galvanic current between lead wire and platinum electrode. The lead electrode was anodic to the platinum electrode in all conditions.

current was 5 times less for 10 mg/L SO₄²⁻ compared to that for 10 mg/L Cl⁻, and the benefits of the relatively low concentration of sulfate was apparent within the first hour (Figure 2-5). Increasing the concentration of sulfate from 10 to 100 mg/L SO₄²⁻ decreased the galvanic current density by 60% (Figure 2-5). Thus, the acceleration of lead dissolution at the anode surface by increasing chloride was confirmed, along with dramatically reduced lead corrosion rates by increasing the sulfate concentration.

Alkalinity and Conductivity. The same experimental setup was also used to test the effects of increasing alkalinity and conductivity on galvanic corrosion of lead. It has been established in literature that increasing conductivity, as would occur when adding bicarbonate or other salts to

water, can also increase galvanic corrosion rates³. With fewer ions in the water to carry the anodic current, very low conductivity water can limit galvanic corrosion.

For example, adding perchlorate, which is not known to form complexes or solids with lead, increased the conductivity of the water. Lead release and galvanic corrosion of lead wire increased (Figure 2-6). For low concentrations of bicarbonate (less than 10 mg/L as CaCO₃ or 25 μS), the effect of conductivity on increasing galvanic corrosion outweighed the pH buffering effect of alkalinity (Figure 2-6). When the alkalinity was above 10 mg/L as CaCO₃ (25 μS), high alkalinity mitigated galvanic corrosion, by presumably forming a protective lead carbonate coating on the anode surface (Figure 2-6). The dependence of lead release on conductivity implies that lead levels are linked to the current in the cell, and this was the observed with the linear relationship between lead in water and current (Figure 2-7).

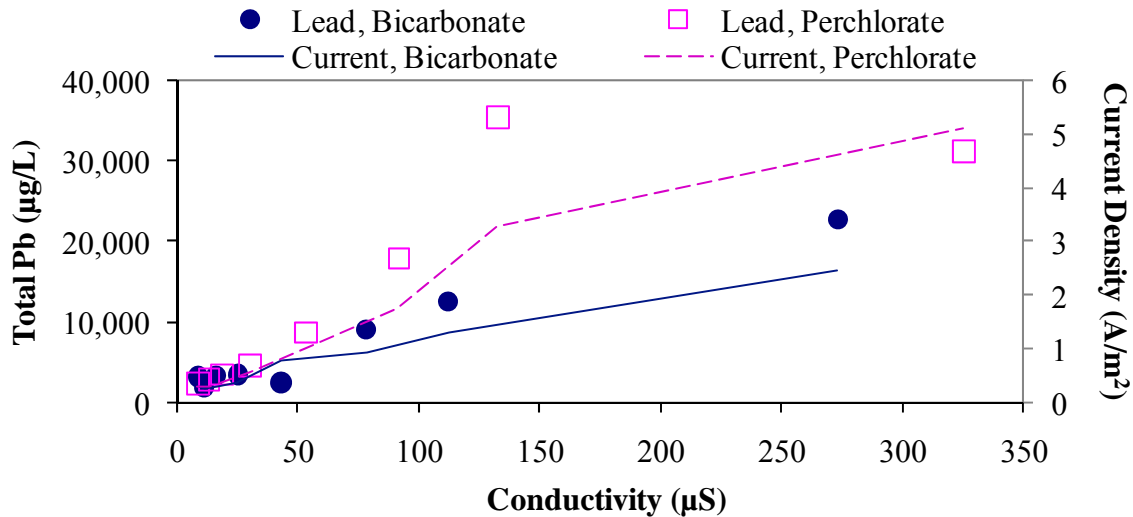


Figure 2-6. Lead release from lead wire (primary axis) and anodic current (secondary axis) as a function of conductivity. Results are after 12 hours of +0.1 V vs. E_{ref} polarization.

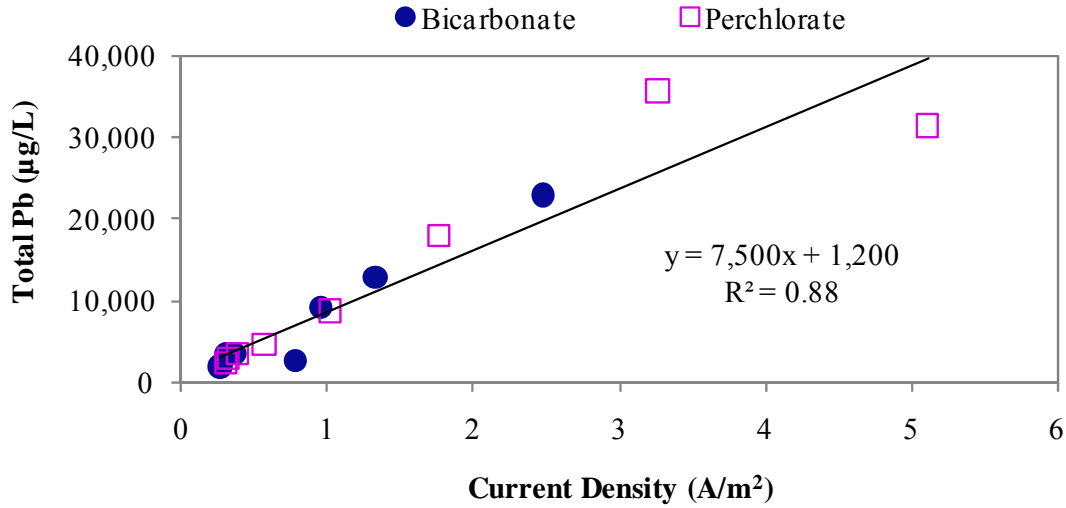


Figure 2-7. Lead release from lead as a function of current for perchlorate and bicarbonate.

Systematic Evaluation of Alkalinity Impacts in Potable Water

The above test with 0-120 mg/L alkalinity as CaCO_3 was repeated, but under more realistic conditions than the mechanistic electrochemical study. Simulated lead soldered joints using copper end caps (Figure 2-3) were exposed to 0-120 mg/L alkalinity as CaCO_3 and two chloride concentrations (2 mg/L Cl or 10 mg/L Cl added to all water). Both pH values of 7.5 and pH 8.5 were evaluated and had similar trends in this study; therefore, only pH 7.5 data are presented herein.

Although dosing 2.5 or 5 mg/L alkalinity as CaCO_3 reduced lead release from solder, the effect of alkalinity relative to water with 0 mg/L as CaCO_3 was not statistically significant until 20 mg/L as CaCO_3 or more was added for both concentrations of chloride evaluated (Figure 2-8). Unlike results from the electrochemical test (Figure 2-6), 20 mg/L as CaCO_3 (43 μS) was enough to reduce galvanic lead corrosion.

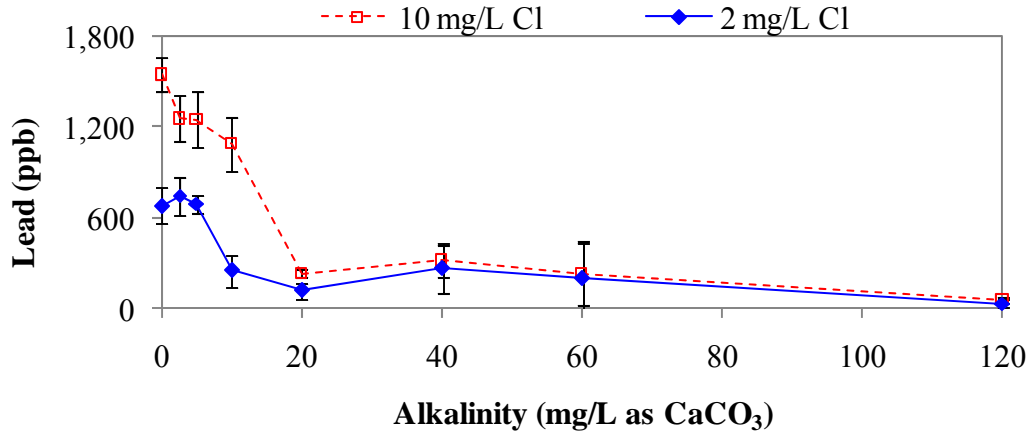


Figure 2-8. Lead release from solder as a function of alkalinity for water with 2 or 10 mg/L Cl at pH 7.5. The lead data for 2 mg/L Cl were the average of Weeks 7-8. The 10 mg/L Cl lead data were average lead in water during Weeks 5 and 6. Error bars represent the 95% confidence intervals.

If the chloride concentration was 10 mg/L versus 2 mg/L, Equation 2-1 predicts that higher alkalinity would be needed to counter the effects of more chloride being transported toward the lead surface, and this was confirmed in this study. Specifically, 20 mg/L as CaCO₃ was dosed to water containing 10 mg/L Cl to reduce the lead release to 250 µg/L, while half the alkalinity (10 mg/L as CaCO₃) was required for 2 mg/L Cl (Figure 2-8). Furthermore, if the alkalinity was 20 mg/L as CaCO₃ or less, water with 10 mg/L Cl significantly increased lead leaching from solder 2-4 times compared to water with 2 mg/L Cl. There was also 3 times more chloride measured near the anode surface than in the bulk water when the alkalinity was 10 mg/L as CaCO₃ or less and the water contained 10 mg/L Cl (results not shown). Moreover, higher lead leaching correlated with higher percentage of the current being carried by chloride ($R^2=0.74$), while more of the current being carried by bicarbonate ion resulted in less lead leaching ($R^2=0.73$).

The transport of bicarbonate competes with chloride and sulfate; therefore, higher alkalinity would be needed to overcome and passivate lead at high chloride concentrations. The required amount of alkalinity would vary from water to water. Competition between chloride and bicarbonate indicates how increasing the alkalinity of water at utilities can have no effect on the galvanic corrosion of lead.

Effect of Alkalinity in Utility Case Studies

Testing of chloride, sulfate, and alkalinity were extended to more realistic conditions using simulated lead soldered joints and water from several different utilities. These experiences indicated that increasing the alkalinity does not always mitigate lead problems when the CSMR of the water was relatively high.

Utility A. For example, increasing the alkalinity of from 25 to 100 mg/L as CaCO_3 had no significant impact on lead release for Utility A water, which had a high CSMR of 2.5 and contained orthophosphate (results not shown). Based on the ion transport equation (Equation [2-1]), increasing the alkalinity from 25 to 100 mg/L as CaCO_3 increased the calculated bicarbonate ion transport from 20% to 45%, while Cl^- transport decreased from 60% to 41%. It was speculated that much higher bicarbonate/alkalinity would be needed before benefits of alkalinity could be achieved. For example, an alkalinity of 200 mg/L as CaCO_3 could increase the amount of bicarbonate transport to 62% versus a transport of Cl^- of 29% for this water, and bicarbonate could begin to outcompete chloride and passivate lead by precipitating lead carbonates at the lead anode surface.

Utility B. In an unusual case (Utility B), increasing the alkalinity from 8 to 20 mg/L as CaCO_3 significantly increased lead release from galvanic solder by 6 times in the low conductivity water containing 8 mg/L Cl^- , 2 mg/L SO_4^{2-} (CSMR 4), and no phosphate (Figure 2-9). Moreover, for the same condition but with 1 mg/L P, lead release increased by 46 times with the addition of 12 mg/L as CaCO_3 . In these cases, greater alkalinity concurrently increased the conductivity by 40% (50 μS vs. 70 μS), which might explain some of the observed increase in galvanic lead corrosion³ and is consistent with other findings in this work (Figure 2-6).

However, when the chloride concentration was increased in Utility B water to 17 mg/L Cl^- (CSMR 8.5) to simulate a NaCl brine leak from an on-site hypochlorite generator, there was

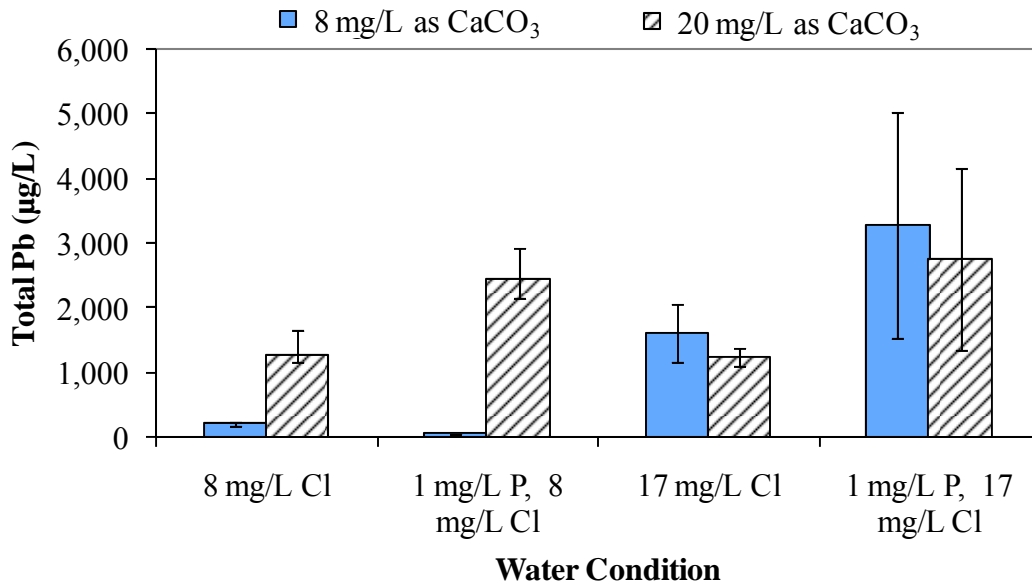


Figure 2-9. Lead leaching from lead solder-copper coupons in the Utility B case study. Light colored bars indicate the lead release at the typical alkalinity level for the utility (8 mg/L as CaCO_3), and the striped bars represent lead leaching in water dosed with bicarbonate (20 mg/L as CaCO_3). Lower chloride data are from Weeks 12-14 of the study, and higher chloride data are from Weeks 18-20 of the study. Error bars represent 95% confidence intervals.

no significant effect of alkalinity (+12 mg/L as CaCO_3) on lead leaching from solder (Figure 2-9). The increase in alkalinity resulted in 25% greater conductivity (90 μS vs. 112 μS). The difference in the effects of alkalinity at the two chloride levels may be due to the conductivity differences. That is, the utility's CSMR 4 water (8 mg/L Cl and 8 mg/L as CaCO_3) had low enough conductivity that galvanic corrosion was limited, but adding bicarbonate allowed significant ion and current transport. In contrast, adding bicarbonate to the CSMR 8.5 water (17 mg/L Cl), which had twice the conductivity of the CSMR 4 water, did not markedly increase the conductivity. Considering Equation (2-1), dosing bicarbonate to the CSMR 8.5 water only increased the amount of bicarbonate transport from 15% to 30%, while chloride transport was estimated to decrease from 78% to 63%.

Utility C. For another utility where desalinated water was blended with groundwater (high CSMR of 1.7), increasing the alkalinity from 80 to 110 mg/L as CaCO_3 increased lead release from solder by 10 times, and the results were significant with greater than 95% confidence (Figure 2-10). In this case, low conductivity was not an issue for this water. Considering ionic transport, the increased alkalinity did not significantly change SO_4^{2-} transport (24% to 21%) or Cl^- transport (52% to 48%), and the HCO_3^- transport was estimated to increase slightly from 23% to 31%. Clearly, the effects of alkalinity on galvanic lead solder corrosion are complicated and are not completely explained by simplistic models presented herein.

CONCLUSIONS

This work established that, even in acidic conditions found at the lead solder surface, sulfate forms precipitates with lead while chloride reacts with lead to form soluble complexes.

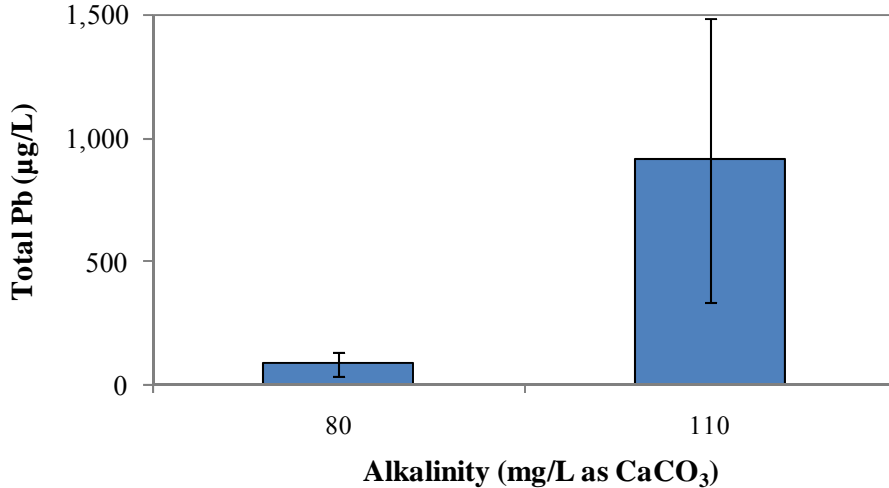


Figure 2-10. Lead release from lead solder connected to copper for a 50:50 blend of desalinated and groundwater. Results are from individual replicates during Week 11 of the study. Error bars represent 95% confidence intervals.

The detrimental effects of chloride and the benefit of sulfate on lead solubility provide a mechanistic explanation for the empirical value of the chloride-to-sulfate mass ratio in predicting trends in lead leaching from solder in at least some circumstances^{1, 2, 6, 13}. Based on calculations of the transport of anions through water, a CSMR above 0.77 would result in more chloride than sulfate being transported to the lead anode, thereby decreasing the mass of sulfate available to precipitate lead and passivate the anode surface.

The transport of bicarbonate ions competes with chloride and sulfate; therefore, higher alkalinity would be needed to overcome and passivate lead at high chloride concentrations, which can accumulate 13 times at the lead solder surface due to galvanic corrosion. This competition with chloride indicates how increasing the alkalinity of the water at utilities can have no effect on the galvanic corrosion of lead. Conceptually, if the alkalinity is increased to a high enough level, the benefits of alkalinity in buffering the pH during galvanic corrosion by forming

lead carbonate solids can be achieved, although the alkalinity required would depend on the water.

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CHAPTER 3: ACCELERATION OF GALVANIC LEAD SOLDER CORROSION DUE TO PHOSPHATE

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ABSTRACT

Although orthophosphate is often effective in reducing lead corrosion, bench-scale tests revealed cases in which even high doses of orthophosphate (1-3 mg/L P) in potable water increased lead and tin release from simulated soldered copper joints. Phosphate increased the galvanic current between tin and copper plumbing materials, especially in water with less than 10 mg/L SO_4^{2-} and when the percentage of the anodic current carried by SO_4^{2-} ion was less than 30%. Tin release was increased more than lead release from 50:50 Pb-Sn solder in these circumstances.

Keywords: tin, lead, alloy, copper, anodic dissolution

INTRODUCTION

Lead Solder Chemistry

Lead contamination of potable water due to galvanic attack of Pb-Sn solder was first demonstrated by Oliphant (1) and Gregory (2), who also discovered high and persistent galvanic currents between copper pipe and lead solder when the chloride-to-sulfate mass ratio (CSMR, or

mg/L Cl^- divided by mg/L SO_4^{2-}) of the water was above about 0.5. Other work by Edwards et al. (3) found more exceedances of the United States Environmental Protection Agency (USEPA) Lead and Copper Rule (LCR) when the CSMR was greater than 0.58. Recent work by Nguyen et al. (4) used theoretical transport considerations to identify a critical CSMR of 0.77, above which galvanic attack on lead solder would be expected to increase markedly. There were also several instances in which elevations of the CSMR above these thresholds increased the LCR 90th percentile lead and caused instances of lead poisoning of children (5-8).

Very corrosive microenvironments with high levels of chloride and low pH (e.g., 2.5) can form at lead solder anode surfaces due to galvanic corrosion between lead solder and copper pipe, perpetuating very high rates of lead corrosion (9). However, higher alkalinity is thought to buffer pH drops associated with galvanic corrosion at lead anode surfaces (10), and higher pH values may also decrease lead solubility (11-13). Lead oxides, which are well known to form protective scaling on lead surfaces, do not typically form on Pb-Sn solder surfaces unless the surface becomes severely depleted of tin (14-16).

Effect of Phosphate on Lead

In low alkalinity water, the optimal pH for orthophosphate inhibition of uniform lead corrosion is between 7.3-8 (13, 17). Orthophosphate has been a very effective inhibitor of lead corrosion in many cases (2, 11, 17-19). However, Oliphant (1) measured no decrease in the galvanic current between lead solder and copper when orthophosphate was dosed in pH 7.4-8.5 water, although the impact of orthophosphate on lead in water was never measured.

Equilibrium modeling can predict the solubility when lead phosphate is the controlling solid over the pH range 3-6 expected at the lead solder anode surface (Figure 3-1). For example,

56 µg/L soluble Pb is present in water at pH 6 water with 1 mg/L orthophosphate as P at equilibrium. However, if the pH decreased to 4, which can occur at lead solder surfaces during galvanic corrosion (9), the predicted soluble lead would increase by 370 times to 21 mg/L Pb. Clearly, soluble lead is expected to increase rapidly if the pH at the lead solder anode surface drops below about pH 4.6, even in the presence of orthophosphate and lead phosphate (Pb₃PO₄) surface scale.

Bulk water concentrations of sulfate are not expected to significantly alter the soluble lead concentration. However, if sulfate concentrated at the lead anode surface (9) 20 times from 10 mg/L SO₄²⁻ in the bulk water to 200 mg/L SO₄²⁻ at the anode, lead sulfate solids could limit the soluble lead to 4 mg/L Pb in the microlayer of pH 4 water at the lead surface (Figure 3-1). Other work with low sulfate (<20 mg/L SO₄²⁻) and low alkalinity water demonstrated that lead concentrations could reach 157 mg/L Pb or higher near lead anode surfaces (9).

