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Mineralogical Evidence of Galvanic Corrosion in Drinking Water Lead Pipe Joints

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Abstract

Galvanic corrosion as a mechanism of toxic lead release into drinking water has been under scientific debate in the U.S. for over 30 years. Visual and mineralogical analysis of 28 lead pipe joints, excavated after 60+ years from 8 U.S. water utilities, provided the first direct view of three distinct galvanic corrosion patterns in practice: (1) no evidence of galvanic corrosion; (2) galvanic corrosion with lead cathode; (3) galvanic corrosion with lead anode. Pattern 3 is consistent with empirical galvanic series (lead→brass→copper in order of increasing nobility) and poses the greatest risk of Pb exposure. Pattern 2 is consistent with galvanic battery reversion. The identification of copper-sulfate minerals (Pattern 2), and lead-sulfate and lead-chloride minerals (Pattern 3) in galvanic zones illustrated the migration of chloride and sulfate toward the anode. Geochemical modeling confirmed the required pH drop from the bulk water level to at least pH 3.0–4.0 (Pattern 2) and pH<5.5 (Pattern 3) in order to form these minerals. Despite joints being over 60 years old, galvanic zones in Pattern 3 were active and possibly posed an important source of lead to drinking water. Importantly, Pattern 3 was not observed in samples from systems representing water qualities favoring PbO₂ formation.

GRAPHICAL ABSTRACT

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Disclaimer

This work has been subjected to U.S. EPA peer and administrative review and has been approved for publication. Any opinions expressed in this paper are those of the authors and do not necessarily reflect the official positions and policies of the U.S. EPA. The authors declare no competing financial interest.

Supporting Information Available

Additional tables summarizing pipe sample and utility water chemistry data, X-ray diffraction patterns, graphics, and geochemical model parameters and outputs are included in the Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Introduction

Drinking water distribution systems in the United States (U.S.) contain mixed metal plumbing, including legacy lead pipe connected to leaded brass or copper pipe. Such connections produce galvanic corrosion cells that have the potential to deteriorate both drinking water quality and pipe mechanical integrity, by inducing preferential dissolution of the anodic metal through galvanic corrosion.

The anode and cathode of the galvanic corrosion cell are established based on the nobility of the dissimilar metals. The less noble metal (i.e., lower electrochemical potential) will act as the anode and will be preferentially oxidized (i.e., corroded), while experiencing a local water pH decrease compared to the bulk water pH (1, 2). The oxidant (e.g., oxygen, free chlorine) will be reduced at the surface of the protected cathodic metal, where a local water pH increase is experienced compared to the bulk water pH (1, 2). Many other factors can influence galvanic corrosion presence and extent, including: reaction kinetics (rate of metal dissolution and scale formation), alloy composition (major constituents, minor constituents, impurities) and pipe scale characteristics (dependence to water quality and electrode potentials), water quality (“corrosivity” to galvanic corrosion) and environment (temperature, flow rate, volume), galvanic couple geometry and joint (number and type of galvanic joints, distances involved, surface shape and condition, area ratio)(3).

The relative importance and longevity of galvanic corrosion as a mechanism of toxic lead release into drinking water in the U.S. has been a subject of debate for over 30 years. A summary of prior work revealed that galvanic effects were deemed short-lived by some researchers, but substantially persistent in the long-term by others (4, 5).

The effects of galvanic lead corrosion have previously been studied in the laboratory by measuring (1) electro-potentials across the galvanic couple or galvanic current across the galvanic couple (6–10), (2) lead contamination of drinking water exposed to the galvanic couple (11–18), or (3) a combination of both (19–25). In most cases lead pipe behaved as the anode, consistent with empirical galvanic series (1, 26, 27). Occasionally, leaded brass or copper was found to behave as the anode instead of lead pipe (28, 29), in which case the possibility for water lead contamination is minimized, because lead pipe behaves as the cathode and is protected from corrosion.

There has been great interest in characterizing the microenvironment near corroding metals. Microelectrodes have been used to measure pH near corroding galvanically-coupled metal surfaces (14, 21, 30, 31). Local pH increases at the cathode and pH decreases at the anode have been observed. The migration of chloride and sulfate anions to the anodic regions, where metal cations are generated, in order to satisfy electroneutrality has also been measured (30).