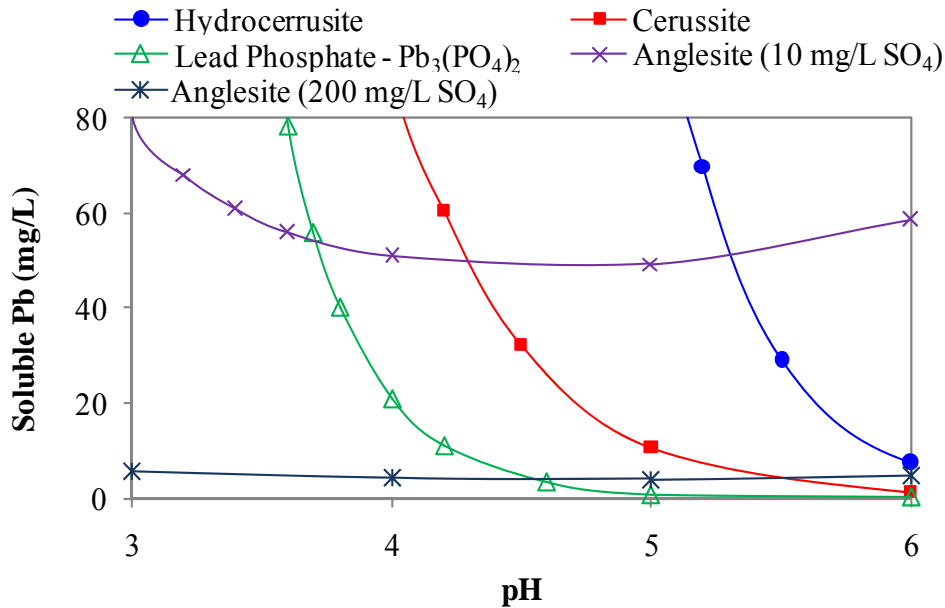


Figure 3-1. Equilibrium soluble Pb(II) between pH 3 and 6 for water with 20 mg/L alkalinity as CaCO₃ when anglesite, hydrocerrusite, cerrusite, or lead phosphate is the dominant solid. The modeled orthophosphate concentration was 1 mg/L P.

Tin Phosphate Chemistry

When tin metal corrodes, Sn(II) is first dissolved from tin metal, and the tin metal eventually completely passivates when Sn(II) at the metal surface oxidizes to Sn(IV) and SnO₂ (20, 21). Tin changes from passive to active corrosion at pH 4-5 (22). Furthermore, Awad (23) found that phosphate can corrode tin, hypothesizing that tin phosphate complexes formed. Later work by others reported formation constants for various tin phosphate complexes (24), and other tin complexes can form with hydroxide and chloride (25). In one study with 3,100 mg/L P, SnOH⁺ and tin phosphate complexes were thought to form (26, 27). Tin carbonate complexes have not been reported (28).

Equilibrium modeling demonstrates the hypothetical extent of tin phosphate complex formation assuming that the available complexation constants are accurate (Figure 3-2). Specifically, if 5 mg/L Sn(II) was released to the water, the soluble tin in water containing 3 mg/L P would be 85 µg/L, or 110 times more soluble tin than expected in water with no phosphate (0.76 µg/L). A large portion of the released tin would precipitate at equilibrium and

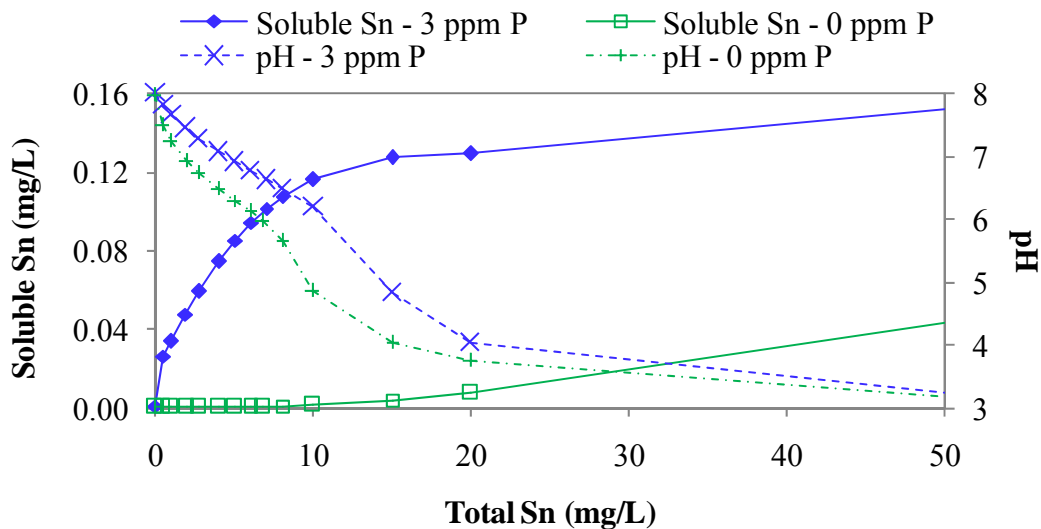


Figure 3-2. Equilibrium soluble Sn and pH due to release of Sn(II) at anode surfaces.

Alkalinity of the water was 8 mg/L as CaCO₃.

form scale in either case. The addition of phosphate also slightly buffers the pH drop associated with the Lewis acidity of tin (Figure 3-2).

The objective of this work is to identify the mechanisms by which phosphate can increase Pb-Sn solder corrosion in building plumbing systems, and to investigate the practical impact of orthophosphate on lead solder corrosion in simulated plumbing joints.

MATERIALS AND METHODS

Experimental Apparatus and Procedure

Macrocells. Simulated joints were prepared with pure tin wires and copper pipes as described elsewhere (9) to track galvanic corrosion occurring between the two metals. Water was changed in the macrocells three times per week (Monday, Wednesday, and Friday) using a “dump-and-fill” protocol (5). Tests were conducted in triplicate.

Soldered 19-mm pipes. Type M 19-mm diameter copper pipes were cut into 305-mm lengths, and one end of each pipe was dipped in molten 50:50 Pb-Sn solder with a depth of 29 mm. The pipes were filled with test water, closed on both ends with silicone stoppers, and tested in triplicate. Water was changed in the pipes three times per week using a “dump-and-fill” protocol (5).

Galvanic solder coupons. The 50:50 Pb-Sn solder-copper coupons for a utility case study was prepared from 25-mm lengths of 50:50 Pb-Sn solder and 13-mm diameter copper coupling as described elsewhere (29). The galvanic lead solder-copper coupons were exposed to 100 mL of each test water in triplicate. The water was changed using a “dump-and-fill” protocol (5) twice

per week (e.g., Monday/Thursday), and weekly composite samples were collected for each water condition at the end of each week. The stagnation time was selected to represent long stagnation times that can occur during weekends in building plumbing and that allow the formation of microclimates that are detrimental to lead corrosion (9).

Galvanic solder end caps. Simulated joints were prepared by assembling a 24-mm diameter copper end cap and a 51-mm length of 19-mm diameter Type M copper pipe as described elsewhere (4). A 152-mm length of 3-mm diameter 50:50 Pb-Sn solder was then melted to form a layer of solder at the bottom of the inner surface of the end cap. The galvanic lead soldered copper end caps were placed into glass containers and exposed to approximately 500 mL of each test water in triplicate. The water was changed using a “dump-and-fill” protocol twice per week (5), and weekly composite samples were collected for each water condition at the end of each week.

Water Chemistry

Macrocells. Treated water, but prior to disinfection, was received at Virginia Tech from the water utilities. Reagent grade chemicals were added to the water including orthophosphate corrosion inhibitor, bicarbonate, sulfate, disinfection with free chlorine, and acid or base for final pH adjustment (Table 3-1). The water from the treatment plant contained 4 mg/L Cl, and all waters were dosed with 10 mg/L Cl after Week 14 of the study to simulate a portion of the chloride that entered the water due to the hypochlorite generator brine leak.

The pH was adjusted with either 0.1 M NaOH or 0.1 M HNO₃ to the target value of pH 7.3 or 9.2. All water was also chlorinated at a dose of 2 mg/L Cl₂. Orthophosphate was dosed from sodium phosphate (Na₂HPO₄). Alkalinity was adjusted with sodium bicarbonate

(NaHCO₃). Chloride and sulfate were added from sodium chloride (NaCl) and sodium sulfate (Na₂SO₄), respectively.

Soldered 19-mm pipes. Water in this test had a CSMR of 1.2, alkalinity of 34 mg/L as CaCO₃, 2 mg/L Al (aluminum solids), 0.3 mg/L TOC from pre-chlorinated NOM, and 1.25 mg/L NH₃-N (Table 3-1). The pH was adjusted to 7.0 or 9.5 ± 0.2 with NaOH or HCl prior to exposure to the soldered pipes. Chloramine concentrations (0 or 5 mg/L Cl₂) and orthophosphate (0 or 3 mg/L as P) were varied in the test water. Chemicals were added as reagent grade salts to distilled and deionized water.

Galvanic solder coupons. The 50:50 Pb-Sn soldered copper coupons (29) were exposed to a utility water with a typical alkalinity of 8 mg/L as CaCO₃ and CSMR of about 4 (Table 3-1). To

Table 3-1. Water chemistry of test waters.

| Test (Apparatus) | Cl ⁻ , mg/L | SO ₄ ²⁻ , mg/L SO ₄ | CSMR ^a | Alkalinity, mg/L as CaCO ₃ | pH | Ortho- phosphate ^b (mg/L P) | Disinfectant (mg/L as Cl ₂) |
|---|--------------------------------|---|--------------------|---|-------------|--|--|
| Mechanism (macrocells) | 4 and 14 | 3-12 | 3-4.7 | 8-58 | 7.3 | 0 or 1 | Free chlorine (2 mg/L) |
| Case Study 1 (soldered 19-mm pipes) | 17 | 14 | 1.2 | 34 | 7 or 9.5 | 0 or 3 | Chloramines ^c (0 or 5 mg/L) |
| Case Study 2 (galvanic lead solder coupons) | 8 (typ.) ^d or 17 | 2 | 4 (typ.) or 8.5 | 8 (typ.) or 20 | 7.3 | 0, 1, 1.8 | Free chlorine (2 mg/L) |
| Case Study 3 (galvanic lead solder end caps) | 10 and 2 (after Week 5) | 0 | -- | 0-120 | 7.5 | 1 | none |

^a chloride-to-sulfate mass ratio (CSMR) provided as mg/L Cl⁻ per mg/L SO₄²⁻.

^b dose(s) evaluated in studies, excluding 0 mg/L P

^c chloramines dose of 4:1 mg Cl₂/mg NH₃-N

^d typical (typ.)

simulate a brine leak that occurred from the on-site hypochlorite disinfectant generator, 9 mg/L Cl from NaCl was added to the water after Week 17 of the study, increasing the CSMR to 8.5. Orthophosphate (NaH_2PO_4) at a dose of 1 mg/L P and 20 mg/L alkalinity as CaCO_3 from NaHCO_3 were also evaluated. The final test waters were adjusted to match the final pH (7.3) and disinfectant dose (2 mg/L free chlorine as Cl_2) used at the treatment plant (Table 3-1). Chemicals were added as reagent grade salts.

Galvanic solder end caps. Water was prepared with 0-120 mg/L alkalinity as CaCO_3 from NaHCO_3 . Chloride was added at a concentration of 10 mg/L Cl (from NaCl) for the first 6 weeks and reduced to 2 mg/L Cl for Weeks 7 through 9 (Table 3-1) to test the effects of two chloride levels. The final pH was adjusted to pH 7.5 or 8.5 by dosing NaOH or CO_2 . Chemicals were added as reagent grade salts to distilled and deionized water.

Analytical Methods

Total metals release was quantified after acidifying water samples with 2% nitric acid for at least 24 hours. Lead, tin, chloride, and sulfate concentrations in the bulk water were measured using an inductively coupled plasma mass spectrometer (ICP-MS) in accordance with Standard Method 3125-B (APHA, 30). Concentrations of chloride and sulfate were cross-checked using DIONEX DX-120 ion chromatography according to Standard Method 4110 (APHA, 30). The pH in the bulk water was measured with an Accumet electrode in accordance with Standard Method 4500- H^+ B (APHA, 30). Electrochemical measurements between the copper pipes and the tin wires in the macrocells were conducted using RadioShack multimeters with 100 Ω

resistance. Galvanic current measured between the anode (tin wire) and the cathode (copper) is an indicator of galvanic corrosion (ASTM, 31).

RESULTS AND DISCUSSION

The adverse effects of phosphate on lead leaching were quantified by comparing lead release to water with and without phosphate as follows:

$$\text{Pb Ratio} = \frac{\text{ppb Pb in water with phosphate}}{\text{ppb Pb in water without phosphate}} \quad \text{Equation (1)}$$

If the calculated ratio is less than 1, dosing phosphate to that specific water mitigated lead corrosion, whereas a ratio greater than 1 indicates that phosphate increased lead release. A similar calculation was done for tin. The calculated ratios were compared to the predicted percentage of the anodic corrosion current carried by transport of sulfate (SO_4^{2-}) ions through solution toward the lead solder anode as described elsewhere (3, 4). There was a tendency for phosphate to increase lead release if the sulfate concentrations were low (<10 mg/L SO_4) or if less than 30% of the carrying current was carried by sulfate ions (Figure 3-3). In some situations the addition of phosphate increased lead release to the water by a factor of 600% (i.e., Pb ratio of 6) (Figure 3-3). Moreover, the detrimental effect of phosphate on tin was even more dramatic, with as much as 14 times more tin in the water after addition of the orthophosphate corrosion inhibitor (Figure 3-3). These results suggest that an attack on the tin phase in 50:50 Pb-Sn solder alloy may be important to explaining the effect of phosphate on solder corrosion.

Mechanism of Phosphate Attack

To understand the increased dissolution of lead-tin solder due to orthophosphate, which was observed in some situations (Figure 3-3), a study was conducted to investigate the galvanic

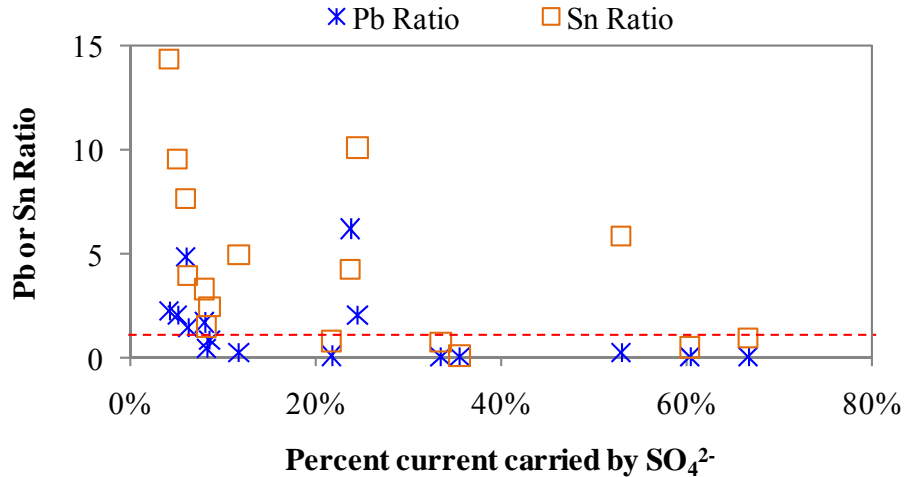


Figure 3-3. Lead (Pb) and tin (Sn) ratios for solder (metal concentration with phosphate divided by metal concentration without phosphate, Equation [1]) as a function of the percentage of current carried by SO_4^{2-} ion. The dashed line at a ratio of 1 indicates the level at which phosphate had no effect on lead or tin release. Data was reprocessed from previous studies (29, 33).

corrosion of pure tin wire connected to copper pipe. Specifically, water from a utility was subjected to a range of alkalinity, pH, and sulfate treatment strategies with and without orthophosphate (Table 3-1) and was tested using a macrocell apparatus (9). The galvanic current and tin concentration in water were tracked.

In half of the test water conditions, the galvanic current increased with the addition of 1 mg/L P, although the results were statistically significant only for the water with 10 mg/L alkalinity as CaCO_3 added (Figure 3-4). However, the tin concentrations increased 3-16 times due to the addition of 1 mg/L P for all of the water conditions (Figure 3-4), although the results

were not significantly different with 95% confidence in two waters (water amended with 10 mg/L SO_4^{2-} or 50 mg/L alkalinity as CaCO_3). Specifically, in the utility water with 18 mg/L alkalinity as CaCO_3 , the tin concentration increased 16 times from 40 ppb Sn to 670 ppb Sn by

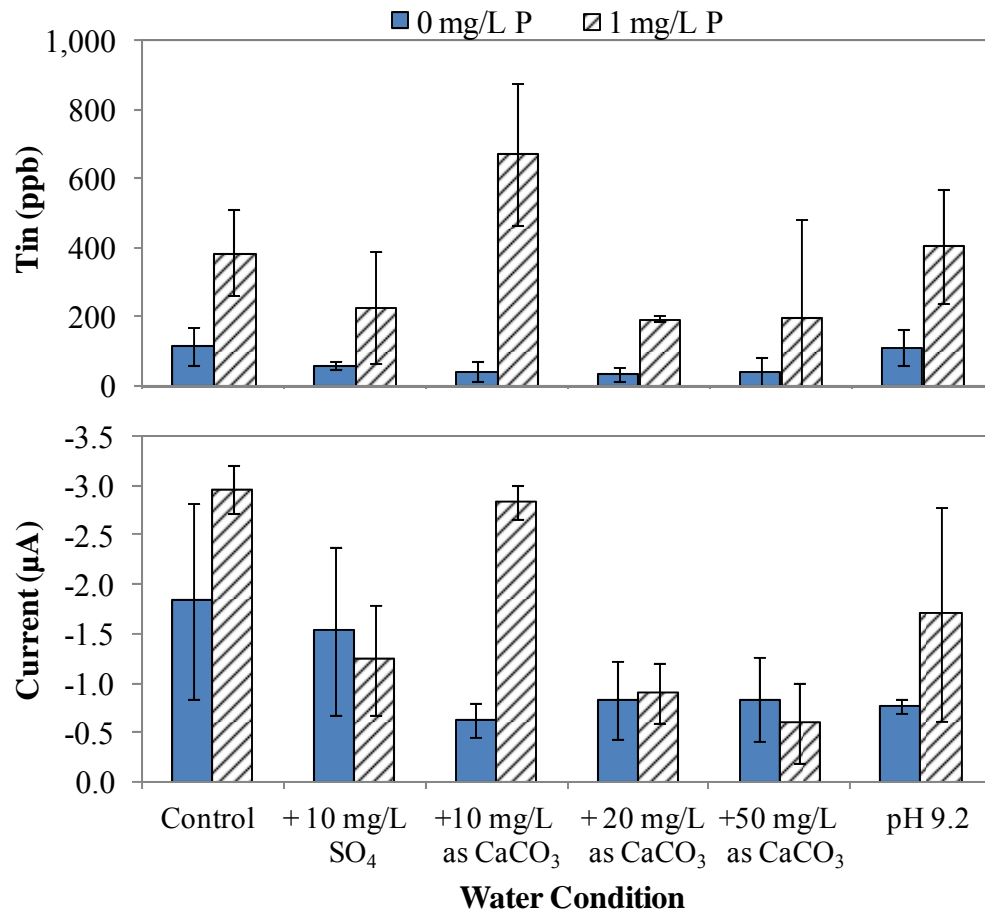


Figure 3-4. Total tin in water and galvanic current between pure tin wire and copper pipe in macrocells. The water had a pH of 7.3 and contained 3 mg/L SO_4^{2-} , 4 mg/L Cl^- , 8 mg/L alkalinity as CaCO_3 , 2 mg/L free chlorine as Cl_2 , unless otherwise specified. Data points are from Weeks 12-14 of the experimental study. Error bars represent 95% confidence intervals.

adding 1 mg/L P (Figure 3-4). Concurrently, the galvanic current increased 4.5 times from 0.6 μA to 2.8 μA (Figure 3-4). The trend in tin concentrations agreed with the predictions based on the current measurements and Faraday's law (results not shown), although a large portion of the oxidized tin likely accumulated in the scale (9). Similar observations of higher current and tin concentrations in water with phosphate were noted in tests with pure tin wire polarized -0.2 V vs. E_{ref} with a platinum counterelectrode (results not shown), and there was high variability in the galvanic current measurements among replicates. These higher tin concentrations and galvanic currents due to the orthophosphate addition in water with low sulfate (3 mg/L SO_4^{2-}) are consistent with previous findings (Figure 3-3). Between 7-21% of the anodic current was carried by sulfate in most of these test waters.

Clearly, the galvanic current sacrificing the Pb-Sn solder anode was increased due to orthophosphate in some cases, which in turn translates to lower pH and higher concentrations of aggressive anions such as Cl^- at the Pb-Sn solder surface (9).

Moreover, the increased lead and tin corrosion of solder at joints can decrease its integrity and cause premature failure in home plumbing (32, 33). The specific factors causing the increase in galvanic current was not identified in this work. However, it is possible that phosphate slowed the transition of Sn(II) to less soluble and more protective Sn(IV), thereby increasing the time for passivation of the metal and the amount of soluble tin in water containing phosphate. Future work is needed to confirm this mechanism.

Case Studies Where Phosphate Increased Lead Solder Corrosion

The macrocell study demonstrated that tin corrosion increased due to phosphate. Consequently, higher tin concentrations at the solder surface and the stronger Lewis acidity of tin compared to lead can promote corrosion of lead release from 50:50 Pb-Sn solder. Although there are numerous instances where phosphate was effective in inhibiting lead corrosion in potable water distribution systems (11, 13, 17-19), the following studies focus on cases where phosphate increased corrosion of Pb-Sn solder.

Case Study 1. In one water with an alkalinity of 34 mg/L as CaCO₃ and a CSMR of 1.2 (Table 3-1), lead release from galvanic 50:50 Pb-Sn solder increased as much as 2 times when 3 mg/L P was dosed. Specifically, in pH 7 water with 5 mg/L chloramines as Cl₂, lead release doubled from 4,580 ppb to 9,220 ppb, but the results were not significant at the 95% confidence level (Figure 3-5). However, tin was more affected than lead by phosphate, and the tin concentration significantly increased 3-10 times when 3 mg/L P was added (Figure 3-5). In the same water in which the lead concentration doubled (pH 7 and 5 mg/L Cl₂), tin release increased by an order of magnitude from 110 ppb to 1,070 ppb. Water at pH 7 appeared to be more affected by phosphate than pH 9.5 water (Figure 3-5). That is, phosphate increased tin release 7-10 times in pH 7 water, whereas an increase of 3-4 times more tin was observed in water at pH 9.5 due to phosphate. There was no evidence that chloramine disinfectant significantly affected solder corrosion for this water.

In addition to higher lead and tin concentrations, more white particles, which were presumably lead and tin colloidal particles, could be observed in the potable water with orthophosphate compared to the same water with no phosphate (ex., Figure 3-6). In this case

study, tin corrosion unambiguously increased due to orthophosphate, which is consistent with observations for pure tin wire (Figure 3-4) and in some previous work with 50:50 Pb-Sn solder (Figure 3-3).

Case Study 2. Consistent with expectations from other studies (2, 11, 13, 17-19), orthophosphate decreased lead corrosion of solder coupons for a utility water with 8 mg/L Cl and

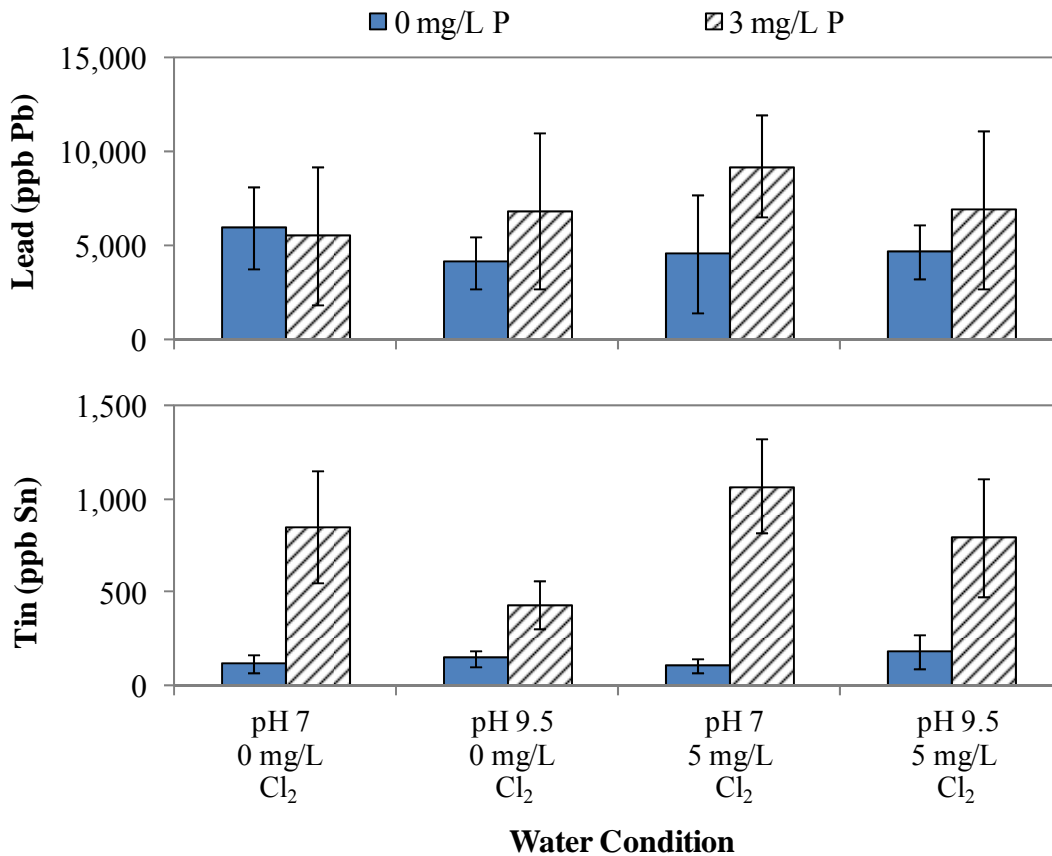


Figure 3-5. Lead and tin release from soldered copper pipes exposed to a water with a CSMR of 1.2, alkalinity of 34 mg/L as CaCO₃, and chloramines disinfectant where indicated. Data are from Weeks 1, 3, 6, and 8 of the study. Error bars represent 95% confidence intervals.

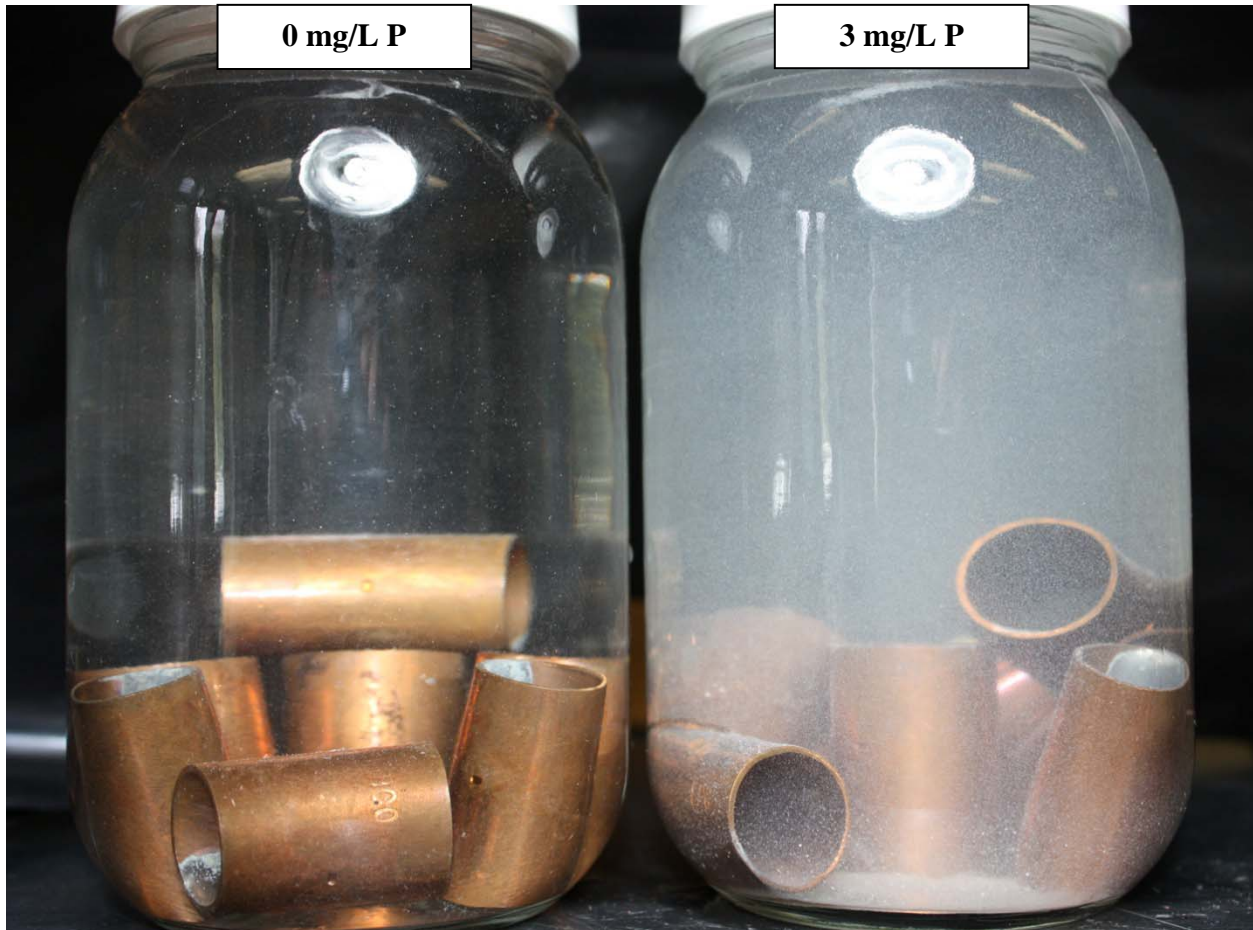


Figure 3-6. Example of white colloidal particles released from galvanic lead solder coupons in pH 7 water with orthophosphate (right) compared to the same water without orthophosphate corrosion inhibitor (left).

8 mg/L alkalinity as CaCO_3 (Figure 3-7). However, in the other test water conditions, including water with a higher alkalinity of 20 mg/L as CaCO_3 or chloride concentration of 17 mg/L Cl, lead release increased by 2 times with the addition of 1 mg/L P. The results were significant at the 95% confidence level for the condition with 20 mg/L as CaCO_3 and 8 mg/L Cl.

Moreover, for the same soldered coupons, tin release increased 2-14 times for all of the test water types due to orthophosphate, and the results were significant at the 95% confidence level, with the exception of the water with an alkalinity of 8 mg/L as CaCO_3 and 8 mg/L Cl. In

the worst case in water with 20 mg/L as CaCO_3 and 17 mg/L Cl, adding 1 mg/L P increased tin release by 14 times from 40 ppb Sn to 580 ppb Sn (Figure 3-7). Furthermore, increasing the alkalinity slightly in this water worsened the effect of phosphate on tin corrosion, even though significant increases in lead corrosion were observed at both alkalinities. Specifically, adding 1 mg/L P to water with an alkalinity of 20 mg/L as CaCO_2 increased tin release 5-14 times, whereas adding phosphate to lower alkalinity water (8 mg/L as CaCO_3) increased tin release 2-9 times (Figure 3-7). Additionally, water with more chloride worsened the effect of phosphate. For example, dosing orthophosphate to water with 8 mg/L Cl increased tin release 2-5 times,

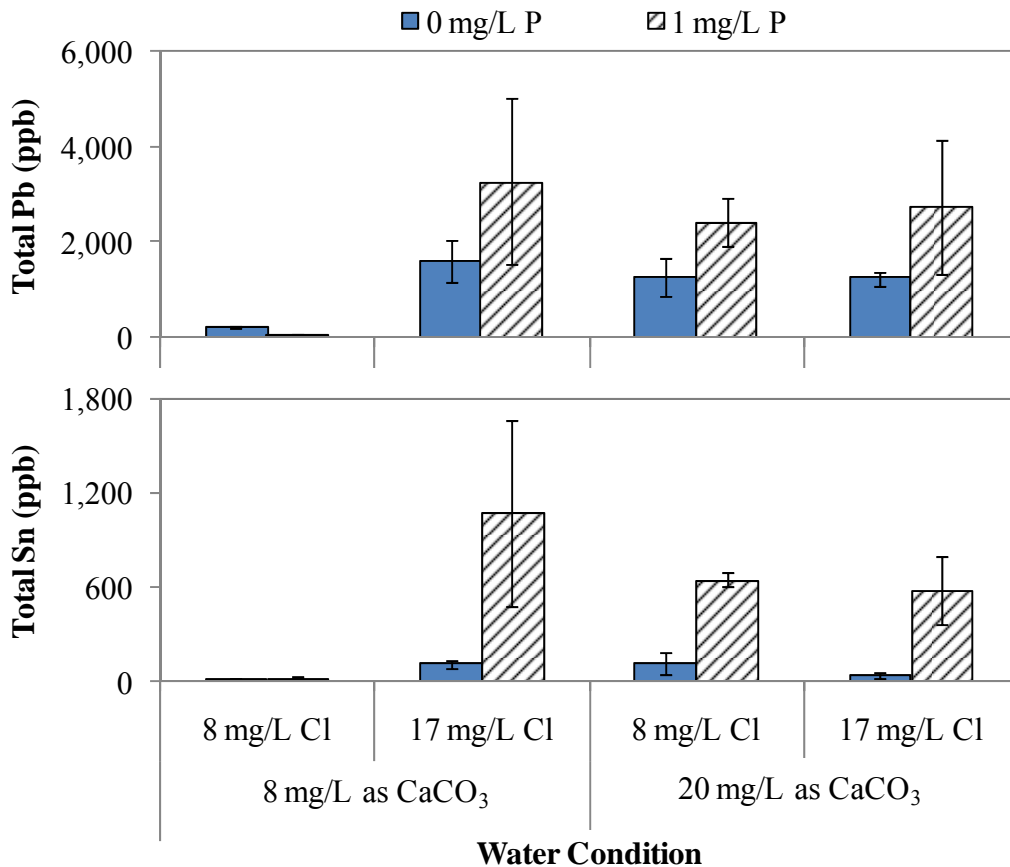


Figure 3-7. Effect of phosphate on total lead and tin release from galvanic 50:50 Pb-Sn solder. Data for 8 mg/L Cl was collected during Weeks 12-14 of the study, while 17 mg/L Cl data was from Weeks 18-20. Error bars represent 95% confidence intervals.

while an increase of 9-14 times more tin was measured in water with 17 mg/L Cl. In summary, for most of the waters tested in this utility study, phosphate significantly increased tin release from 50:50 Pb-Sn solder, and increases in lead release were also observed.

Case Study 3. In water containing 2 mg/L Cl and alkalinity in the range of 0-120 mg/L as CaCO₃, lead release from soldered end caps increased between 30% and 950% due to phosphate, and the results were statistically significant for all conditions, with the exception of 40 and 60 mg/L alkalinity as CaCO₃ (Figure 3-8). For example, lead release increased by a factor of 4

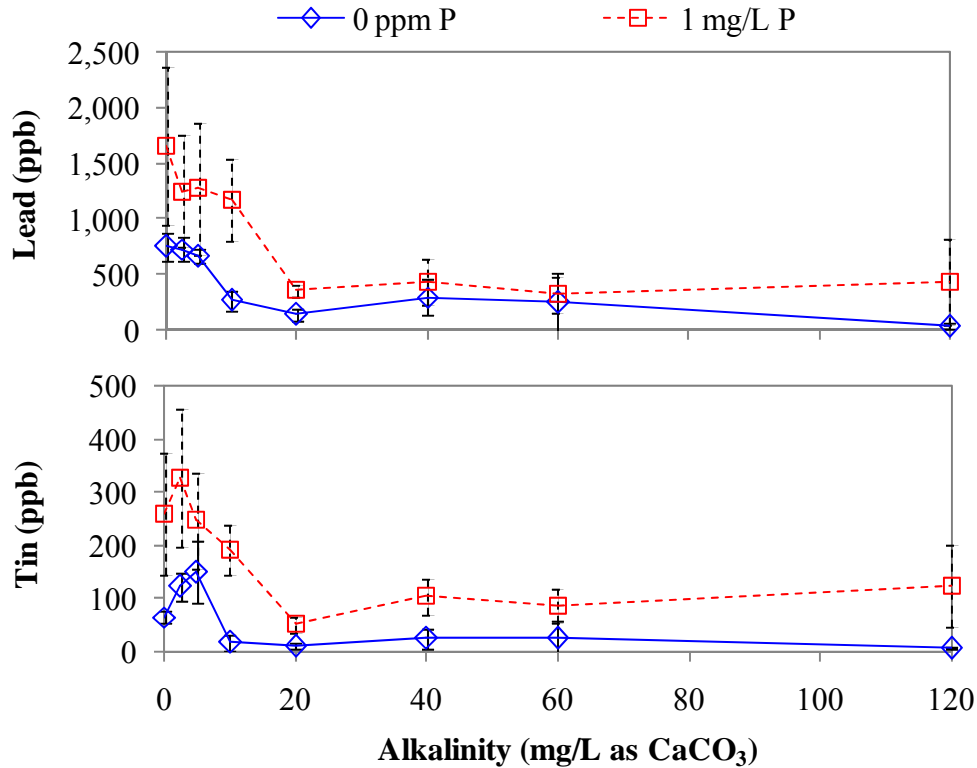


Figure 3-8. Lead (top) and tin (bottom) released from galvanic lead solder-copper end caps as a function of alkalinity. The water contained 2 mg/L Cl, and the data points are average concentrations from the triplicates during Weeks 7-8. Error bars denote 95% confidence intervals.

from 270 ppb Pb to 1,170 ppb in water with 10 mg/L as CaCO₃ when 1 mg/L P was added (Figure 3-8). Moreover, higher alkalinity did not reduce the effect of phosphate, although less lead was measured in water with lower alkalinity. For example, lead in water with 120 mg/L as CaCO₃ increased an order of magnitude from 40 ppb to 440 ppb Pb when phosphate was added. However, much higher alkalinity might mitigate lead corrosion (4).

Completely consistent with the other case studies, the effect of phosphate on tin release was more dramatic than lead, with increases from 65% to more than 2,000% more tin in this water when 1 mg/L P was added. Specifically, 1 mg/L P increased tin release by an order of magnitude from 18 ppb Sn to 190 ppb Sn in water with 10 mg/L alkalinity as CaCO₃ (Figure 3-8). Moreover, the largest impact of phosphate was observed at the highest alkalinity level (120 mg/L as CaCO₃), in which case tin release increased 20 times from 6 ppb Sn to 125 ppb Sn with the addition of phosphate. Phosphate significantly increased tin release for all alkalinity levels at the 95% confidence level, with the exception of water with 5 mg/L as CaCO₃.

To further compare the relative effect of phosphate on lead and tin release among the alkalinity levels and the two chloride concentrations in this study, the ratio of lead or tin release with phosphate versus without phosphate (Equation [1]) was calculated. In this case study, the Pb and Sn ratios were not significantly affected by the chloride concentration in this study (2 or 10 mg/L Cl) (Figure 3-9). The Pb ratios for most of the conditions were between 1 and 4 and was as high as 12 for 120 mg/L as CaCO₃, indicating that phosphate increased lead release in these test waters. The Sn ratios were higher than those calculated for lead and were between 1 and 10 in most cases, again indicating that tin was more affected by phosphate than lead (Figure 3-9). Higher chloride (10 mg/L vs. 2 mg/L Cl) worsened the effect of phosphate on tin when the alkalinity was 5 mg/L as CaCO₃ or less (Figure 3-9), which is consistent with findings in Case

Study 1 with low alkalinity water (Figure 3-7). In summary, dosing 1 mg/L P significantly increased lead and tin release from soldered end caps in this case study, and the impact of orthophosphate was worse for tin. Additionally, higher chloride in low alkalinity water worsened the phosphate effect.

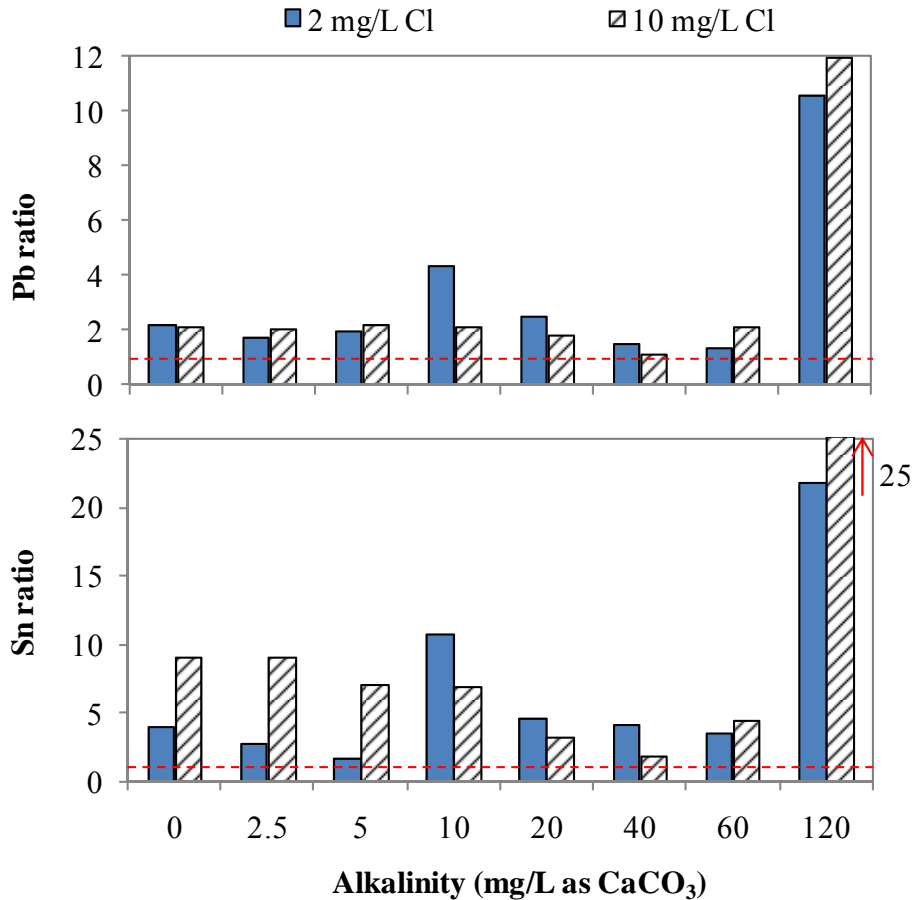


Figure 3-9. Lead ratio (top) and tin ratio (bottom) for 2 and 10 mg/L Cl and alkalinity ranging between 0 and 120 mg/L as CaCO₃. The lead ratio was defined as lead release to water with phosphate divided by lead release without phosphate (Equation [1]), and the tin ratio was the same formula but with tin release. The water contained no sulfate. Data for 2 and 10 mg/L Cl were from Weeks 7-8 and Weeks 5-6, respectively. The dashed line at a ratio of 1 indicates the level at which phosphate had no effect on lead or tin release.