These observations are somewhat analogous to iron tuberculation (32) and to a larger extent to pitting corrosion of copper in water, where attack at the copper anode or “pit” produces a local acidic microenvironment rich in copper ions (33). In these phenomena, corroding metal and hydrogen cations are generated at the anodic metal floor. Chloride and sulfate ions are drawn to the anodic region to achieve electroneutrality by diffusing through a membrane-like barrier cover layer, and a “cap” develops over the pit consisting of copper-sulfate and chloride compounds reflective of the acidic environment below it (2, 33–40). Sometimes the caps fail over time, exposing residual structures of multiple-mineral phase deposits reflecting their microenvironment. In a number of case studies, the aggressive (often highly acidic) pit solution dissolved through the pipe wall and caused leaks. In other cases, sectioned pieces of pipe revealed either stable (over timeframes of interest) pit cap mounds, or remnants of pipe structures that were breached or which became dormant.

Prior knowledge on galvanic lead corrosion was built upon relatively short-term experiments, spanning from 7 hours at bench-scale (18) to 48 months at pilot scale (41). With a few exceptions utilizing excavated lead pipes (15, 17), these experiments utilized brand new lead materials (e.g., lead pipe, lead-tin solder or lead wire) and brand new copper or brass materials (e.g., copper pipe, copper wire or brass coupon), typically exposed to synthetic tap water under controlled dump-and-fill or water flow regimes. Commercially available connectors between lead and copper (i.e., various plastic couplings and nondielectric or dielectric brass couplings) have only recently been tested in experiments (17, 22), as opposed to the typically used laboratory simulants (often an externally wired plastic spacer placed between the dissimilar metals).

These experimental conditions could not fully capture the complex mixed metal dimensions, configurations and ages encountered in actual water distribution systems, nor the complex water use patterns and water chemistries that control galvanic phenomena in practice. As a result, experimental materials and/or experimental conditions may have prohibited the significant development of pipe corrosion solids as they would actually occur in the field after decades of pipe use. Furthermore, none of the previous studies examined the mineralogy of corrosion scales at galvanic junctions, which can provide a direct view of galvanic corrosion presence and extent.

The goal of this work was to employ comprehensive visual and mineralogical characterization of pipe scales at galvanically connected lead-brass or lead-copper joints, excavated from different U.S. water distribution systems after long periods of service, in order to: (1) directly confirm the presence or absence of galvanic corrosion, (2) conclusively identify which metal in the galvanic cell behaved anodically (i.e., corroded) over time, and (3) identify mineral phases at the galvanic junction as opposed to the remaining pipe surface,

to gain mechanistic insights on possible galvanic microlayer effects and associated implications.

Materials and Methods

Pipe samples.

Twenty-eight lead pipe joints, connected to either leaded brass or copper pipe, were obtained from eight water utilities after 60–114 years of use (Table 1). Most pipes were connected with lead-tin solder (wiped or cup joint). A limited number of samples were connected with a leaded brass fitting (flare or compression joint). Photographs of the four different joint types are available in Supplemental Information (SI figure S1). These pipe samples represent the first methodical examination of actual excavated lead galvanic joints in North America. They reflect “samples of opportunity” obtained from certain drinking water utilities interested in pipe scale analyses, rather than a geographically and statistically representative pipe collection across the U.S. From these twenty-eight samples, three samples will be described in detail, illustrating the three distinct galvanic corrosion patterns identified in this research. A summary of results is tabulated for the rest of the samples.

Drinking Water Quality

Utilities D and G treated ground water, while the remaining utilities treated surface water. Drinking water quality leaving the plant varied among the eight water utilities (Table 2). The pH ranged from 7.4 to 9.4 on average, and the alkalinity ranged from 20 to 300 mg/L as CaCO_3 . Residual disinfectant was either chlorine (ranging from 0.3 to 1.4 mg/L) or monochloramine (ranging from 1.4 to 2.0 mg/L). Utilities A and G dosed orthophosphate as a corrosion inhibitor, while Utility B dosed a low concentration of hexametaphosphate as an antiscalant, not as a corrosion inhibitor. The remaining utilities did not dose a phosphate chemical.