CONCLUSIONS

- Dosing of orthophosphate occasionally creates significant adverse consequences on galvanic corrosion of lead bearing plumbing materials connected to copper tube. Because orthophosphate often has profound benefits in reducing lead release during uniform corrosion, the net impacts of orthophosphate on overall lead release including brass and lead pipe can be complicated.
- The tendency toward adverse consequences of orthophosphate on galvanic corrosion of lead increased if the sulfate concentration was less than about 10 mg/L SO_4^{2-} or if the percentage of the current carried by SO_4^{2-} was less than 30%.
- In cases where orthophosphate exacerbated galvanic corrosion of 50:50 Pb-Sn solder, tin release was more strongly affected than lead.
- In certain waters, dosing orthophosphate increased the galvanic current and tin release from pure tin connected to copper pipe, which can be expected to reduce anode surface pH to a level where it cannot be passivated.
- Consistent with other work, phosphate had a more detrimental effect on corrosion of Pb-Sn solder at pH 7 than at pH 9.5 in one water tested.
- Higher alkalinity did not mitigate the adverse effects of phosphate, but more lead and tin corrosion did occur at lower alkalinity.
- Higher concentrations of chloride in low alkalinity water (<10 mg/L as CaCO_3) also worsened the effects of phosphate on solder corrosion.

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CHAPTER 4: NITRATE ACCELERATED CORROSION OF LEAD SOLDER IN POTABLE WATER SYSTEMS

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ABSTRACT

Although nitrate is generally believed to have little effect on lead corrosion, bench-scale tests in this work revealed that increasing nitrate in the range of occurrence in potable water (0-10 mg/L N) can dramatically increase lead leaching from simulated soldered pipe joints. Lead in water created slightly increased galvanic currents between solder and copper pipe, but nitrate also altered the nature of the attack in a manner that caused solder particles to detach into the water. Chloramine decay and the associated conversion of ammonia to nitrate could create much higher lead contamination of potable water from solder in some cases.

Keywords: Pitting corrosion, oxidation, anodic dissolution

INTRODUCTION

Nitrate (NO_3^-) concentrations in drinking water are increasing in some areas of the country due to fertilizer run-off, release of other nitrogen containing compounds from industry, and nitrification in chloraminated systems [1-4]. The U.S. Environmental Protection Agency (USEPA) has established a maximum contaminant level (MCL) of 10 mg/L $\text{NO}_3\text{-N}$ due to

concern over adverse health effects [5, 6]. While many water supplies contain less than 0.1 mg/L $\text{NO}_3\text{-N}$, exceedances of the nitrate MCL are not uncommon and may be increasing [7].

It is commonly believed that nitrate generally has little or no effect on corrosion of pure lead pipe or lead solder [8]. However, prior studies of galvanic corrosion due to the physical connection between lead solder and copper pipe noted that the surface potential was very unstable in water with greater than 1 mg/L $\text{NO}_3\text{-N}$ [9]. Although Gregory [9] did not measure the effects of nitrate on metals release, follow-up research by Dudi [10] noted a significant increase in lead release from leaded brass when 10 mg/L $\text{NO}_3\text{-N}$ was dosed. Higher lead leaching has also been reported after nitrifying bacteria reduced pH and converted ammonia to nitrate [4, 11-13]. However, Zhang [14] determined that the adverse effect of nitrification for pure lead pipes was attributable to the reduced pH instead of the formation of nitrate from ammonia.

Other work on lead corrosion in water with high pH and high nitrate concentrations found that nitrate contributed to the breakdown of passivating scale and created non-uniform corrosion. Rehim [15] and Amin [16] noted that increasing nitrate concentrations, albeit at levels far higher than drinking water (0 to 3,500 mg/L $\text{NO}_3\text{-N}$), increased the current density in electrochemical cells with lead anodes. Those authors and others also observed more pitting corrosion on lead surfaces [15, 16] and tin surfaces [17] with higher nitrate concentrations, but increasing alkalinity and phosphate mitigated the nitrate induced pitting to some extent [16, 18]. This is consistent with other work where phosphate was effective in inhibiting lead corrosion [9, 19-22]. Additionally, higher alkalinity is believed to buffer pH drops that occur during galvanic corrosion at lead anode surfaces [10], and more alkaline pH values generally decrease lead solubility [21, 23, 24].

In light of the observations regarding potential adverse impacts of nitrate on aspects of lead corrosion, this work was designed to: 1) determine if changes in nitrate in the range commonly encountered in potable water (0-10 mg/L) could adversely affect lead corrosion and lead contamination of potable water; and 2) isolate possible abiotic impacts of nitrification on lead leaching from soldered joints in systems practicing chloramination. Because Zhang [14] confirmed the conventional wisdom that slight changes in nitrate (0-2 mg/L N) had little or no effect on lead leaching from lead pipe alone, potential impacts on galvanic corrosion of lead solder:copper joints was a focus of this research.

MATERIALS AND METHODS

Experimental Apparatus

Macrocells. The simulated copper pipe joint macrocells were designed to allow measurement of the galvanic current between 50:50 Pb-Sn solder and copper. The macrocell was constructed with 50:50 Pb-Sn solder wire and copper pipes as described elsewhere [25]. The copper-to-solder ratio was approximately 34:1.

Solder Coupons. The second apparatus was a galvanic lead solder:copper coupon simulating lead solder in a typical copper pipe joint in a home, which was assembled by melting a 25-mm length of 3-mm diameter 50:50 Pb-Sn solder to a 25-mm length of 13-mm diameter copper pipe coupling [26]. The approximate solder-to-copper wetted surface area was 1:7.3. The solder coupons were placed in glass containers and exposed to 100 mL of each test water, and each condition was tested with at least three replicates.

Water Chemistry and Testing Sequence

Work was conducted in four phases. Phases 1 and 2 were carried out using macrocells, and Phases 3 and 4 were conducted using solder coupons. Test water in Phases 1 through 3 had 24 mg/L alkalinity as CaCO_3 (from NaHCO_3), 21 ± 1 mg/L Cl^- (from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), 45 ± 3 mg/L SO_4^{2-} (from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and MgSO_4), and a chloride-to-sulphate mass ratio (CSMR) of about 0.47 (Table 4-1). Similar water was used in Phase 4, but the chloride concentration was increased in some water conditions to represent chloramine decay in a distribution system (Tables 4-2 and 4-3).

When chloramine disinfectant was added in Phases 2 through 4, a 4:1 mg $\text{Cl}_2/\text{mg N}$ ratio was used. Nitrate was added as NaNO_3 , and all chemicals were added as reagent grade salts to distilled and deionised water. The pH of all conditions was adjusted to 7.7 ± 0.1 by adding CO_2 before placing the water in the test cells.

Phase 1. The macrocells were exposed to approximately 110 mL of each test water (Table 4-1), and water was changed using a static “dump-and-fill” method [27].

Phase 2. Waters with 0, 1, 2.5, and 10 mg/L $\text{NO}_3\text{-N}$ were tested in triplicate with macrocells for a period of 10 days in Phase 2 (Table 4-1), and no disinfectant was added. The conductivity ranged from 172 μS to 311 μS due to differences in the nitrate concentration (Table 4-1). The water was changed three times (every 3 or 4 days) using a “dump-and-fill” method [27].

Triplicate samples were collected, and each sample was analyzed for lead.

Table 4-1. Summary of water quality used in Phases 1, 2, and 3.

| Parameter | Target Nitrate (mg/L NO ₃ -N) | | | | |
|--|--|------|------|------|------|
| | 0 | 1 | 2.5 | 5 | 10 |
| Actual nitrate (mg/L NO ₃ -N) | 0 | 0.93 | 2.4 | 5 | 11 |
| Chloride (mg/L Cl ⁻) | 22 | 21 | 21 | 21 | 21 |
| Sulphate (mg/L SO ₄ ²⁻) | 46 | 48 | 43 | 44 | 45 |
| CSMR ^(a) | 0.47 | 0.44 | 0.49 | 0.49 | 0.47 |
| Alkalinity (mg/L as CaCO ₃) | 24 | 24 | 24 | 24 | 24 |
| Conductivity (μS) | 172 | 177 | 251 | 273 | 314 |

^(a) Chloride-to-sulphate mass ratio (CSMR).

Phase 3. This phase of the study tested whether increasing nitrate from 0 mg/L to 10 mg/L NO₃-N increased lead release from solder coupons. Water with 0, 1, 2.5, 5, and 10 mg/L NO₃-N (Table 4-1) were selected to represent the typical range found in drinking water and was disinfected with chloramine (3.5 mg/L Cl₂). The test waters were exposed to solder coupons in five replicates for 9 weeks. The water was changed using a static “dump-and-fill” protocol [27] twice per week (Monday and Thursday) to simulate “worst-case” 3-day stagnation conditions encountered in school plumbing systems over weekends. At Week 9 after the lead concentration did not decrease significantly with time, which suggested that the system had reached pseudo steady-state, individual samples were collected from each of the five replicates to indicate the relative error among the replicates.

Phase 4. The simulated abiotic effect of nitrification in a system using chloramine disinfectant was tested in Phase 4 with solder coupons in triplicate. The test waters were selected to simulate the extreme change in nitrogen chemistry that could occur as water leaves a treatment plant and passes through a distribution system. That is, chloramine (NH_2Cl) first decays to chloride and ammonia (NH_3), followed by conversion of ammonia to nitrite (NO_2^-) and nitrate (Table 4-2).

To examine a “worst-case” scenario based on results from Phase 3, where the corrosive nitrate threshold occurred with 2.5 mg/L $\text{NO}_3\text{-N}$, all water in Phase 4 were dosed with 1.25 mg/L $\text{NO}_3\text{-N}$. Therefore, if nitrification occurred in water with 4 mg/L chloramine as Cl_2 and 1 mg/L $\text{NH}_3\text{-N}$ (4:1 ratio of mg Cl_2 /mg $\text{NH}_3\text{-N}$), 1 mg/L $\text{NO}_3\text{-N}$ would form (or a total of 2.25 mg/L $\text{NO}_3\text{-N}$) and likely would be corrosive to lead solder. The six water conditions evaluated in Phase 4 were designed to simulate the extremes that could be encountered in a groundwater system with chlorine, chloramine, and various stages of chloramine decay/nitrification, but at a constant pH of 7.7 to isolate changes in ammonia speciation (Table 4-3).

Table 4-2. Summary of reactions and effects of chloramine decay on chloride, nitrate, and nitrite concentrations.

| Reaction | Balanced Equation | Key Impact |
|------------|---|---|
| Reaction 1 | $3 \text{NH}_2\text{Cl} \rightarrow \text{N}_2 + \text{NH}_3 + 3\text{Cl}^- + 3\text{H}^+$ | Increase in chloride (2 mg/L Cl^- per 1 mg/L Cl_2) and formation of $\text{NH}_3\text{-N}$ |
| Reaction 2 | $\text{NH}_4^+ + 1.9\text{O}_2 + 0.069\text{CO}_2 + 0.0172 \text{HCO}_3^- \rightarrow 0.0172\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.983\text{NO}_2 + 0.966\text{H}_2\text{O} + 1.97\text{H}^+$ | Increase in nitrite (1 mg/L $\text{NO}_2\text{-N}$ per 1 mg/L $\text{NH}_3\text{-N}$) |
| Reaction 3 | $\text{NO}_2 + 0.00875\text{NH}_4^+ + 0.035\text{CO}_2 + 0.00875\text{HCO}_3^- + 0.456\text{O}_2 + 0.00875\text{H}_2\text{O} \rightarrow 0.00875\text{C}_5\text{H}_7\text{O}_2 + \text{NO}_3^-$ | Increase in nitrate (1 mg/L $\text{NO}_3\text{-N}$ per 1 mg/L $\text{NO}_2\text{-N}$) |

[4, 28, 29]

Table 4-3. Summary of water conditions in Phase 4.

| Parameter | Water Condition | | | | | |
|---|----------------------|-----------------------------------|---------------------------------|---|--|--|
| | Control ^a | Free Cl ₂ ^b | NH ₂ Cl ^c | Cl ⁻ +NH ₃ ^d | Cl ⁻ +NO ₂ ^{-e} | Cl ⁻ +NO ₃ ^{-f} |
| Target nitrate (mg/L NO ₃ -N) | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 2.25 |
| Target nitrite (mg/L NO ₂ -N) | 0 | 0 | 0 | 0 | 1 | 0 |
| Target total chlorine (mg/L Cl ₂) | 0 | 1 | 4 | 0 | 0 | 0 |
| Target ammonia (mg/L NH ₃ -N) | 0 | 0 | 1 | 1 | 0 | 0 |
| Chloride prior to disinfectant decay (mg/L Cl) | 21 | 21 | 21 | 28 | 28 | 28 |
| Sulphate (mg/L SO ₄ ²⁻) | 42 | 41 | 41 | 41 | 40 | 41 |
| CSMR ^(g) | 0.50 | 0.51 | 0.51 | 0.68 | 0.70 | 0.68 |
| Conductivity (µS) | 192 | 204 | 223 | 235 | 243 | 241 |
| Conductivity after increase ^(h) (µS) | 283 | 292 | 311 | 323 | 332 | 332 |

^a Control water was the 1.25 mg/L NO₃-N from Table 4-1.

^b Control water dosed with 1 mg/L chlorine disinfectant.

^c Control water dosed with chloramine disinfectant (4 mg/L as Cl₂), 4:1 ratio Cl₂:NH₃-N.

^d Chloraminated control water after Reaction 1 (Table 4-2).

^e Chloraminated control water after Reaction 2 converted to nitrite (Reaction 1+ Reaction 2; Table 4-2)

^f Chloraminated control water after Reaction 3 (Table 4-2).

^g Chloride-to-sulphate mass ratio (CSMR).

^h After 6 weeks, base-level nitrate was increased from 1.25 mg/L to 5 mg/L NO₃-N.

After Week 6 of Phase 4, the nitrate concentration was increased by 3.75 mg/L NO₃-N for all of the water conditions (Table 4-3), increasing the nitrate concentration to at least 5 mg/L NO₃-N for all water.

Analytical Methods

Collected samples after exposure to the macrocells or solder coupons were acidified with 2% nitric acid for at least 24 hours to dissolve metals and analyzed with an inductively coupled plasma mass spectrometer (ICP-MS) according to Standard Method 3125-B [30]. The pH in the bulk water was measured with an electrode according to Standard Method 4500-H⁺ [30]. Ammonia was measured using the salicylate method on a Hach DR 2700 spectrophotometer, according to Standard Method 4500-NH₃ [30]. Total and free chlorine were measured on a Hach DR 2700 spectrophotometer in accordance with Standard Method 4500-Cl [30]. Nitrate and nitrite were measured using DIONEX DX-120 ion chromatography, according to Standard Method 4110 [30]. Galvanic current measurements between the copper pipes and solder in the macrocells were conducted using RadioShack multimeters with 100 Ω resistance. In the convention of this work, negative currents indicated that the lead solder was the anode and was being sacrificed while the copper pipe was the cathode and was being protected.

RESULTS AND DISCUSSION

Mechanistic Study

The magnitude of the galvanic current between the solder and copper pipe increased from approximately 20 μA to 35 μA when the nitrate (NO₃⁻) concentration increased from 0 to 10 mg/L NO₃-N (Figure 4-1). This doubling in the amount of current between the lead solder and

copper could be due to the higher nitrate concentration or the concurrent doubling in the conductivity [8]. A two-tailed t-test confirmed the relationship between higher nitrate (or higher conductivity) and the higher galvanic current with greater than 95% confidence.

The trend in galvanic currents in Phase 1 was confirmed by lead in water measurements in Phase 2. The lead released from lead solder in the macrocells increased nearly 2 times from 1,100 ppb Pb to 2,100 ppb Pb when nitrate increased from 0 to 10 mg/L N (Figure 4-2). The impact of higher nitrate was relatively low in these short-term tests with separate anode and cathode arrangements, and follow-up testing used more realistic simulations of lead solder:copper joints using solder coupons.

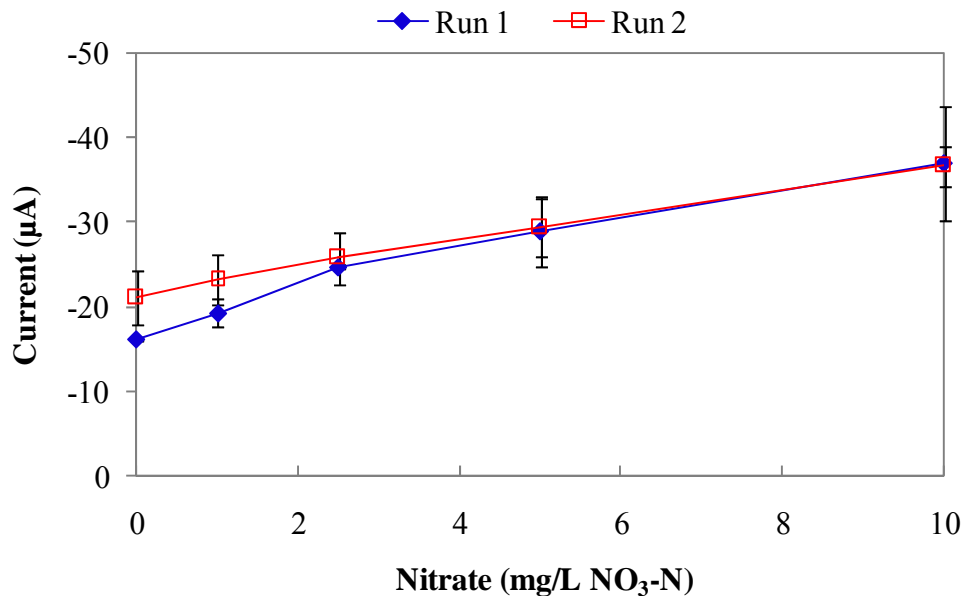


Figure 4-1. Impact of increasing nitrate in macrocells on galvanic current in Phase 1. Error bars represent 95% confidence intervals. Negative currents indicate that lead solder was sacrificed and that the copper pipe was protected.

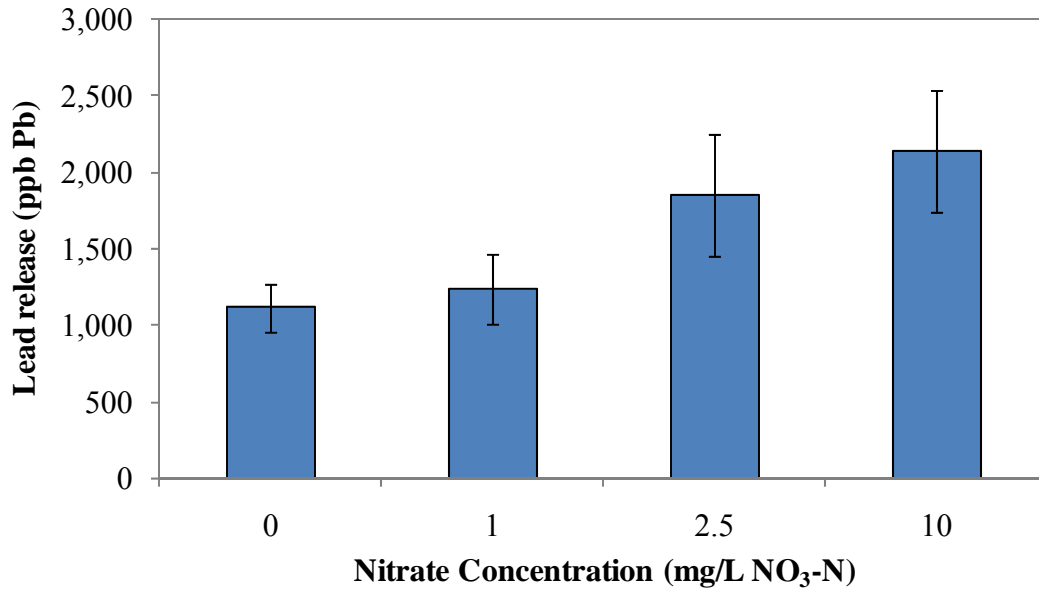


Figure 4-2. Lead in water after 3-4 days of stagnation as a function of the nitrate concentration in macrocells in Phase 2. Error bars represent 95% confidence intervals.

Effect of Nitrate on Galvanic Lead Solder Coupons

Essential trace nutrients to inhibit nitrification [31, 32] were not added to the water, and a nitrogen mass balance (i.e., nitrate, nitrite, and ammonia) in the third phase of testing indicated no significant changes in nitrite, total ammonia, or nitrate during the tests after accounting for trace residual nitrate from glassware due to nitric acid washing (Table 4-4). Thus, significant biological activity was not occurring.

Increasing the nitrate concentration from 0 to 10 mg/L NO₃-N dramatically increased lead leaching from solder coupons. Consistent with expectations, the condition with 0 mg/L NO₃-N had the lowest lead release with 18 ppb Pb at Week 9 (Figure 4-3). When the nitrate concentration was increased from 0 to 1 mg/L NO₃-N, lead release to the water increased by 2 times to 29 ppb Pb. Moreover, increasing nitrate to 2.5 mg/L NO₃-N increased lead in water to

Table 4-4. Nitrate and ammonia values measured before and after a stagnation period during Phase 3. Nitrite values were always below detection (<0.1 mg/L NO₂-N).

| Target Nitrate (mg/L NO ₃ -N) | Nitrate (mg/L NO ₃ -N) | | Ammonia (mg/L NH ₃ -N) | |
|---|-----------------------------------|-------|-----------------------------------|-------|
| | Before | After | Before | After |
| 0 | 0.00 | 0.24 | 0.89 | 0.82 |
| 1 | 0.93 | 1.66 | 0.89 | 0.80 |
| 2.5 | 2.37 | 2.58 | 0.91 | 0.78 |
| 5 | 4.98 | 5.59 | 0.88 | 0.82 |
| 10 | 10.68 | 11.03 | 0.92 | 0.80 |

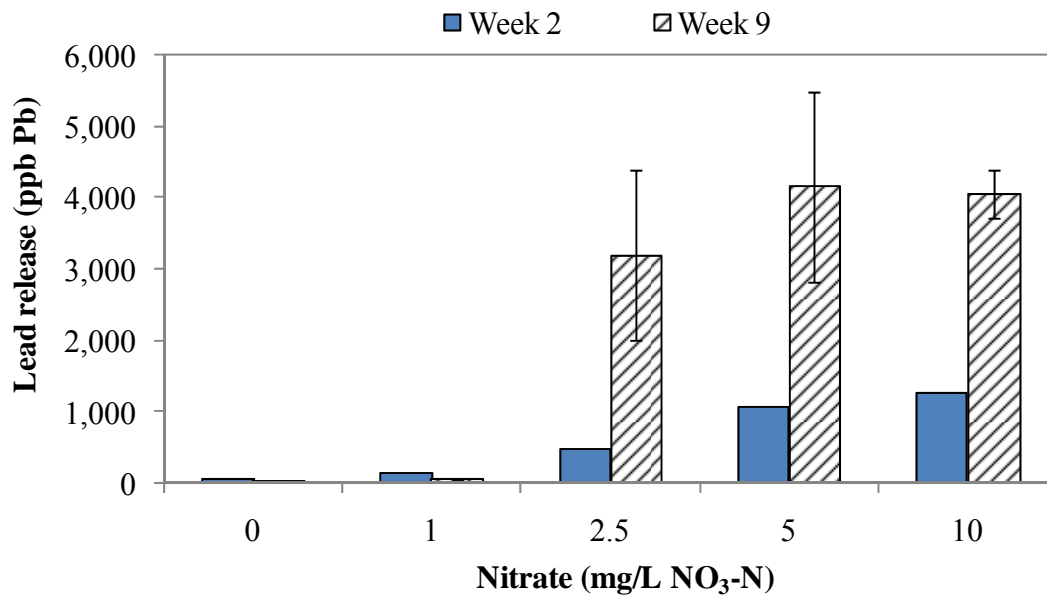


Figure 4-3. Effect of increasing nitrate on lead release from solder coupons in Phase 3.

Results are shown from Week 2 and Week 9 of the study. Error bars represent 95% confidence intervals for Week 9.

3,500 ppb Pb, or **194 times** relative to water with no nitrate. Further increases in nitrate had lower impact on lead corrosion, but greater nitrate concentrations still increased the average lead release (although the differences were not statistically different). Compared to Week 2, these lead concentrations for water containing at least 2.5 mg/L NO₃-N resulted in at least 3 times more lead at Week 9 than at Week 2, suggesting that the impact of higher nitrate concentrations could worsen with time. In contrast, the conditions with low nitrate (0-1 mg/L NO₃-N) had about 65-80% less lead in water at Week 9 than Week 2. T-tests with triplicate data from Week 9 confirmed that the highest three nitrate conditions (2.5, 5, and 10 mg/L NO₃-N) released significantly more lead with greater than 95% confidence than the lower two nitrate conditions (0 and 1 mg/L NO₃-N).

Increasing the conductivity by adding nitrate to the water can explain some of the increases in galvanic lead corrosion [8]. However, a parallel study with the same water but with chloride (from NaCl) instead of nitrate added to the water found much lower lead release for the same conductivity (results not shown). Specifically, lead release in water with the same conductivity as the test water with 10 mg/L NO₃-N (311 μS) had 32 times less lead or 140 ppb Pb at Week 9 (results not shown) compared to the 10 mg/L NO₃-N water. That is, nitrate was more corrosive than chloride for this water type, and the much increased lead contamination of the water from nitrate was not explained by higher conductivity alone.

Visually, the solder coupons exposed to 10 mg/L NO₃-N in Phase 3 were corroded to a much greater extent than solder coupons without nitrate (Figure 4-4). Moreover, the water with more nitrate caused pieces of the lead solder to peel away from the surface of the copper coupling, and the surface of the solder became non-uniformly corroded. In some cases, pieces of metallic solder were observed to detach from the solder coupon into the water. The

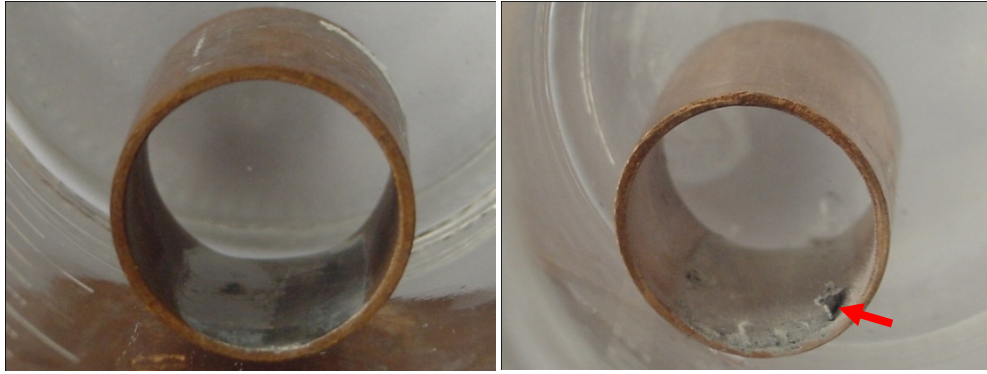


Figure 4-4. Galvanic lead solder coupons after 6 weeks of exposure to 0 mg/L NO₃-N (left) and 10 mg/L NO₃-N (right) in Phase 3.

measurements of lead in water confirmed the visual observations of aggressive attack on the lead solder. It is possible that the 50:50 Pb-Sn solder was attacked through intergranular corrosion, which is a well-known mechanism for nitrate-induced corrosion of steel and silver [33, 34]. Nitrate was not part of the cathodic reaction because the nitrate concentration did not decrease after stagnation (Table 4-4), which was a mechanism observed by others in the corrosion of tin in low pH (3.5) canned food [35].

Clearly the impacts of nitrate in the longer-term testing with solder coupons were dramatically worse than observed in testing with the macrocell (Phases 1 and 2). Specifically, solder coupons exposed to 2.5 mg/L NO₃-N water had 8.6 times more lead leaching at Week 2 than the control water without nitrate (Figure 4-3). In contrast, the same change in the nitrate concentration in the macrocell test resulted in only 1.7 times more lead release and galvanic current (Figure 4-2). The effect of nitrate appears to be attributable to a highly localized attack on the lead solder, which caused pieces of solder to fall into the water, because relatively slight increases in galvanic current due to the nitrate (or concomitant increase in conductivity) were observed in the macrocell arrangement. Other possible explanations for the discrepancy include:

1) differences due to melting of the solder in the solder coupon, versus using unmelted Pb/Sn solder wire in the macrocell, 2) larger physical distance between the lead solder wire and the copper pipe cathode in the macrocell ($\frac{1}{2}$ cm path length through water) compared to the simulated joint (direct connection of 0 cm). In any case, results suggest that in actual joints found in a potable water system, the nitrate effect could sometimes be severe.

Effect of Disinfectants and Simulated Nitrification on Lead Release

The impacts observed in Figure 4-3 raised serious concerns about whether changes in nitrogen speciation occurring in systems using chloramine disinfectant could affect lead leaching from solder in homes. A series of tests was designed to simulate biological consequences of nitrification by examining abiotic changes in nitrogen chemistry that can occur in a distribution system as water leaves a treatment plant and passes through a distribution system [4]. That is, chloramine (NH_2Cl) first decays to chloride (Cl^-) and ammonia (NH_3), followed by conversion of ammonia to nitrite (NO_2^-) and nitrate (Table 4-2). These simulated reactions were evaluated at two levels of nitrate: (1) less than 2.5 mg/L N, and (2) greater than 5 mg/L N.

Conditions with less than 2.5 mg/L $\text{NO}_3\text{-N}$. The control condition, which had 1.25 mg/L $\text{NO}_3\text{-N}$, released 110 ppb Pb from the solder coupons (Figure 4-5). Disinfectant dosing of either free chlorine or chloramine significantly decreased lead leaching relative to the control water with no disinfectant. Specifically, dosing 1 mg/L free chlorine disinfectant (as Cl_2) decreased lead leaching by about 50%, whereas 4 mg/L chloramine (as Cl_2) decreased lead leaching by about 75% (Figure 4-5). During stagnation in this bench-scale test, the free chlorine decayed 100% to chloride, whereas the chloramine decayed about 90%.

In the test simulating complete decay of chloramine to Cl^- and NH_3 , lead leaching increased to about 190 ppb Pb, or 1.7 times more than the control condition and 7.2 times more than the chloramine condition. In the condition representing complete conversion of chloramine to NO_3^- and Cl^- , lead leaching increased to 520 ppb Pb, which was 4.7 times more lead than the control condition, and 20 times more lead than the chloramine condition (Figure 4-5).

Interestingly, the condition simulating complete conversion of chloramine to Cl^- and NO_2^- was similar to the control condition, but was about 3.7 times higher than the chloramine condition (Figure 4-5).

T-tests confirmed all the trends with greater than 95% confidence with Bonferroni correction. The results illustrate that even without accounting for the potentially important

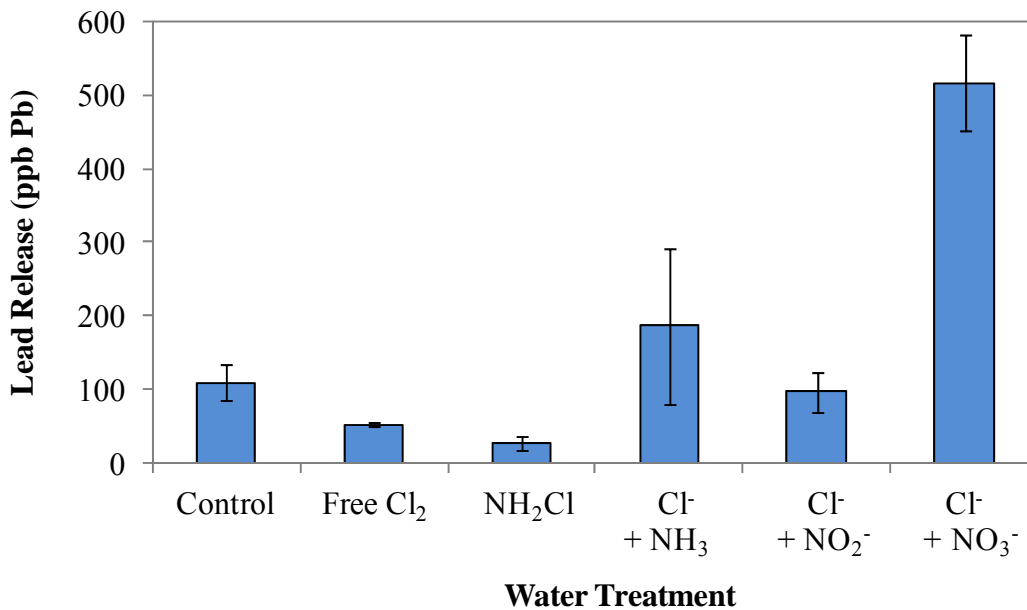


Figure 4-5. The effect of disinfectant decay on lead release from solder coupons in Phase 4.

The simulated joints were exposed to test waters in Table 4-3. Error bars represent 95% confidence. Results are shown from Week 6 of Phase 4.

impacts of reduced pH due to nitrification [14], corrosivity of water to solder in chloraminated systems can change markedly as it passes through the distribution system, especially if nitrification occurs with formation of nitrate (Figure 4-5). This has important consequences for selection of sampling sites for Lead and Copper Rule Compliance and for understanding human exposure to elevated lead.

Conditions with greater than 5 mg/L NO₃-N. To examine impacts of chloramine decay and nitrification in a system starting with a higher concentration of nitrate (Table 4-3), nitrate was dosed to a base level of 5 mg/L NO₃-N six weeks into Phase 4. Within one week, lead leaching increased by 2-12 times for all conditions due to the greater nitrate concentration (results not shown). Moreover, the lead release increased 2.5-144 times after two weeks at the higher nitrate concentration compared to the results at less than 2.25 mg/L NO₃-N (Figure 4-6). The previous trends observed at lower concentrations of nitrate were qualitatively different. Specifically, for the system with greater than 5 mg/L NO₃-N, water with chloramine had the highest lead, whereas the condition simulating complete conversion to nitrate had the lowest lead release (Figure 4-6). These observations reinforces the findings of Dudi [10], who discovered that nitrate caused very erratic lead leaching from brass.

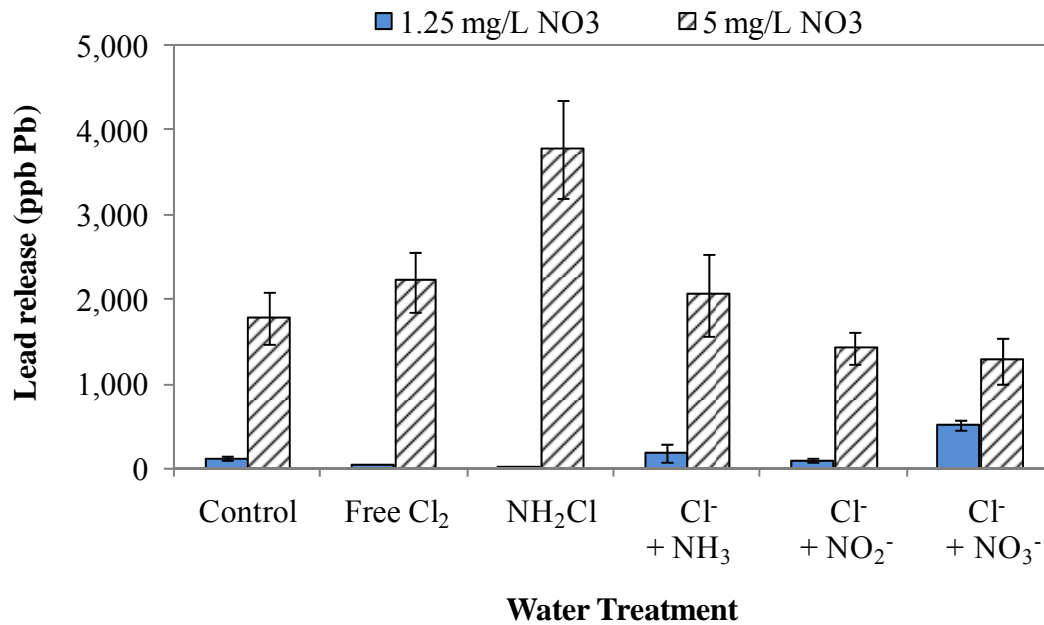


Figure 4-6. The effect of increasing base-level nitrate from 1.25 mg/L to 5 mg/L NO₃-N on lead release from solder coupons in Phase 4. Error bars represent 95% confidence intervals.

Light coloured bars show lead release prior to nitrate increase at Week 6 of the study, and striped bars are lead release two weeks after nitrate was increased in all water (Week 8).

CONCLUSIONS

- There was an increase in galvanic current with greater nitrate concentrations in short-term tests with macrocells, which also corresponded to a doubling of conductivity and lead leaching.
- Increasing the nitrate concentration in water from a low level (0-1 mg/L NO₃-N) to a high level (2.5-10 mg/L NO₃-N) could result in dramatic increases in lead leaching from galvanic copper:lead solder coupons. The impact appeared to be due to non-uniform corrosion, as small pieces of solder were observed to detach into the water.

- In a water with a low concentration of nitrate (<2.25 mg/L $\text{NO}_3\text{-N}$) and disinfected with chloramine, corrosivity of the water to lead solder could increase due to changes in nitrogen speciation as would occur from chloramine decay and biological nitrification. Addition of chlorine and chloramine decreased lead leaching relative to a control condition without oxidants. These trends were altered in a water that already contained high nitrate (>5 mg/L $\text{NO}_3\text{-N}$).

ACKNOWLEDGMENTS

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CHAPTER 5: CHLORIDE-TO-SULFATE MASS RATIO: PRACTICAL STUDIES IN LEAD SOLDER GALVANIC CORROSION

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ABSTRACT. The impact of the chloride-to-sulfate mass ratio (CSMR) on lead leaching from 50:50 lead-tin solder galvanically coupled to copper in stagnant conditions was examined using bench-scale testing and data from water utilities. The CSMR was significantly altered by coagulant changeover, blending of desalinated seawater, anion exchange, and sodium chloride brine leaks from on-site hypochlorite generators. Consistent with prior experiences, increasing the CSMR in the range of 0.1 to 1.0 could produce dramatic increases in lead leaching from lead-tin solder galvanically coupled to copper. Utilities should be alert to such problems if the CSMR is altered.

INTRODUCTION

Lead corrosion is sometimes severely impacted by seemingly innocuous changes in drinking water treatment, and in a few cases has been linked to elevated blood lead levels in children (Renner et al, 2006; Edwards et al, 2007; Edwards et al, 2009; Renner, 2009). The literature reveals numerous instances in which higher chloride-to-sulfate mass ratio (CSMR) was linked to increased galvanic corrosion and associated problems with lead solder pipe joints (Oliphant, 1983; Gregory, 1990; Edwards et al, 1999; Edwards et al, 2007). The CSMR is expressed as a ratio of mg/L chloride (Cl^-) to mg/L sulfate (SO_4^{2-}). For example, in a water with

10 mg/L Cl^- and 20 mg/L SO_4^{2-} , the CSMR is 0.5. Levels of CSMR exceeding about 0.6 have been associated with accelerated lead solder corrosion (Oliphant, 1983; Gregory, 1990; Edwards et al, 1999; Edwards et al, 2007).

Galvanic Corrosion. The problems attributed to higher CSMR result from accelerated galvanic corrosion of lead pipe:copper or lead solder:copper connections in water distribution systems. When lead is connected to copper, lead is typically sacrificed while copper is protected. Oliphant first showed that galvanic currents between lead solder and copper pipes increased with higher CSMR, although lead in water was never measured (1983). Supporting Oliphant's findings, Edwards et al observed higher lead in water when lead solder was connected to copper in water with a high CSMR of 1.4-4.5 (2007), but the CSMR had little effect for lead solder alone. The galvanic corrosion dropped the pH to as low as 2.5 and concentrated chloride as much as 11 times at the solder surface compared to bulk water concentrations during periods of stagnation, allowing the attack on the lead-bearing material to proceed without passivation (Edwards et al, 2007; Nguyen et al, 2010b). In certain waters with high CSMR, galvanic currents are sustained at levels greater than $2 \mu\text{A}/\text{cm}^2$, which creates a highly corrosive micro-environment at the surface of the lead solder anode (Nguyen et al, 2010b). Specifically, concentration of chloride at the anode surface can produce soluble complexes with lead, whereas concentration of sulfate can form a precipitate that can protect the lead surface even at very low pH (Nguyen et al, 2010b). Other research by Reiber suggested that galvanic corrosion was short-lived (1991; 2006), based on surface potential and current measurements between lead solder and copper, but this was for waters that were amended by addition of sulfate or under continuous flow conditions (AwwaRF, 1996). Reiber (1991; 2006) also did not measure lead

release to water. Work by Porter et al (1995) observed significant impacts of galvanic corrosion of lead solder on lead leaching and corrosion rates; however, effects of the CSMR on the magnitude of the problem was not quantified.

Changes in the CSMR. Studies by Oliphant (1983) and Gregory (1990) determined that a CSMR of greater than 0.5 increased galvanic corrosion of lead solder connected to copper. An independent study by Edwards et al (1999) found that higher chloride relative to sulfate correlated with higher 90th percentile lead levels for certain utilities with relatively high pH and low alkalinity water. Edwards et al (1999) identified a CSMR threshold of approximately 0.58, below which 100% of the utilities surveyed met the United States Environmental Protection Agency (USEPA) Lead and Copper Rule (LCR). Above that threshold, only 36% of the utilities surveyed were in compliance with the LCR.

A recent report, summarized herein, has documented how the CSMR can be profoundly altered by routine events such as coagulant changeover, implementation of anion exchange treatment, an accidental sodium chloride (NaCl) brine leak from an on-site hypochlorite generator, blending of desalinated water into a distribution system, and even application of road salt (Nguyen et al, 2010b). Some of these changes resulted in exceedance of the EPA lead action level and were only resolved when the CSMR was lowered (Edwards et al, 2007; Edwards et al, 2008); however, without head-to-head testing, the links between the higher CSMR and the higher lead in water cannot be considered unambiguous. Similarly, a few prior studies have shown that stabilized desalinated water treated with reverse osmosis membranes had a relatively high CSMR and can increase lead leaching (Taylor et al, 2005; Tang et al, 2006; Blute et al, 2008). But results in the prior work could not be clearly tied to the change in the CSMR, given

that other water quality parameters affecting lead leaching, such as pH and alkalinity, were also changing among the different blends.

The goal of this work was to conduct simple tests that could be easily deployed at water utilities to quickly examine impacts of changes to the CSMR on lead leaching from simulated lead soldered joints. Moreover, the test was used to verify the practical experiences of several water utilities, who believed that their higher lead in water resulted from higher CSMR. Finally, in some cases, the test was also used proactively to screen for potential lead corrosion problems that might result from possible treatment changes.