Important ion concentrations (e.g., Cl^- & SO_4^{2-}) were also quite variable when available, but data were fairly limited. As a result, the chloride-to-sulfate mass ratio (CSMR), a water quality factor deemed important in affecting galvanic corrosion (8, 20, 28, 30, 42) was not calculated herein. Meaningful calculations of the CSMR were not possible for several reasons: the chloride and sulfate concentrations were not available at Utility C; only single chloride/sulfate concentrations were available at Utilities D and E with no additional data on possible variability; and the chloride/sulfate data at remaining Utilities were not always paired.

What is more, these summarizations (Table 2) characterize relatively recent drinking water quality information, over the timeframe of a small number of years. They may not necessarily reflect a consistent water quality throughout the lifetime of excavated pipe joints, which generally extends from decades to more than a century. Overall, drinking water quality is very important in the analysis, but such data are rather limited in this kind of observational research.

Sample preparation

Pipe joints were extracted by the water utilities' personnel and shipped to the US EPA's (Environmental Protection Agency) AMSARC (Advanced Materials and Solids Analysis Research Core) laboratory in Cincinnati, Ohio. Utilities were instructed to cap the ends of the moist excavated pipes for shipment to the laboratory, consistent with other AMSARC studies (43). Upon receipt, the pipe samples were prepared and corrosion scales were harvested using methods described in detail previously (43, 44). The discrimination of scale layers and other structures for subsampling was mainly based on color and/or textural change in scale composition.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was used to identify the main crystalline solids present in the scales. Amorphous (i.e., poorly crystalline) solids were not identifiable by PXRD. Powder samples were top-loaded into silicon or quartz zero background sample holders. In cases with very little material, a small amount of the powdered sample was made into a slurry with amyl acetate and pipetted onto a quartz zero background plate. The amyl acetate was evaporated prior to sample analysis. PXRD patterns were obtained using two different diffractometers. The first is a Scintag SDS 2000 theta-/theta diffractometer using Cu K α radiation generated at 1.6 kW (40 kV, 40 mA). Scans were performed in step scan mode with a step size of 0.02 ° 2 θ , and a 1–3s count time. The second instrument is a PANalytical X-pert Pro using Cu K α radiation (45 kV, 40 mA) and an X'celerator RTMS detector. Scans were performed in continuous scan mode, from 10 – 90° 2 θ at a scan speed of 0.03556°/s. Pattern analysis for crystalline mineralogical composition was performed using JADE software (Versions 7–9, Materials Data Inc.) and the 1995–2002 ICDD PDF-2 database. The methodology employed could often detect, but not quantify, the presence of poorly-ordered or amorphous solids in the scale.

Geochemical Modeling of Scale Microenvironments

To explore the hypothesis that active galvanic corrosion at lead-containing joints could result in local environments that could aggravate lead release, illustrative lead and copper phase diagrams were constructed using The Geochemist's Workbench standard software (Aqueous Solutions LLC, Champaign, IL). The principle tool used was the Act2 module for the preparation of activity-pH diagrams, representing anodic or cathodic regions of the joints. Solid phases were chosen based on observed presence, or by literature suggestions of minerals characterized as having potential for rapid formation and metastability in short timeframes under environmentally-relevant aquatic system conditions that could be analogous to the scale microenvironments. Equilibrium constants were taken from compilations of lead and copper species used in previous US Environmental Protection Agency (EPA) studies (45, 46), and they are tabulated in the Supporting Information (Model Outputs S1, S2 and S3).

Bulk water chemistry characteristics were a starting point for the computations of the thermodynamic activities, though limited knowledge existed of the finished water constituent concentrations over time for most systems. Particularly, pH, chloride, sulfate and bicarbonate anions have been shown in many of the cited references to be key factors in

promoting or mitigating galvanic corrosion current flow (31–39), and concentration gradients have been shown to form under conditions where corrosion product buildups cause the creation of semi-permeable membrane layers that preferentially permit or restrict their passage through the membranes and accumulated deposit material.

Background dissolved inorganic carbonate (DIC), chloride and sulfate concentrations were selected as an approximation of the chemistries of the systems whose samples were examined. Phase diagrams for lead and copper were prepared to identify hypothetical estimate combinations of water chemistry (pH, sulfate, chloride) that would be necessary at the microenvironments (as opposed to bulk water) in order to reproduce the observed solids, assuming at least a metastable equilibrium has been achieved within the scale.

As with any equilibrium or near-equilibrium model simulations of real environmental systems, considerable uncertainty exists in many important parameters that can shift predicted phase boundaries by an order of magnitude or more (47, 48). Examples of those parameters include accuracy and applicability of thermodynamic equilibrium constants, the difference between thermodynamic activity and concentration, kinetics of mineral precipitation and dissolution reactions, degree of crystalline order and crystallite size, tendency for formation of metastable phases, lattice substitutions, and neglect of temperature adjustment. Therefore, the use of the phase diagrams for hypothesis plausibility testing could only be approached in a qualitative and conceptual way. Developing a rigorous validated internally-consistent suite of thermodynamic data for the suite of lead and copper minerals observed in these samples was beyond the scope of this study.

Results and Discussion

Based on visual examination and detailed solids and surface analyses, three general galvanic corrosion patterns were observed: (1) no evidence of galvanic corrosion was present; (2) galvanic corrosion was evident and lead pipe was cathodic relative to the connected anodic brass or copper pipe; or (3) galvanic corrosion was evident and lead pipe was anodic relative to the connected cathodic brass pipe (Figure 1, Table 1).

Where galvanic corrosion was not evident (Pattern 1), uniform corrosion was observed on each pipe surface, herein termed the “background zone”. Where galvanic corrosion was evident (Patterns 2 and 3) pipe section surfaces were divided into two distinct zones: the “galvanic” and the “background” zone. Visual features considered when defining the zones included scale structure, morphology, shape, thickness, roughness and color. The galvanic zone was defined as the region adjacent to the pipe joint and extending outward to a location where the influence of galvanic interactions was not apparent based on visual examination (see illustrative Figure S2 for visual determination of the galvanic and background zones in one galvanic joint sample).

The galvanic zone included an anodic and cathodic region, defined by the nature of the corresponding corrosion by-products and the extent of corrosion attack. For example, the presence of solids typically associated with low pH conditions and the excessive mounding of corrosion by-products covering zones of local metal degradation or pits suggested an

anodic zone, where the potential for lead release is enhanced. The background zone was the remainder of the pipe surface that did not appear to be impacted by galvanic corrosion (Figure S2). The features in this region were consistent in nature and reflected general uniform corrosion.

The galvanic corrosion patterns of twenty-eight galvanic pipe couples collected from eight water utilities are summarized in Table 1. A mix of patterns were observed across and even within utilities. Three pipe joints, representative of the three corrosion patterns (Figure 1, Table 3), are described in detail below.

Pattern 1-No evidence of galvanic corrosion (Sample D1)

Sample D1 was comprised of lead and copper pipes joined by a yellow brass compression fitting (Figure 1a). Thus, there were two galvanic connections (lead-brass, brass-copper) represented in the sample. Scales at the point of contact of these metals were mineralogically identical to those of the respective adjacent pipes. This indicated that uniform corrosion of lead, brass and copper was taking place, without evidence of additional galvanically-driven corrosion. The mineralogy of uniformly corroded metal surfaces (i.e., background zones in the absence of any galvanic zones) is summarized in Table 3 and discussed below, whereas details are offered in Supporting Information (Figures S3, S5-S7).

The lead pipe scale consisted of three layers (L1, L2 and L3). The outermost layer (L1) consisted of local, small patches of brownish colored scale, containing the Pb(IV) oxide plattnerite and possibly scrutinyite. Based on observations of other pipes received from this utility, these patches may be remnants of a previously more extensive coating. The middle, white/cream colored layer (L2) consisted predominantly of cerussite, with minor hydrocerussite, and plumbonacrite. The innermost (L3) layer was composed of litharge.

On the brass fitting, the scale consisted of malachite with minor cerussite. Scales on the copper pipe were composed of malachite overlying a thin layer of cuprite. The lead pipe showed a thickened litharge layer at the joint.