MATERIALS AND METHODS

This section is divided into 3 subsections to describe the following: (1) the test protocol with descriptions of the galvanic lead solder coupons and procedure for water changes; (2) test waters that were evaluated and the treatment techniques in the lab or at the treatment plant for each utility study; and (3) analytical methods that were used to analyze samples.

Bench Test Protocol. A 1” length of 3-mm diameter 50:50 lead (Pb)-tin (Sn) solder was placed on the inner edge of a 1” length of ½” diameter copper couplings (Figure 5-1). The wetted surface area ratio of lead solder-to-copper was approximately 1:7.3. The galvanic lead solder:copper coupons were placed in glass containers and exposed to 100 mL of each water in triplicate. The water was changed using a static “dump-and-fill” protocol twice per week (Monday/Thursday or Tuesday/Friday) as was conducted by Edwards et al (2007). Although the average stagnation time in buildings between flow events is on the order of 30 minutes, a longer stagnation time of 72-96 hours (3-4 days) was selected in this study to represent that which often

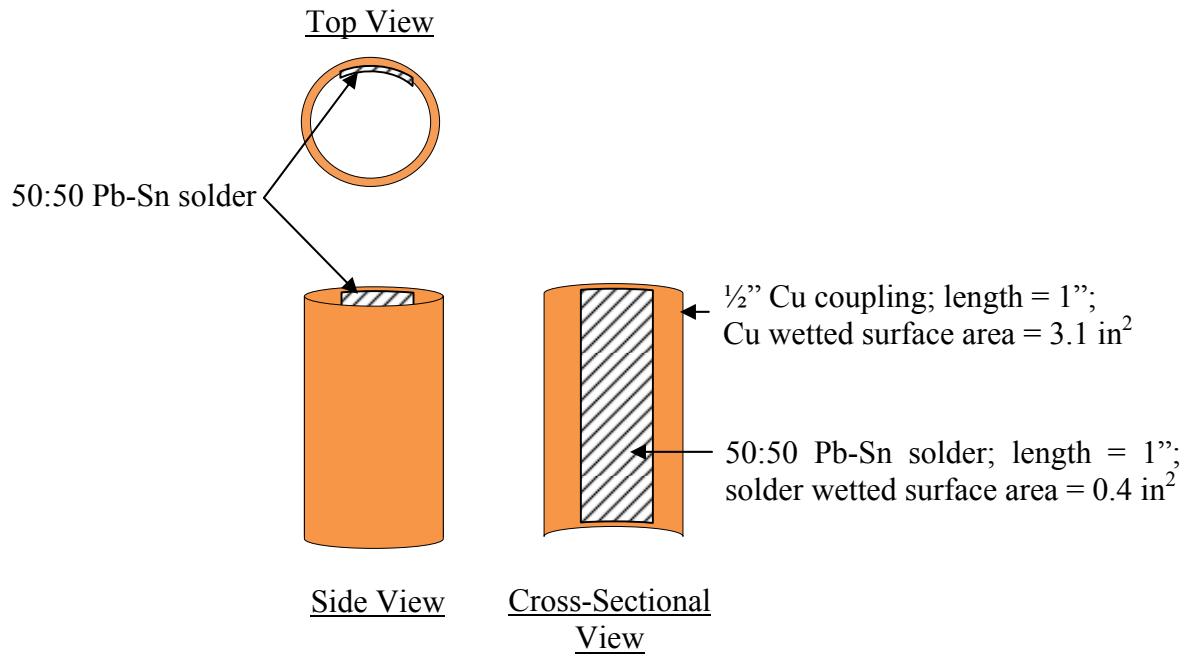


Figure 5-1. Top, side, and cross-sectional schematic views of copper coupling with 50:50 lead-tin solder. The solder was applied on the inside surface of the coupling.

occurs in many buildings such as schools over weekends or vacations. Weekly composite samples were collected for each water condition at the end of each week. After the lead concentration did not decrease significantly over time, which indicated that the coupons had stabilized or reached pseudo steady-state, water from individual replicates were analyzed to determine statistical confidence intervals. Each study lasted at least 5 weeks (Table 5-1).

Test Water Treatment. Water was shipped to Virginia Tech from each of the six participating water utilities (Table 5-2) and subjected to various treatment strategies (Table 5-1). Raw water from Utilities 1, 2, and 3 were treated by coagulation and filtration at bench-scale to simulate the full-scale treatment to the extent possible. In the Utility 4 study, distribution system water was obtained, and anion exchange treatment was simulated at bench-scale. Water from

Utility 5 was obtained from the plant, and potential corrosion inhibitors were dosed to the water. Water from Utility 6 was obtained from the current distribution plant, and finished desalinated water was obtained from the utility's pilot desalination plant. Sodium bicarbonate (NaHCO_3) was added to Utility 6's desalinated water to increase the alkalinity from 25 mg/L to 40 mg/L as

Table 5-1. Treatment change evaluated, experimental duration, and target corrosion inhibitor doses, pH, and disinfectant concentrations for each utility.

| Utility | Treatment Change Evaluated | Total Weeks Evaluated | Target pH | Corrosion inhibitor (Dose) | Disinfectant (Dose) | Other Treatment |
|---------|------------------------------|-----------------------|------------|---|---|--|
| 1, NC | Coagulation* | 5 | 7.3 | Ortho-phosphate (1 mg/L P) | Free Chlorine (2.5 mg/L Cl_2) | -- |
| 2, NC | Coagulation, anion exchange* | 7 | 8.0 | None | Chloramines (3.5 mg/L Cl_2) | Fluoride (0.9 mg/L F) |
| 3, NC | Coagulation* | 9 | 7.7 | Ortho-phosphate (1 mg/L P) | Chloramines (3.5 mg/L Cl_2) | -- |
| 4, ME | Anion exchange* | 11 | 7.0 or 5.5 | None | None | -- |
| 5, TN | Brine leak** | 20 | 7.3 or 8.7 | Varied (0 or 1 mg/L ortho-phosphate as P) | Free Chlorine (2 mg/L Cl_2) | -- |
| 6, CA | Desalination*** | 8 | 8.2 | None | Chloramines (3.5 mg/L Cl_2) | Desalinated water dosed with NaHCO_3 **** |

* Coagulation and/or anion exchange was conducted in the lab.

** NaCl brine leak simulated by adding 12 mg/L Cl.

*** Desalinated water and current distribution water from the treatment plant was shipped to Virginia Tech for tests. Blending of the two waters, alkalinity addition, disinfection, and pH adjustment was conducted in the lab.

**** Dosed to reach 40 mg/L as CaCO_3

Table 5-2. Typical water quality of raw water or partially treated water from each utility.

| Parameter | Water Utility | | | | | | |
|---|---------------|-----------|-------|-----------|-----------|---------------|-------------------|
| | 1, NC | 2, NC | 3, NC | 4, ME | 5, TN | 6 Current, CA | 6 Desalinated, CA |
| Typical pH | 7.3 | 8.0 | 7.7 | 7.0 | 7.3 | 8.2 | 8.2 |
| Alkalinity (mg/L as CaCO ₃) | 40 | 35 | 25 | 12 | 8 | 125 | 25 |
| Chloride (mg/L Cl) | 14 | 9 | 12 | 4.4 | 3 | 50 | 87 |
| Sulfate (mg/L SO ₄) | 9 | 13 | 16 | 4.1 | 2 | 68 | 0.85 |
| Nitrate (mg/L N) | <i>BD</i> | <i>BD</i> | 0.44 | 0.08 | <i>BD</i> | 0.12 | <i>BD</i> |
| Phosphate (mg/L P) | 0.35 | 0.1 | 0.041 | <i>BD</i> | <i>BD</i> | 0.001 | <i>BD</i> |
| Sodium (mg/L) | 12 | 28 | 12 | 2.4 | 7.1 | 67 | 68 |
| Calcium (mg/L) | 5.4 | 6.2 | 9.3 | 8.6 | 2 | 29 | 0.015 |
| Magnesium (mg/L) | 2.1 | 2.5 | 3.7 | 0.4 | 0.63 | 6.9 | 0.018 |
| Silica (mg/L) | 5.5 | 0.8 | 3.8 | 5.2 | 2.2 | 6.6 | 0.077 |

BD = Below Detection

calcium carbonate (CaCO₃).

For all water conditions, the pH, corrosion inhibitor dose, and disinfectant concentrations were adjusted prior to exposure to the plumbing materials (Table 5-1). Monosodium orthophosphate (NaH₂PO₄) at a dose of 1 mg/L as phosphorus (P) was used for Utilities 1, 3, and

5. To reach target pH values (± 0.1), 0.1 M sodium hydroxide (NaOH) was added to increase the pH, or acid was added in the form of 0.1 M nitric acid (HNO₃) for Utilities 1, 2, 5, and 6 or carbon dioxide (CO₂) for Utilities 3 and 4 to decrease the pH (Table 5-1). Prior to the work for Utilities 3 and 4, but after the Utility 1, 2, and 5 studies, nitrate (NO₃⁻) was found to increase lead leaching (Gregory, 1990; Stone et al, 2009). Although nitrate is expected to have limited effects on lead leaching in this work because no more than 0.1 mg/L NO₃-N was added to the water from nitric acid, CO₂ was used in subsequent studies. When chloramines were dosed, a 4:1 mg chlorine (Cl₂)/mg ammonia as nitrogen (NH₃-N) ratio was used in all cases except for Utility 6, which had a ratio of 5:1 mg Cl₂/mg NH₃-N. Chemicals were added as reagent-grade salts.

Coagulation (Utilities 1, 2, and 3). Waters coagulated at bench-scale were treated with coagulation, sedimentation, and filtration. 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 using jar tests. Deep bed filtration was simulated using glass wool filters. 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 between coagulants were the same as those noted by the utilities in treating the actual waters using deep bed sand filters. Aside from the coagulant type and dose, each test water was treated identically. Within each case study, the pH (± 0.1) and alkalinity (± 5 mg/L as CaCO₃) of the finished water was the same, and the total organic carbon removal was about the same for all coagulants within each study.

The CSMR increased for water treated with coagulants containing chloride (e.g., polyaluminum chloride and ferric chloride) because the coagulants added chloride and no sulfate. In contrast, sulfate-based coagulants resulted in lower CSMR because sulfate was increased but not chloride. For coagulant blends, such as ferric sulfate/aluminum chlorohydrate, both sulfate and chloride were added; however, the particular proprietary blend evaluated in this study added much more chloride than sulfate to the water, thereby increasing the CSMR.

Utility 1, NC. Within the last few years, Utility 1 has implemented four different coagulants with varying chloride and sulfate levels, and high lead measurements in 13% of samples collected from homes and schools coincided temporally with use of chloride-based coagulants. At least one sample contained 79 ppb Pb (Hewlitt, 2007). To potentially enhance coagulation while maintaining a relatively low CSMR, Utility 1 was interested in testing a new proprietary type of coagulant that contained a ferric sulfate polymer blend. Therefore, five coagulants were evaluated for Utility 1 water: (1) aluminum sulfate (alum), (2) ferric chloride, (3), a ferric sulfate/aluminum chlorohydrate blend, (4) ferric sulfate, and (5) a ferric sulfate polymer blend (Table 5-3).

Utility 2, NC. Four types of coagulants were tested including: (1) ferric chloride, (2) ferric sulfate, (3) ferric chloride/ferric sulfate blend resulting in a CSMR of 0.4, and (4) ferric chloride/ ferric sulfate blend resulting in a CSMR of 1.1. Anion exchange in combination with a third of the typical dose of ferric sulfate or ferric chloride was also evaluated. At bench-scale, the anion exchange treatment was simulated in batch treatment using the same method used for Utility 4 at bench-scale for consistency within this work. The CSMR in Utility 2's water that was

Table 5-3. Finished water chloride and sulfate after coagulation.

| Utility | Coagulant | Chloride (mg/L Cl) | Sulfate (mg/L SO ₄ ²⁻) | CSMR* |
|---------|---|-----------------------|--|------------|
| 1, NC | Alum | 14 | 32 | 0.4 |
| | Ferric chloride | 28 | 9 | 3.0 |
| | Ferric sulfate / aluminum chlorohydrate blend | 18 | 10 | 1.8 |
| | Ferric sulfate | 13 | 30 | 0.4 |
| | Ferric sulfate polymer blend | 14 | 32 | 0.4 |
| 2, NC | Ferric chloride | 55 | 12 | 4.5 |
| | Ferric sulfate | 15 | 72 | 0.2 |
| | Ferric chloride + AE** | 52 | 4 | 13 |
| | Ferric sulfate + AE** | 31 | 22 | 1.4 |
| | Ferric chloride/ Ferric sulfate blend | 22 | 64 | 0.4 |
| | | 40 | 37 | 1.1 |
| 3, NC | 100% Alum | 16 | 40 | 0.4 |
| | 100% PACl*** | 22 | 12 | 1.8 |
| | Alum and PACl*** Blend | 21 | 30 | 0.7 |
| | | 22 | 24 | 0.9 |
| | | 23 | 18 | 1.3 |

*Chloride-to-sulfate mass ratio (CSMR)

** Anion Exchange (AE)

*** Polyaluminum chloride (PACl)

pre-treated with ferric sulfate increased from 0.2 to 1.4, and water pre-treated with ferric chloride increased from 4.5 to 13 as a result of the chloride-based anion exchange treatment (Table 5-3).

Utility 3, NC. Utility 3 currently coagulates using alum but wanted to use some level of polyaluminum chloride (PACl) to enhance the removal of natural organic matter. In the past, switching completely to PACl resulted in LCR exceedances (Edwards et al, 2007). Therefore, five types of coagulation treatment were evaluated for effects on lead leaching: (1) alum, (2) PACl, (3) alum/PACl blend with a resulting CSMR of 0.7 (4) alum/PACl blend with a resulting CSMR of 0.9, and (5) alum/PACl blend with a resulting CSMR of 1.3.

Anion exchange for arsenic removal (Utility 4). Fifteen gallons of untreated well water were collected at a point prior to arsenic removal from Utility 4. Five gallons of this water were subjected to no anion exchange treatment and pH adjustment to 7.0 to simulate the original distribution system water that did not have a lead problem (i.e., before implementation of anion exchange treatment). The remaining ten gallons of water were treated by anion exchange in a batch process to simulate impacts of arsenic treatment without a column based on a protocol used by Singer et al (2002). Chloride-based anion exchange resin was mixed with the water from Utility 4 at a ratio of 1.7 mL of resin per 1 L of treated water at 100 RPM for 30 minutes, followed by 30 minutes of settling. Bio-Rad AG 1-X8 resin (50-100 mesh size) in the chloride form was used for this study. Prior to its use, the resin was rinsed several times with deionized water to remove excess chloride. Half of the water treated with anion exchange was reduced to pH 5.5 by bubbling CO₂ to simulate the low pH that occurred in practice after frequent anion exchange column regeneration. After pH adjustment for all three water conditions, no further

treatment of the water was conducted, as occurs in practice. Thus, three water conditions were tested for Utility 4: (1) well water with no arsenic treatment at 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. After the 6-week study, the anion exchange treated condition at pH 5.5 was adjusted to pH 7.0 for a 5-week period.

Arsenic in the water was reduced from 4.5 to 1.8 ppb arsenic (As) as a result of the treatment. The anion exchange treatment increased chloride from 4.4 mg/L to 13.2 mg/L Cl^- and decreased sulfate from 4.1 mg/L to 1.7 mg/L SO_4^{2-} , effectively increasing the CSMR from 1.1 to 7.8 (Table 5-4). Using this method, less arsenic and sulfate was removed from the water compared with anion exchange through a column, which typically removes more arsenic and is the method used in practice by Utility 4. As a result, if arsenic and sulfate were removed more efficiently in practice and replaced with chloride from the resin, the CSMR after treatment would be higher than in this study. 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.

Table 5-4. Summary of water quality for Utility 4.

| Condition | Arsenic ($\mu\text{L As}$) | Chloride (mg/L Cl^-) | Sulfate (mg/L SO_4^{2-}) | CSMR* |
|----------------------------------|--|---|---|--------------|
| No anion exchange | 4.5 | 4.4 | 4.1 | 1.1 |
| Anion exchange treatment, pH 7.0 | 1.8 | 13.2 | 1.7 | 7.8 |
| Anion exchange treatment, pH 5.5 | 1.8 | 13.2 | 1.7 | 7.8 |

* Chloride-to-sulfate mass ratio (CSMR)

Brine leak (Utility 5). Test water was obtained from the UV channel of Utility 5's treatment plant and subjected to a number of corrosion control strategies including the addition of poly-orthophosphate blend corrosion inhibitor, orthophosphate, and alkalinity (Nguyen et al, 2010a). However, only 3 conditions with and without the simulated brine leak are described in this work: (1) pH 8.7, (2) pH 7.3, and (3) pH 7.3 with 1 mg/L orthophosphate as P. The treated water from Utility 5 typically has a chloride concentration of 3 mg/L Cl^- and a very low sulfate concentration of about 2 mg/L SO_4^{2-} . However, the chloride in the treated water increased five times to 15 mg/L Cl^- when the brine solution from the hypochlorite generator leaked into the water. To investigate the possible impacts of this leak at the utility, solder coupons were initially exposed to water with 3 mg/L Cl^- for 17 weeks, followed by exposure to water with 15 mg/L Cl^- for 3 weeks to simulate the effect of the accidental brine leak. Simulation of the brine leak from the on-site hypochlorite generator was accomplished by adding chloride as sodium chloride.

Desalination (Utility 6). Utility 6 shipped groundwater and seawater desalinated by multiple stage nanofiltration to Virginia Tech. The alkalinity of the desalinated water was adjusted to 40 mg/L as CaCO_3 by adding NaHCO_3 prior to blending with groundwater. Distribution water (groundwater) and desalinated water were blended at four different ratios: (1) 100% distribution or current water, (2) 25% desalinated water and 75% distribution water, (3) 50% desalinated water and 50% distribution water, and (4) 75% desalinated water and 25% distribution water (Table 5-5).

To specifically evaluate the effects of chloride and sulfate in the blends, two additional tests were conducted. For one batch of distributed groundwater, chloride (22 mg/L Cl^- added as calcium chloride or CaCl_2) was added to match the chloride concentration that was present in the

highest desalinated water blend, or 25% distributed and 75% desalinated water blend. Likewise, for one aliquot of 25% distributed and 75% desalinated water, sulfate (52 mg/L SO_4^{2-} added as calcium sulfate or CaSO_4) was added to match the sulfate level present in the 100% distribution water (Table 5-5).

Analytical Methods. The water samples that were collected after exposure to the lead solder coupons were acidified with 2% HNO_3 for at least 24 hours to dissolve metals. The samples were analyzed for elements such as lead, chloride, sulfate, and phosphate with an

Table 5-5. Summary of finished water quality for Utility 6.

| Blend | Chloride (mg/L Cl^-) | Sulfate (mg/L SO_4^{2-}) | CSMR* | Alkalinity (mg/L CaCO_3) |
|--|-----------------------------------|---------------------------------------|------------|---------------------------------------|
| 100% Distribution | 54 | 66 | 0.8 | 125 |
| 25% Desalinated: 75% Distribution | 62 | 50 | 1.2 | 104 |
| 50% Desalinated: 50% Distribution | 71 | 35 | 2.0 | 83 |
| 75% Desalinated: 25% Distribution | 81 | 18 | 4.5 | 61 |
| 100% Distribution + Cl^{**} | 76 | 69 | 1.1 | 125 |
| 75% Desalinated: 25% Distribution + SO_4^{**} | 75 | 70 | 1.1 | 61 |

* Chloride-to-sulfate mass ratio (CSMR)

** The two blended waters with the lowest and highest CSMR were amended with chloride and sulfate, respectively, to produce CSMR 1.1 water.

inductively coupled plasma mass spectrometer (ICP-MS) in accordance with Standard Method 3125-B (APHA, 1998). The pH in water samples was measured with an electrode according to Standard Method 4500-H⁺ (APHA, 1998). Ammonia was measured using a Hach DR 2700 spectrophotometer salicylate method according to Standard Method 4500-NH₃ (APHA, 1998). Total and free chlorine were measured on a Hach DR 2700 spectrophotometer according to Standard Method 4500-Cl (APHA, 1998).

RESULTS AND DISCUSSION

Effect of Coagulation. It has already been established that in a few cases, the type of coagulant used to treat water is a major factor controlling the CSMR and lead leaching from solder-copper galvanic couplings (Edwards et al, 2007). This work extended the testing to many other waters where similar problems were suspected (Table 5-3). The magnitude of lead release varied among the utilities and is attributed to the differences in the pH, alkalinity, disinfectant type, corrosion inhibitor (if any), and silica. A key finding is that increasing the CSMR in each of the case studies definitively increased the lead leaching from solder, in some cases by orders of magnitude.

Utility 1, NC. To evaluate the effect of each coagulant on lead leaching and to test one new type of coagulant for the utility, five different types of coagulants in treated waters were compared head-to-head in terms of lead leaching from solder. Consistent with theory and practical experience at this utility, lead leaching increased with higher CSMR of the water. The ranking from least to most lead leaching was: (1) ferric sulfate, leaching 60 ppb Pb, (2) alum, leaching 140 ppb Pb, (3) the ferric sulfate polymer blend, leaching 200 ppb Pb, (4) ferric

chloride, leaching 530 ppb Pb, and (5) the ferric sulfate/aluminum chlorohydrate blend, leaching 790 ppb Pb (Figure 5-2).