Pattern 2-Galvanic corrosion evident with lead pipe cathodic relative to anodic brass or copper (Sample A2)

Evidence of severe localized brass corrosion at the connection of lead and brass pipes in Sample A2 indicated that the red brass pipe was the anode in the galvanic couple (Figure S2). The brass pipe exhibited excessive dealloying across the entire pipe wall cross section in the ~1.0 to 1.5 cm immediately adjacent to the joint, as evidenced by conversion of the metallic brass to a brittle reddish and pale blue-green material composed of cuprite and posnjakite (Figure 2a; Table 3, also Supporting Information Figures S2 and S8). Thinner surface corrosion and localized pitting extended ~6 cm upstream from the end of the pipe. The brass galvanic zone was dominated by thick blue-green or yellowish green irregular deposits of brochantite, nakauriite, and malachite (Figure S9). Anglesite was locally present within the galvanic zone, mainly co-occurring with cuprite in the dealloyed pits and the extensively dealloyed end of the pipe. Here the anglesite was micro-crystalline and disseminated throughout the cuprite matrix, suggesting that the lead was likely sourced from the brass alloy rather than the lead pipe. Porous copper scales, consisting of similar minerals

to those on the adjacent brass pipe, extended onto the lead pipe surface (Figure 2a, S2). In addition, numerous 100 μm diameter spheroids composed of radiating euhedral crystals of antlerite occurred within the void spaces in the copper solids.

The predominant scale morphology and mineralogy in the brass background zone changed dramatically from the thick galvanic deposits to smoother textured grayish blue-green deposits composed of mushistonite, a copper-tin hydroxide (Table 3, Figure S2). The tin likely originated from the brass pipe, which contained 5.6 % tin in pristine sections and 14.8 % tin in dealloyed sections of Sample A2 (Table S2, Figure S4). Table S2 and Figure S4 compare the elemental composition of a reference red brass to the elemental composition of Sample A2 in pristine and dealloyed sections, in order to illustrate the extent of red brass dealloying experienced at this joint. Changes in elemental composition in this dealloyed brass section reflect the preferential mobilization of zinc and copper, leading to relative increases in the remaining concentrations of tin and lead.

The lead pipe exhibited no visible pitting, thus constituting the cathode in this galvanic corrosion cell. In the galvanic zone, litharge occurred beneath the thick deposit of copper solids. The background scale mineralogy on the lead pipe was predominantly plattnerite, with minor scrutinyite, calcium lead phosphate and hydrocerussite overlying litharge (Table 3). In this example the plattnerite reflects a legacy scale formed under prior free chlorine disinfection, which had not entirely decomposed after five to six years of monochloramine disinfectant.

Pattern 3-Galvanic corrosion evident with lead pipe anodic relative to cathodic brass (Sample E1)

Lead pipe was the anode in Sample E1, as evidenced by severe localized lead corrosion. Galvanic zone pitting occurred across a ~2 cm area at the joint (Figure 3a). In places the entire 1/4"-thick lead pipe wall had dissolved, such that the corrosion pit impinged on the lead-tin solder used to seal the joint. The thick shell of outermost material covering the galvanic zone was largely composed of hydrocerussite, which, along with cerrussite also comprised the bulk of the background surface scale deposits on the rest of the lead pipe (Table 3, Figures S11 and S12). Beneath the outer cap was a middle zone consisting of euhedral crystals of anglesite, as well as leadhillite, susannite and laurionite. These minerals formed large crystals in the void space beneath the outer cap. These same lead sulfate and hydroxychloride phases also occurred in the deepest part of the corrosion pit, within void spaces of the extensively corroded lead pipe wall.

The adjacent red brass pipe showed no evidence of locally enhanced corrosion, and had only a very thin layer of scale deposits across its entire surface. The background scale mineralogy on the brass pipe was predominantly nanocrystalline cassiterite, with local pockets of cuprite overlain by mushistonite and brochantite (Figure S13).

Model Prediction of Mineral Assemblages

Figures 2b, 2c and 3b are illustrative examples of geochemical modeling, meant to demonstrate water quality conditions necessary to form the minerals observed in anodic zones of Galvanic Patterns 2 and 3. The modeling exercise illustrated that for certain

minerals to be present in the microenvironments, local water quality conditions had to be appropriate and different from the bulk drinking water.

For the array of minerals identified in Pattern 2 (i.e., Sample A2), geochemical modeling illustrated that a pH gradient from about 7.7 (for malachite) to 4.0 (brochantite) and as low as at least 3.0–4.0 (antlerite) would be necessary to form the observed copper minerals (Figure 2b), depending upon the actual amount of soluble copper and likely some concentration of sulfate in the microenvironment. The low acidic pH needed to form antlerite (pH 3.0–4.0) is much lower than the reported average bulk water pH of 7.7 for Utility A. Conditions at a corroding brass anode of a galvanic connection could therefore produce a condition analogous to pitting corrosion of copper. In addition, sulfate (log a of -2 equals ~ 960 mg/L, and log a of -1 equals 9600 mg/L in Figure 2c) and copper (log a of -3 , -2 , -1 equals ~ 64 mg/L, 640 mg/L, 6400 mg/L respectively in Figure 2b) should be present in significant quantities to form the identified copper sulfate solids of Pattern 2 (Figure 2c).