Statistically, the water conditions coagulated with ferric sulfate or the ferric sulfate polymer blend had lower lead release from lead solder than the other conditions (p -value < 0.05). On average, water treated with the sulfate-based coagulants (ferric sulfate, alum, and the ferric sulfate polymer blend) released 4.9 times less lead than water treated with the chloride-based coagulants (ferric chloride and ferric sulfate/aluminum chlorohydrate blend). Coagulation with the ferric sulfate/aluminum chlorohydrate blend did not decrease lead leaching compared to coagulation with a 100% chloride-based coagulant because the sulfate contributed by the ferric sulfate was not sufficient to decrease the CSMR to a non-corrosive level (Table 5-3). Consistent with theory, lead leaching to water was positively correlated with the CSMR (Figure 5-3).

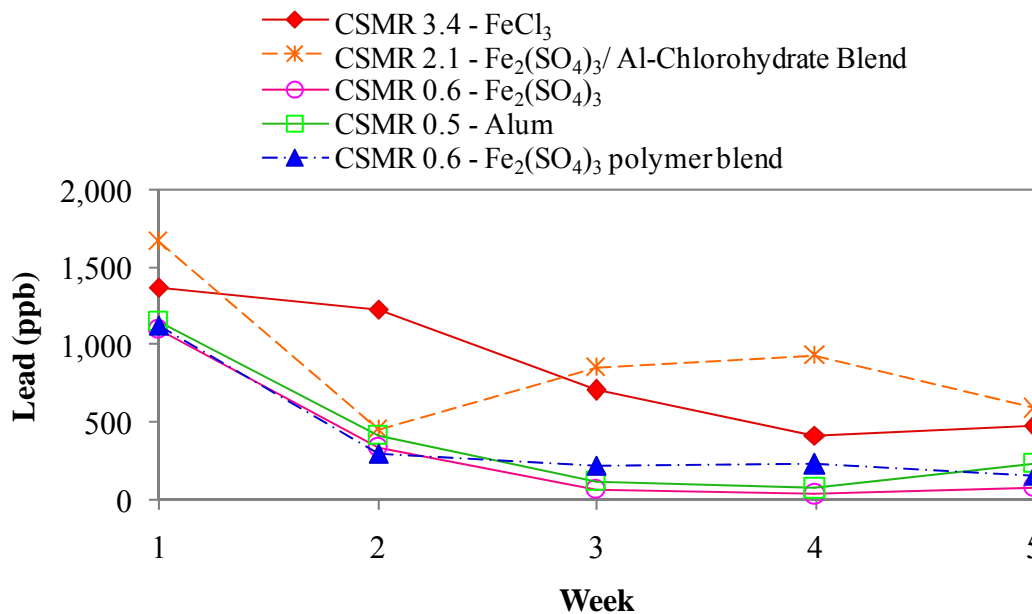


Figure 5-2. Lead release as a function of time for Utility 1. The coagulant chemicals are denoted as follows: ferric chloride (FeCl_3), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), and aluminum sulfate (alum).

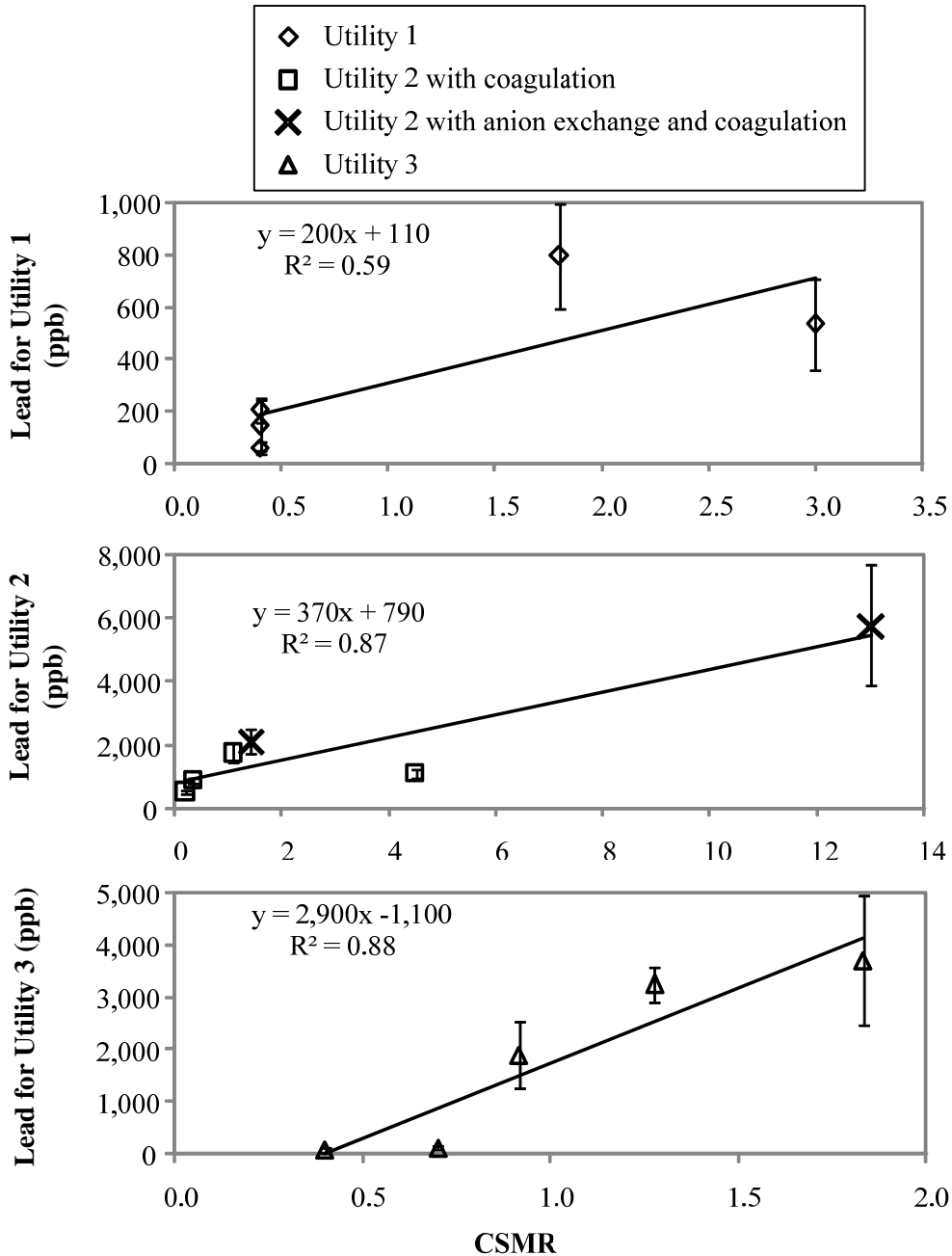


Figure 5-3. Lead release as a function of the chloride-to-sulfate mass ratio (CSMR) for waters treated with coagulation. Utilities 1 and 3 water contained orthophosphate corrosion inhibitor while Utility 2 did not. Chloramine disinfection was used by Utilities 2 and 3, and Utility 1 used free chlorine. Error bars represent 95% confidence intervals. Results are the averages of triplicates for each water condition during Week 5 for Utility 1, Week 7 for Utility 2, and Week 9 for Utility 3.

Utility 2, NC. Four coagulants (ferric chloride, ferric sulfate, ferric chloride/ferric sulfate blend at low CSMR, and ferric chloride/ferric sulfate blend at high CSMR) in treated waters, and two coagulants in conjunction with anion exchange treatment, were compared head-to-head in terms of lead leaching from solder connected to copper. With the exception of the solder coupons exposed to water treated with 100% ferric chloride, higher CSMR correlated with increased lead release (Figure 5-3). The water with the lowest CSMR, the 100% ferric sulfate condition with a CSMR of 0.2, resulted in the least amount of lead release of about 520 ppb Pb. By doubling the CSMR to 0.4, the lead release increased 1.7 times to a concentration of 880 ppb Pb. Water treated with the coagulant blend (CSMR 1.2) caused 1,730 ppb Pb release, or an increase in 3.4 times compared to ferric sulfate (CSMR 0.2). The water treated with ferric chloride (CSMR 4.0) had lead release that was not statistically different from that at a CSMR of 1.2, but all other results were different at greater than 95% confidence.

Utility 3, NC. Bench-scale tests were conducted to determine if blending alum and PACl coagulants was possible to obtain benefits of PACl while also maintaining a lower CSMR. Consistent with theory, CSMR had a positive correlation with lead release (Figure 5-3). For instance, the lowest CSMR condition (100% alum with a CSMR of 0.4) had the lowest lead release at 70 ppb Pb. Increasing the CSMR to approximately 0.9 increased lead release 26 times up to more than 1,900 ppb Pb compared to the alum-treated water. The highest CSMR level of 1.8 (100% PACl) caused lead concentrations 44 times higher than the lowest CSMR condition (100% alum), releasing about 3,200 ppb Pb. The trends were confirmed at greater than 95% confidence. For this utility, increasing the CSMR from 0.4 to 0.7 did not result in a significant increase in lead. Therefore, these results indicate that in this water, higher CSMR blends of PACl

and alum generally increased lead release. However, the blended coagulant with a CSMR of 0.7 was not significantly different from the 100% alum condition (CSMR 0.4), and the utility could use a small amount of PACl without markedly increasing the lead in water.

Effect of Anion Exchange Treatment: *Utility 2, NC.* The utility was considering anion exchange in combination with coagulation to remove natural organic matter (NOM) from the water. The use of anion exchange significantly increased the CSMR (Table 5-3).

The anion exchange treatment, in conjunction with lower doses of both ferric sulfate and ferric chloride coagulant, increased lead release. Furthermore, the lead leaching to water correlated with increases in the CSMR (Figure 5-3). The lead release in the ferric sulfate-treated water increased from 700 ppb to 2,400 ppb Pb (a 3.4X increase) with anion exchange as the CSMR increased from 0.2 to 1.4. When water was treated with anion exchange and with a third of the typical ferric chloride dose used at the treatment plant, lead release increased from 1,500 ppb to 11,000 ppb Pb (a 7X increase) as the CSMR increased from 4.5 to 13. It was concluded that anion exchange might be problematic in this water because it dramatically increased the CSMR and lead leaching.

Utility 4, ME. Consistent with suspicions at Utility 2, a dramatic increase in lead release for Utility 4 was observed in water treated with anion exchange. Anion exchange treatment increased lead release an average of 47 times during Week 6 of the study from 40 ppb to 1,830 ppb Pb (Figure 5-4). This illustrates that the 66 times increase of lead in water above the LCR action level of 15 ppb, which was observed in apartments supplied by this utility (Edwards et al, 2007), are within the realm of possibility.

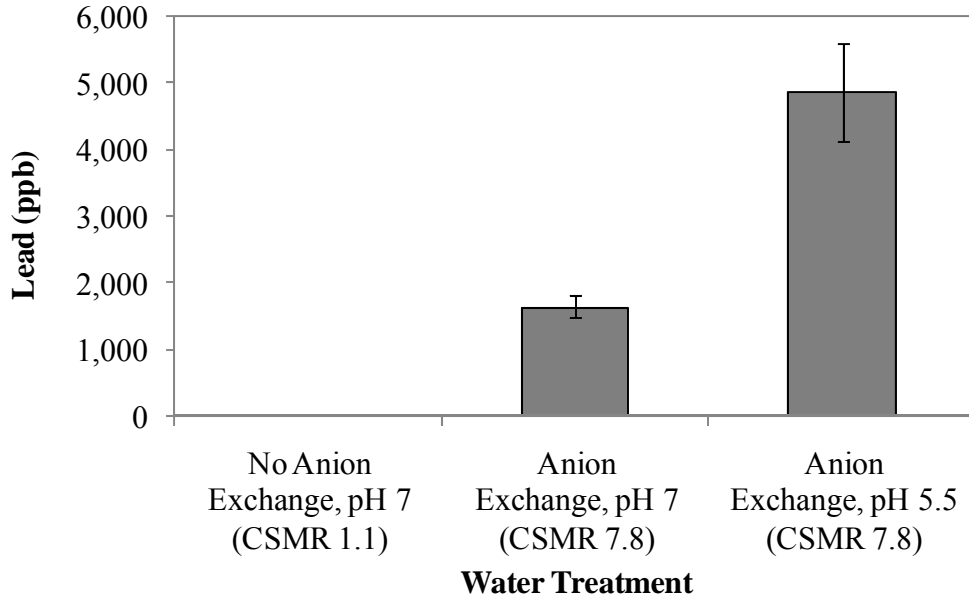


Figure 5-4. Effects of anion exchange and pH reduction on lead release for Utility 4. Results are shown from Week 6 of the study. Error bars represent 95% confidence intervals.

The combined effect of higher CSMR and lower pH resulted in even higher lead leaching than from high CSMR alone. Decreasing the pH from 7.0 to 5.5 increased lead in the water from 1,830 ppb to 4,800 ppb Pb (Figure 5-4). To further illustrate the exacerbating effect of lower pH, the pH 5.5 anion exchange-treated water was increased to pH 7.0 for a period of 5 weeks. After about 3 weeks, the lead release decreased to the level that had been observed for the condition at pH 7.0 for the duration of testing (Figure 5-5).

Anion exchange treatment, and the resultant increase in the CSMR, by itself was enough to cause a dramatic increase in lead release; however, the decrease in pH also contributed to serious problems in this water.

Effect of Brine Leak (Utility 5). In most of the conditions evaluated for Utility 5, the simulated brine leak, or increasing chloride from 3 mg/L Cl^- to 15 mg/L Cl^- , caused an increase

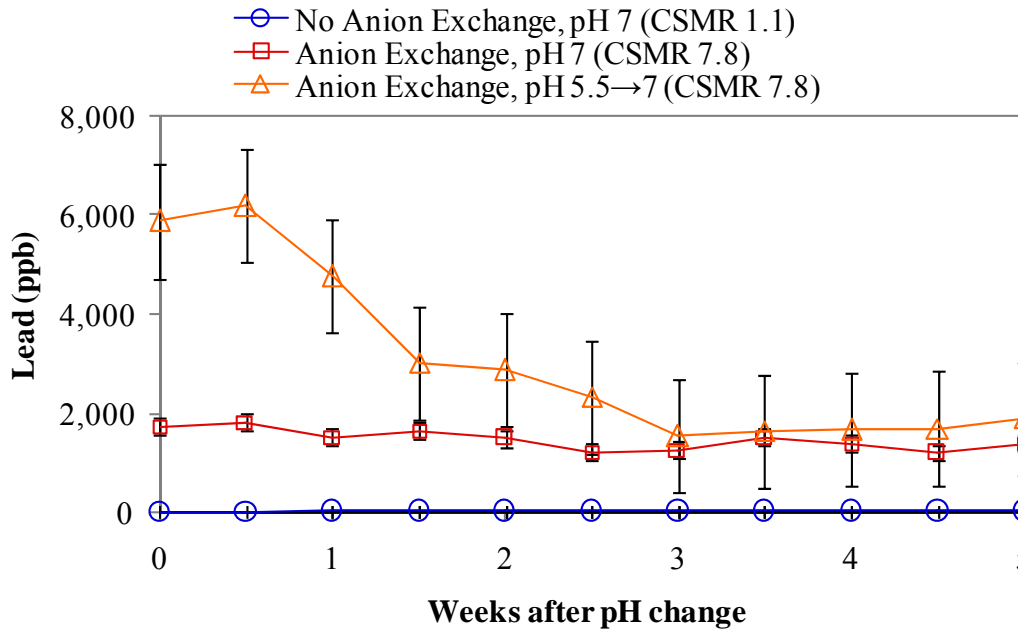


Figure 5-5. Lead concentration as a function of time after increasing the pH from 5.5 to 7.0 for anion exchange-treated water for Utility 4. The error bars are also shown in Figure 5-4, which was one week before the pH change.

in lead release, regardless of the pH or corrosion inhibitor (Figure 5-6). In this case, although alkaline pH was expected to decrease lead solubility (Schock, 1989; Dodrill et al, 1995; Lin et al, 1997) increasing the pH from 7.3 to 8.7 did not eliminate the chloride effect on lead release and did not reduce lead leaching at either chloride concentration. Similar observations were noted by Dodrill et al (1995), who found that increasing the pH in low alkalinity water did not affect the 90th percentile lead, although benefits were observed when the pH was increased above pH 8.4. At the typical low chloride concentration of 3 mg/L Cl, dosing orthophosphate caused the least amount of lead release (62 ppb Pb) amongst all conditions tested. In contrast, the same condition with the simulated brine leak caused 62 times more lead and resulted in the highest lead release of 3,270 ppb Pb. Additional analysis suggested that mostly particulate lead (>0.45 μm) was

released from 50:50 Pb-Sn solder into the water, but the specific proportions of particulate and soluble lead would vary on the water type.

Clearly, changes in the CSMR can produce profound changes in lead leaching even in systems with orthophosphate corrosion inhibitor, consistent with practical data gathered by Edwards et al (2007). Moreover, the 90th percentile lead for Utility 5 dropped 70% after the plant consecutively: (1) reduced the NaCl brine leak, and (2) began dosing orthophosphate, although the field results are confounded by the implementation of the two changes. However, this bench-scale testing for the utility unambiguously demonstrates that reducing the chloride concentration had the largest impact in decreasing lead in water. Specifically, the simulated elimination of the

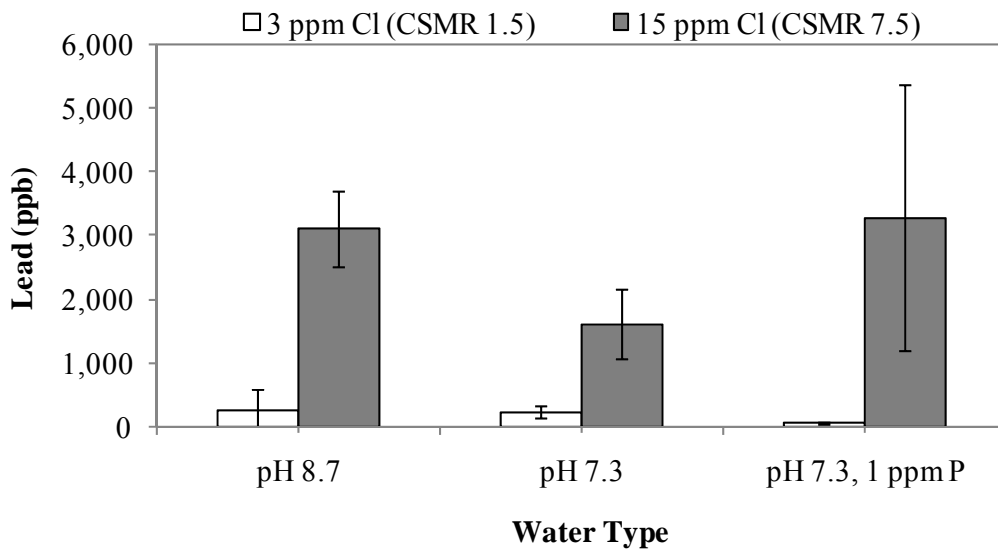


Figure 5-6. Effect of simulated brine leak (+12 mg/L Cl) on lead release from galvanic lead solder for Utility 5. Results are shown as an average of three weeks prior to chloride increase (Weeks 12-14) and the average of the final three weeks of the study (Weeks 18-20). Typical water contained 8 mg/L as CaCO₃. Chloride was increased at Week 18. Error bars represent 95% confidence intervals.

brine leak at bench-scale (chloride concentration decreased from 15 mg/L to 3 mg/L) resulted in 78% less lead in water, and an additional 6% decrease in lead release from solder was achieved by dosing orthophosphate (0 mg/L P versus 3 mg/L P in water containing 3 mg/L Cl) (Figure 5-6). That is, a total of 84% less corrosion of lead occurred at bench-scale after the chloride concentration was reduced and orthophosphate was dosed, with a large portion of the reduction attributed to decrease in the chloride concentration. The slight difference in the percent decrease in lead in the field (70%) versus that at bench-scale (84%) as a result of the treatment changes might be from other factors, such as amount of lead exposed to water in home plumbing and lead source in tested homes in the field.

Effect of Desalination (Utility 6). Blending desalinated water with the current distribution water clearly increased lead release from the solder coupons. The current distribution water with no desalinated water had relatively low lead of 20 ppb, but the blend with 75% desalinated or nanofiltered water exhibited high lead levels of 1,300 ppb Pb, which is an increase of 65 times (Figure 5-7). Even a blend with 25% nanofiltered water increased the amount of lead in the water by 16 times compared to the current distribution water. These results were consistent with trends observed by Tang et al (2006) and Taylor et al (2005).

The increased corrosivity of the nanofiltered water was consistent with expectations based on the high CSMR and the lower alkalinity of the water compared to the current distribution water (groundwater) (Table 5-2). To isolate the effects of chloride and sulfate, when the current distribution water was dosed with enough chloride to equal the chloride concentration in the 75% desalinated water (Table 5-5), the lead concentration was increased 3 times (Figure 5-7). When the 75% desalinated water was dosed with sulfate to match the current distribution

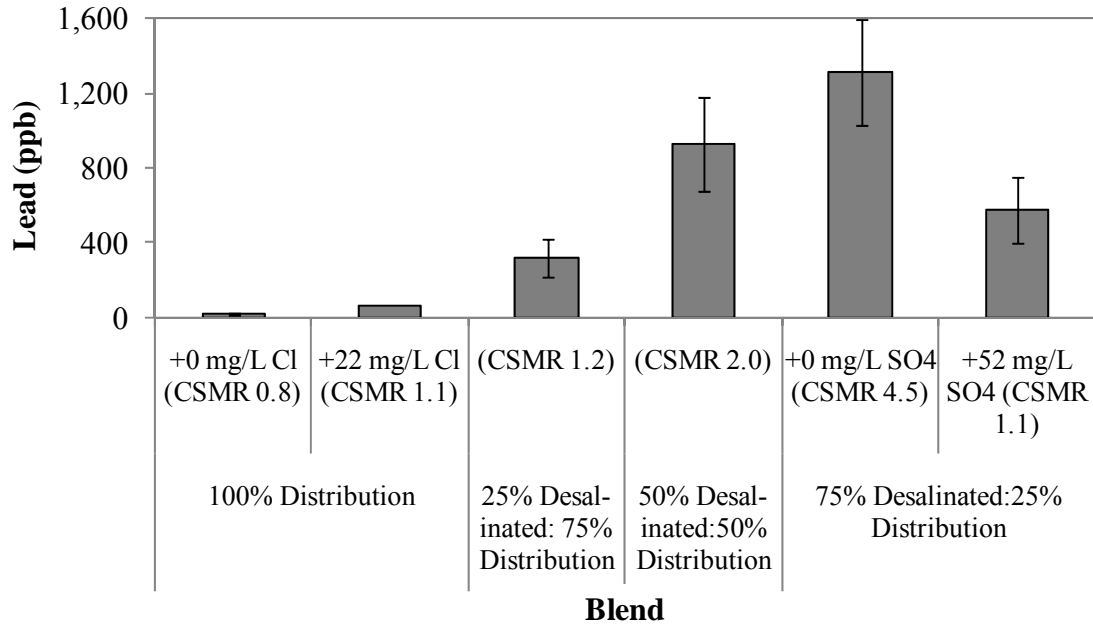


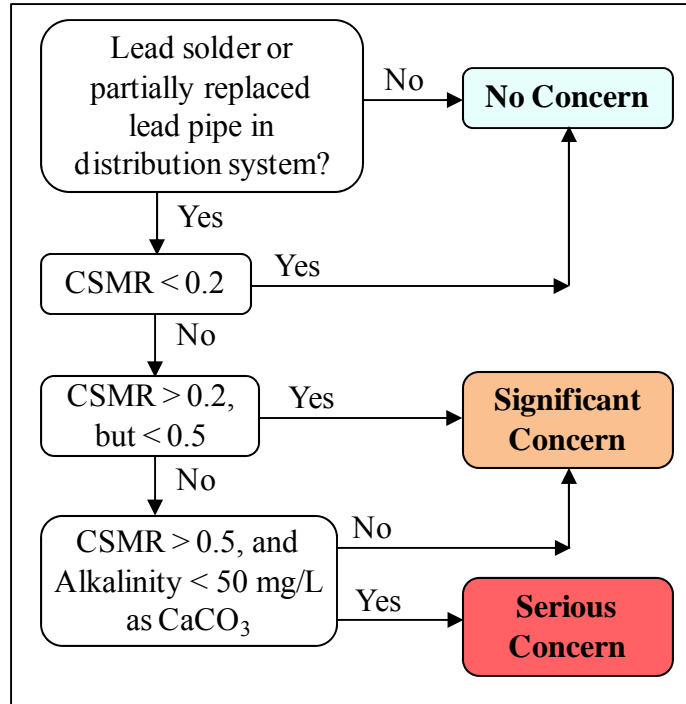
Figure 5-7. Effect of desalinated water on lead release for Utility 6. Results are shown from week 8 of the study. Error bars represent 95% confidence intervals.

water (Table 5-5), the lead released was decreased 2.3 times (Figure 5-7). Comparing the two amended waters with the same CSMR of 1.1 (current distribution water amended with 22 mg/L Cl and the 75% desalinated water blend amended with 52 mg/L SO₄), the 75% desalinated water blend with sulfate added had 9 times more lead than the current distribution water with chloride added. The much lower lead release in the current distribution water could be attributed to the higher alkalinity (Schock, 1989), silica concentration (Gregory, 1990), and hardness (Boffardi et al, 1991) of the current distribution water. While these factors played a key role in its reduced corrosivity of the current distribution water relative to lead leaching from the desalinated water blends, the change in chloride and sulfate of the water was also a major factor.

SYNTHESIS

This work demonstrates that the CSMR can be altered by treatment changes such as switching from a sulfate-based coagulant to a chloride-based coagulant, implementing anion exchange treatment for arsenic or NOM removal, the use of desalinated seawater, and a NaCl brine leak from an on-site hypochlorite generator. Although there is not a direct relationship between absolute lead concentrations from the bench-scale tests and concentrations measured in water in the field, the test protocol in this work can indicate the relative effect of treatment changes at utilities on lead release. For example, if a utility's current 90th percentile lead was 10 ppb, and bench-scale testing indicates that a prospective treatment strategy has 5 times more lead leaching than the current treatment in the head-to-head test, then an action level exceedence would not be unexpected if the treatment alternative was implemented.

On the basis of the results herein and other experiences (Edwards et al, 2007; Nguyen et al, 2010a; Nguyen et al, 2010b), a "decision tree" was developed to judge if altering the CSMR may be of no concern, significant concern, or a serious concern to utilities, using the calculated CSMR of their water and information regarding distribution system materials (Figure 5-8). For example, if a utility had no lead solder or partially replaced lead pipe materials in the distribution system and the CSMR was below 0.2, this work would not predict lead problems from the mechanism of lead corrosion that is described herein. In contrast, if a utility's water had a CSMR greater than 0.5 and an alkalinity of less than 50 mg/L as CaCO₃, then the utility could potentially have serious lead problems following treatment changes that increase the CSMR. Therefore, the greatest concerns are at utilities with homes containing lead solder or partially replaced lead pipe, and 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



Source: Nguyen et al, 2010a.

Figure 5-8. Level of lead corrosion concern for utilities relative to the chloride-to-sulfate mass ratio (CSMR), alkalinity, and lead sources in the system.

considering treatment changes that increase the CSMR above 0.5 examine potential impacts on lead release using the simple protocols described in this work. Most of the tests can detect the potential for serious adverse impacts after a few weeks of bench-scale testing.

CONCLUSIONS

- A simple bench-scale test was developed that could rapidly screen for significant changes in lead leaching from various water treatment changes. In the cases where field data on relationships between coagulant changes and 90th percentile or other lead leaching data were available, the short-term tendencies from the bench-scale tests were in qualitative agreement with practical utility experiences and longer-term test results.

- In every water tested, increasing the CSMR in the range of 0.1 to 1.0 increased lead leaching from galvanic lead solder:copper coupons. If the CSMR was over the range of 1.0, sometimes increasing the CSMR further had little additional adverse effect, although severe lead corrosion problems were generally occurring.
- The CSMR can increase from the following changes: (1) switching from a sulfate-based coagulant to a chloride-based coagulant, (2) implementing anion exchange treatment, (3) use of desalinated seawater, and (4) a NaCl brine leak from an on-site hypochlorite generator. Changes (1) and (2) increase the chloride in water while reducing the amount of sulfate added to the water, (3) decreases sulfate more than chloride, and (4) adds chloride to the water.
- Using anion exchange treatment, even in conjunction with a sulfate-based coagulant can increase the CSMR and lead release significantly.
- Dosing orthophosphate did not protect utilities from lead corrosion problems associated with elevated CSMR.
- Utilities that are considering treatment changes that increase the CSMR should test prospective changes prior to implementation if the following apply: (1) lead solder is used to connect copper pipes in the distribution system and in homes, (2) the water has low alkalinity (less than about 50 mg/L as CaCO₃), and (3) the final CSMR will be greater than 0.2. A quick test could be conducted using the protocol used in this work to indicate the relative effect of the changes on lead corrosion.

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APPENDIX A

Supporting Information:

Corrosive micro-environments at lead solder surfaces arising from galvanic corrosion with
copper pipe

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Experimental procedures, one table, and seven figures are included.

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Supporting Information 1

Experimental Procedure for Case Study 1

Test water from Utility 1 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 polyaluminum chloride (PACl) or aluminum sulfate (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. The PACl coagulant was provided by Utility 1. Doses, timing of addition and duration of treatments were selected to simulate the full-scale treatment practice to the extent possible. Since PACl adds chloride to the water, it increases the ratio of chloride to sulfate whereas alum adds sulfate thereby decreasing the ratio.

To simulate future reservoir water quality conditions when road salts enter the source water at higher concentrations, 16 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 1 over the last 15 to 20 years, with an increase in Cl⁻ 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: (1) alum-treated water (CSMR 1.4), (2) PACl-treated water (CSMR 5.3), and (3) PACl-treated water with simulated road salt (CSMR 8.5).

Supporting Information 2

Experimental Procedure for Case Study 2

Test water was obtained at Virginia Tech by shipments of Utility 2 treated water from the UV channel of the treatment plant. Collected water was separated into aliquots and subjected to various treatments (Table S-1). Chemicals added to the water included orthophosphate corrosion inhibitor, bicarbonate, sulfate, disinfection with free chlorine, and acid or base for final pH adjustment. The water from the treatment plant contained 4 mg/L Cl, and all waters were dosed with 10 mg/L Cl after Week 14 to simulate a portion of the chloride that entered the water due to the hypochlorite generator brine leak.

The pH was adjusted with either 0.1 M NaOH or 0.1 M HNO₃ to the target value of pH 7.3 or 9.2. All water was also dosed with free chlorine at a concentration of 2 mg/L Cl₂. Orthophosphate was dosed from sodium phosphate (Na₂HPO₄). Alkalinity was adjusted with sodium bicarbonate (NaHCO₃). Chloride and sulfate were added from sodium chloride (NaCl) and sodium sulfate (Na₂SO₄).

Table A-1: Water quality conditions tested for Utility 2

| Water Type | | pH | Conductivity (μS) | Alkalinity (mg/L as CaCO ₃) | Cl ⁻ (mg/L) | SO ₄ ²⁻ (mg/L SO ₄) | Si (mg/L) | Phosphate (mg/L P) |
|---|--------------|-----|-------------------|---|------------------------|---|-----------|--------------------|
| Current Water | No Phosphate | 7.3 | 68 | 8 | 14 | 3 | 2.8 | 0.0 |
| | Phosphate | 7.3 | 72 | 8 | 14 | 3 | 2.8 | 1.0 |
| Current Water + 10 ppm Sulfate | No Phosphate | 7.3 | 91 | 8 | 14 | 12 | 2.8 | 0.0 |
| | Phosphate | 7.3 | 96 | 8 | 14 | 12 | 2.8 | 1.0 |
| Current Water + 10 mg/L alkalinity as CaCO ₃ | No Phosphate | 7.3 | 83 | 18 | 14 | 3 | 2.8 | 0.0 |
| | Phosphate | 7.3 | 88 | 18 | 14 | 3 | 2.8 | 1.0 |
| Current Water + 20 mg/L alkalinity as CaCO ₃ | No Phosphate | 7.3 | 102 | 28 | 14 | 3 | 2.8 | 0.0 |
| | Phosphate | 7.3 | 107 | 28 | 14 | 3 | 2.8 | 1.0 |
| Current Water + 50 mg/L alkalinity as CaCO ₃ | No Phosphate | 7.3 | 167 | 58 | 14 | 3 | 2.8 | 0.0 |
| | Phosphate | 7.3 | 172 | 58 | 14 | 3 | 2.8 | 1.0 |
| Current Water at pH 9.2 | No Phosphate | 9.2 | 71 | 8 | 14 | 3 | 2.8 | 0.0 |
| | Phosphate | 9.2 | 78 | 8 | 14 | 3 | 2.8 | 1.0 |

Supporting Information 3

Experimental Procedure for Case Study 3

The case study lasted a total of 11 weeks. The simulated copper joint macrocells were exposed to synthetic water with low and high CSMR, which were 0.2 and 16, respectively. 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. 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.

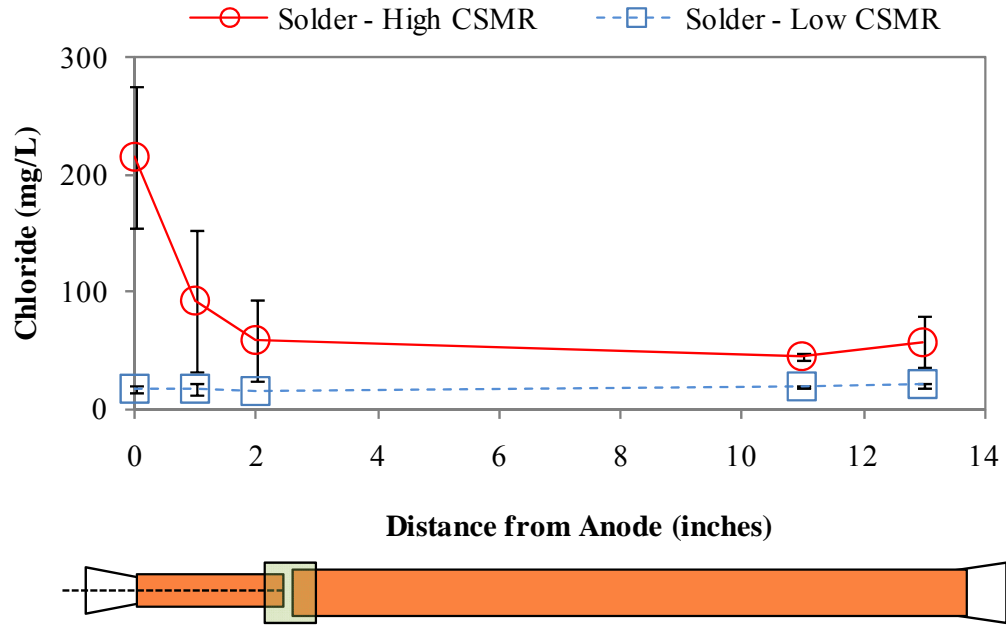


Figure A-3: Chloride microelectrode measurements as a function of distance from the lead solder anode for low and high CSMR waters in Case Study 3. Data are from the 10th week of the study, and error bars represent the 95% confidence intervals.

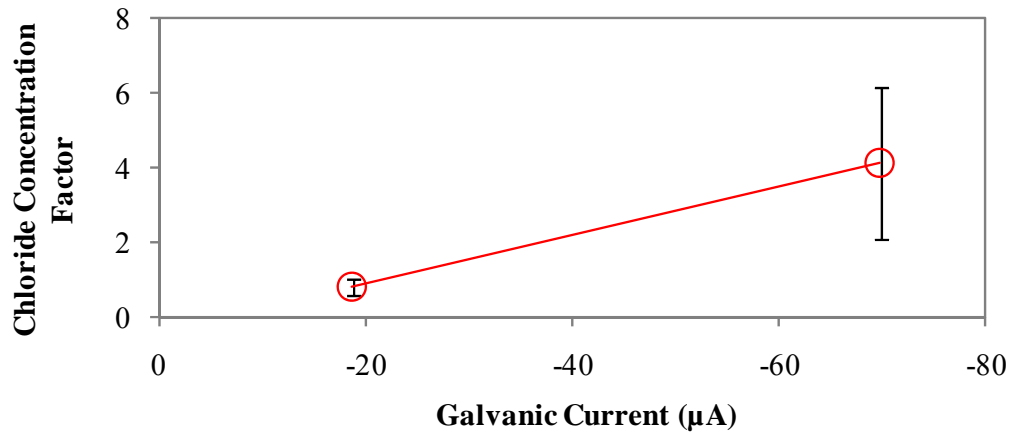


Figure A-4: Chloride concentration factor measured with a chloride microelectrode as a function of galvanic current in Case Study 3 for 50:50 Pb/Sn solder. The two points represent low and high CSMR water conditions at Week 10 of the case study, and error bars represent the 95% confidence intervals.

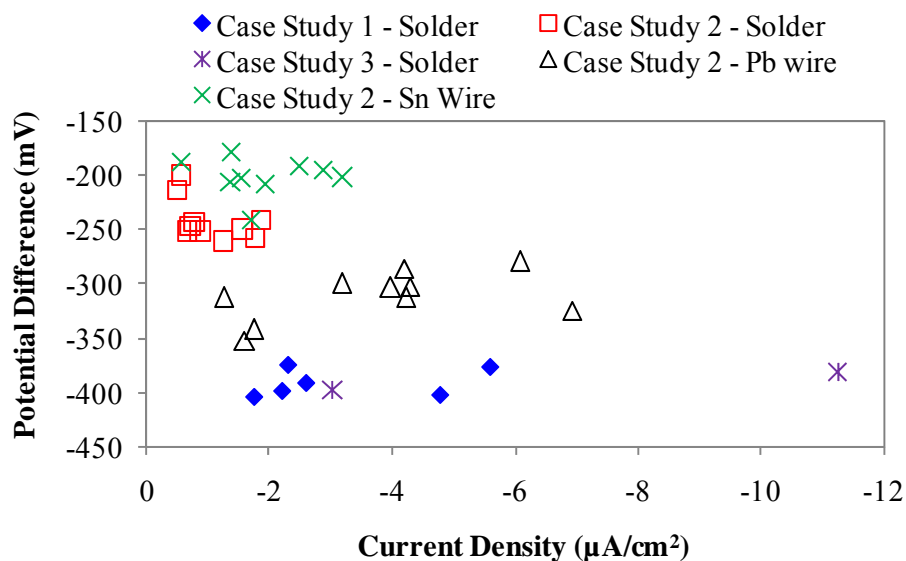


Figure A-5: Potential difference measured between the copper pipes and the anode wire (solder, pure lead, or pure tin) as a function of galvanic current density.

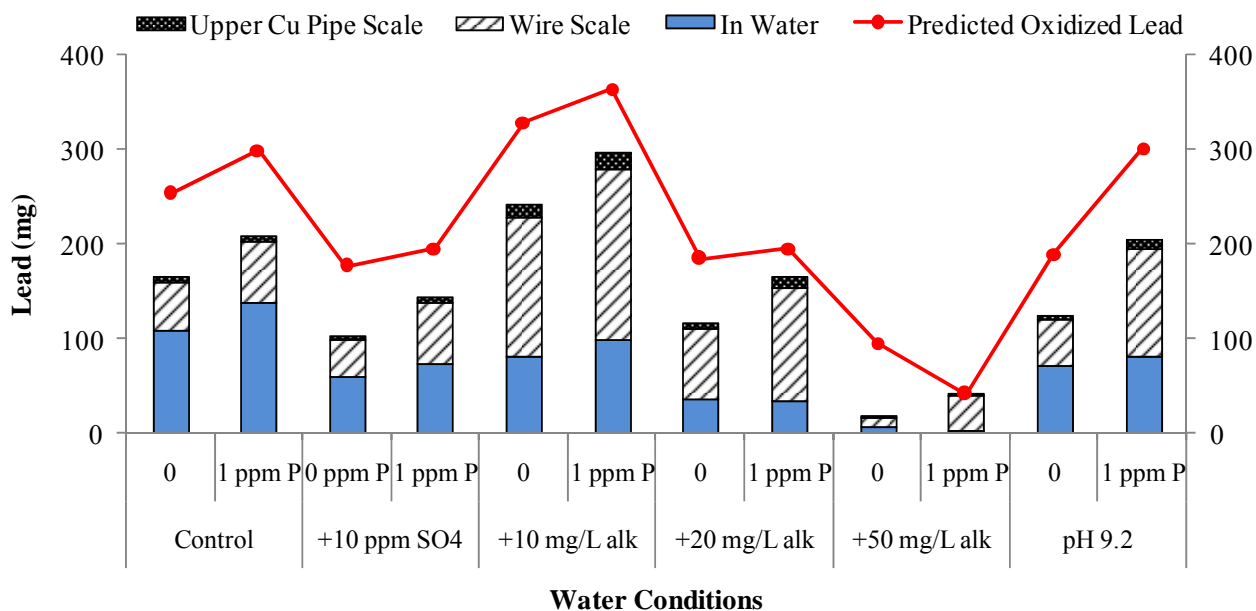


Figure A-6: Mass balance of total released lead from pure lead wires in Case Study 2. Scale from the lead wire and upper copper pipe section were recovered, weighed, and dissolved to determine the mass of lead in the scale. The total mass of lead released into the water throughout the study was determined from the weekly samples. The current measurements were used to predict the oxidized lead based on Faraday's law. The scale on the lower copper pipe was not recovered and may account for the difference between the predicted and measured lead.

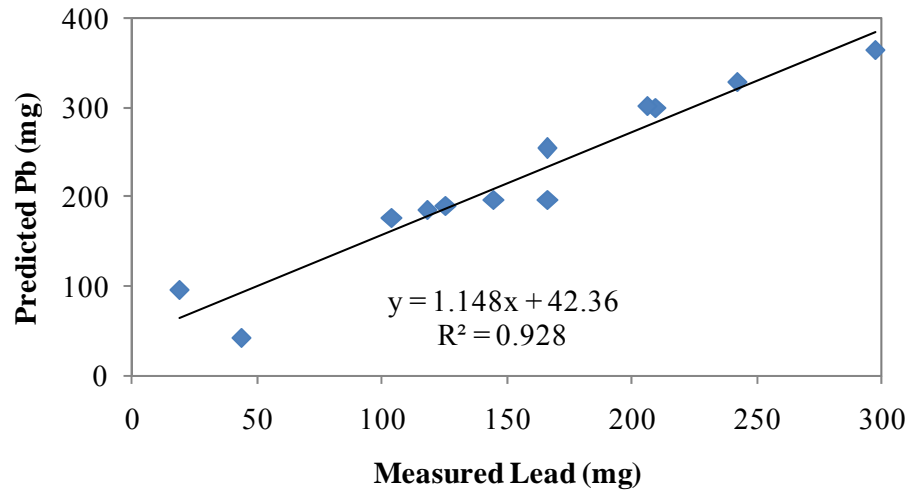


Figure A-7: Comparison of the predicted released lead based on Faraday's law versus the lead accounted in the water, lead wire scale, and upper copper pipe scale for lead wire in Case Study 2.