For Pattern 3 (Sample E1, Figure 3b), the starting point bulk water concentrations of Utility E of sulfate, chloride and soluble lead provided sufficient quantities in the model to predict the formation of the observed lead solids, though some additional concentration in the scale microenvironment is possible. Anglesite and laurionite were predicted to form at pH < 5.5 , a substantial decrease from the bulk water pH of 7.4. This would represent a local pH drop around the lead anode, shifting the lead solubility diagram to pH conditions that favor dissolved Pb(II) presence (Figure 3b) and thus increased potential for lead contamination of drinking water.

Overall, geochemical modeling, in conjunction with the PXRD mineral observations, support the theory and other researchers' experimental observations of lower pH and ion migration toward the anode of the galvanic couple.

Pb(II) and Pb(IV) oxidation state on lead anode/cathode behavior

Table 1 summarizes the galvanic corrosion patterns identified across all pipe samples. Lead was never the anode in samples from drinking water systems which currently have, or had, decades-long consistency of treatment that favored the development of stable Pb(IV) scales as observed on their lead pipes (Utilities A & B in Table 1). Lead (IV) scales are much less soluble than Pb(II) scales, and form on lead pipes when the water chemistry facilitates a consistently high and stable oxidation reduction potential and surface corrosion potential (49).

Utility C is unique in that it started to develop Pb(IV) scales on the lead pipes following a treatment change in 2006, which increased pH from ~ 8.1 to ~ 9.3 . The 2006 conversion of lead minerals on lead pipes from Pb(II) to Pb(IV) phases, had immediate impacts on galvanic corrosion reversion (lead pipe switched from anode to cathode of the galvanic cell). Specifically, five samples collected before the treatment change showed evidence of galvanic lead corrosion (i.e., the lead pipe was the anode) whereas brass was the cathode. Brass fittings from six galvanic connections sampled after this change showed evidence of galvanic brass corrosion (i.e., localized brass pitting and dealloying at the brass anode) whereas lead was the cathode. These temporal observations from multiple galvanic joints

within Utility C support the notion that drinking water quality can affect galvanic lead corrosion, and that galvanic lead corrosion is a dynamic process sensitive to water treatment changes even in joints which had been in service for 70+ years at Utility C. Experimental work has also shown copper coupons becoming anodic to lead coupons over time as Pb(IV) solids accumulated on the lead in the presence of free chlorine under continuous flow (29).

Utility F exhibited mixed results, with no evidence of galvanic corrosion in some joints and with evidence of galvanic brass corrosion (i.e., brass was the anode) in others, although most joints were excavated in the same year. This utility has zones of differing water chemistry within the distribution system, due to mixing of waters from different sources. The three samples (F2, F3, F5) with evidence suggesting brass as being the anode, had well-developed Pb(IV) scales on the lead pipe surface. Conversely, samples F1 and F4 which had abundant hydrocerussite in addition to the Pb(IV) scales on the lead pipe, exhibited no clear evidence of galvanic corrosion. These spatial observations from several galvanic joints within Utility F suggest that the presence and extent of galvanic corrosion ties back to local water quality conditions within the distribution system. By extension, water systems that have multiple zones of different water qualities may have different manifestations of galvanic corrosion within them.

Importance of galvanic corrosion based on excavated lead joints

This work reconciles the seemingly conflicting prior research expectations summarized by Giammar et al. (4) by demonstrating that extremes in lead pipe behavior are possible across real excavated galvanic joints. Specifically, mineralogical evidence supports the creation of a sustained galvanic cell (Patterns 2 and 3) in most systems that were studied, consistent with electrochemical theory and the majority of prior experimental work. The absence of a galvanic cell (Pattern 1) was limited to a relatively small number of samples, although three of the eight water systems had at least one such sample.

In the majority of cases where galvanic corrosion was evident, lead was found to behave either as the anodic metal (Pattern 3), consistent with empirical galvanic series of lead→brass→copper in order of increasing nobility (1, 50), or as the protected cathodic metal (Pattern 2), consistent with galvanic battery reversion possibly depending on certain water quality and/or flow conditions (29). In the latter situation, empirical galvanic series as reported in seawater (50) or in unspecified water conditions (1) may not reflect the environment of interest. Matsukawa et al. (27) found that lead was more noble (i.e., had lower measured potential) than copper in a specific flowing tap water quality in Japan, while the opposite was true in flowing seawater. Because the direction and magnitude of galvanic attack is a complex combination of anode-to-cathode surface area ratio, distance between coupled metals, temperature, water flow velocity, water quality and condition of the metal surfaces (50), empirical galvanic series may not always reflect these complexities but offer a useful starting point.

Anodic lead corrosion (Pattern 3) is consistent with empirical galvanic series and was aggressive in the joints where it was observed. This pattern deserves further discussion, as it poses the greatest risk of drinking water lead contamination. This is because lead release into the water from uniform lead pipe corrosion under bulk water conditions is exacerbated

by the additional mechanism of galvanically-driven lead corrosion under more aggressive localized water conditions around the lead anode. Over time, galvanic attack penetrated deeply into the lead pipe wall to pose a presumably significant public health risk and a potential risk of eventual joint failure. Despite joints being over 60 years old, the findings suggest that galvanic zones were still active at the time of extraction and posed an important source of lead to drinking water.

The formation of certain minerals (e.g., anglesite, antlerite, laurionite) reflected an aggressive water quality in their vicinity (e.g., acidic pH, elevated sulfate and chloride levels). Because it is practically impossible to measure these important water quality parameters in the water microlayers surrounding real pipe joints when they are in service underground, theoretical solubility modeling proved an invaluable tool in gathering mechanistic insights. Solids identified at anodic sites were relatively soluble and some are being reported in drinking water systems for the first time (e.g., antlerite).

Localized corrosion mechanisms that are galvanically driven may be very different than those arising from uniform corrosion or formation of scale deposits on lead pipes. Therefore, a certain set of water quality conditions may be detrimental for galvanic lead release but not necessarily for lead release from uniform corrosion. By extension, a specific corrosion control treatment may be beneficial in controlling one lead release mechanism but not necessarily the other.

From a public health standpoint, galvanic Pattern 3 poses the greatest lead exposure risk. The exact conditions that promote this pattern versus the other two patterns are not fully understood, although our observations suggest it is not prominent in Pb(IV) systems. As such, a conservative plumbing approach would be to avoid direct lead connections with other metals/alloys, during partial lead service line replacements, maintenance work, or whenever opportunity arose, especially in lead-plumbed distribution systems dominated by Pb(II) chemistry instead of Pb(IV) chemistry.

Although not as concentrated a source of lead as pure lead pipe, leaded brass alloys can also exacerbate lead release if they behave as the anode at galvanic junctions. As a result, Pattern 2 in brass-lead joints sampled herein is not galvanic risk free, since uniform corrosion of the leaded brass is exacerbated by galvanic corrosion of the leaded brass anode. Pattern 1 represents the best-case scenario of uniform lead corrosion only (from lead pipe or leaded brass in the samples analyzed here), and still requires approaches to control drinking water lead exposure from uniform lead corrosion. It is also uncertain whether potential water treatment changes at the plant would trigger galvanically-driven corrosion in the future for samples that fell under Pattern 1.

Galvanic corrosion in a broader context

The observational results reported here show the complexity of mixed metal plumbing interactions in actual distribution systems, and give evidence to the widespread importance of galvanic lead corrosion. Unfortunately, it was impossible to capture the array of connection fittings that are available for modern partial lead service line replacements, and

the array of water chemistries across the US, plus all of the combinations of other factors known to affect galvanic corrosion (3) within this limited set of “samples of opportunity.”

The water quality data limitations in terms of incomplete analytical characterizations of the bulk water over time, (e.g., missing Cl^- & SO_4^{2-} , infrequent pH measurements in the distribution system, *etc.*) exemplify the limited resources at some small and medium US water utilities. They only rarely conduct comprehensive and statistically representative analyses of their treated drinking water quality parameters that can affect lead corrosion and participate in pipe scale formation. Data were especially missing for parameters not required by regulation. This in turn makes it challenging to draw conclusions about the influence of specific water quality parameters to the galvanic pipe observations that were described here.

Crystalline solids identified at galvanic joints were key indicators of the three observed galvanic patterns. Sharp PXRD profiles with low intensity baselines indicated that crystalline rather than amorphous solids were dominant in this set of samples. Still, the potential role of amorphous (i.e., non-crystalline) material should be explored in the future, as they are known to be important lead pipe scale components in many water systems (51–53).

Future studies would highly benefit from collecting a complete suite of water quality information, in order to determine the exact water chemistry limits that produce different mineral assemblages, such as elucidating conditions that promote Pb(II) versus Pb(IV) solids in pipe scales, or those that promote mixed sulfate, chloride and carbonate-containing minerals in the galvanic corrosion zones. Selection of pipe samples representing sufficient representations of potentially important influential factors such as joint type, would help refine and clarify the relative roles of the different influential factors in governing or mitigating lead release.

In addition to impacting potential Pb health effects, the accumulation of corrosion by-products at galvanic junctions may obstruct water flow, and the extreme weakening of plumbing materials at anodic sites may compromise the integrity and lifespan of plumbing infrastructure. As such, future research should aim to develop electrochemical reaction models to predict the amount and direction of reactions at metal to metal joints across drinking water chemistries, and develop knowledge to enable adjustment of corrosion control to minimize the impact of galvanic corrosion on lead release into drinking water, in addition to minimization of uniform lead corrosion.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Three lead pipe joints, representative of the three observed galvanic corrosion patterns. Pattern 1: No galvanic corrosion (a), Pattern 2: Galvanic corrosion with lead cathode (b), and Pattern 3: Galvanic corrosion with lead anode (c). The scale bar is 1 cm, with mm subdivisions.

Figure 2.

Cu^{2+} phase diagram (b) and SO_4^{2-} phase diagram (c), predicting formation of solids that were identified at a lead pipe joint representative of lead cathodic galvanic corrosion Pattern 2 (a). The scale bar is 1 cm. Abbreviated minerals are explained in Table 3. Solubility calculations in 2b assumed ionic strength of zero, chloride=28 mg/L, sulfate=48mg/L, DIC=21mg/L, whereas 2c assumed Cu=100mg/L, chloride=28 mg/L, DIC=21mg/L. All solubility calculations assumed 25°C, because of the absence of temperature-dependence functions or enthalpies of formation for key copper aqueous and solid species.

Figure 3. Pb^{2+} phase diagram (b), predicting formation of minerals that were identified at a lead pipe joint representative of lead anodic galvanic corrosion Pattern 3 (a). The scale bar is 1 cm. Abbreviated minerals are explained in Table 3. Solubility calculations in Figure 3b assumed 25°C, ionic strength of zero, chloride= 50 mg/L, sulfate= 9 mg/L, DIC= 8 mg/L.

Table 1.

Summary of lead-brass and lead-copper joints, obtained from water utilities A-H from 2004 to 2010. Multiple joints were occasionally obtained from the same utility over time.

Utility	Sample	Pipe Materials ¹	Galvanic Pattern ²	PbO ₂ Present	Joint Type ³	Installed	Extracted	Years in service
A	A1	brass - lead	2	Yes	wiped	1924	2006	82
	A2	brass - lead	2	Yes	wiped	1913	2006	93
	A3	brass - lead	2	Yes	wiped	1945	2005	60
B	B1	copper - lead	2	Yes	wiped	1926	2007	81
	B2	copper - lead	2	Yes	wiped	1926	2007	81
	B3	brass - lead	2	Yes	wiped	?	2005	?
	B4	brass - lead	2	Yes	wiped	?	2005	?
C	C1	brass - lead	3	No	cup	1891	2005	114
	C2	brass - lead	3	No	cup	1916	2005	89
	C3	brass - lead	3	No	cup	1912	2005	93
	C4	brass - lead	3	No	cup	1934	2005	70
	C5	brass - lead	3	No	cup	1910	2005	95
	C6	brass - lead	2	Yes	cup	1932	2008	76
	C7	brass - lead	2	Yes	cup	1922	2008	86
	C8	brass - lead	2	Yes	cup	1911	2008	97
	C9	brass - lead	2	Yes	cup	1910	2008	98
	C10	brass - lead	2	Yes	cup	1911	2009	98
	C11	brass - lead	2	Yes	cup	1910	2009	99
D	D1	copper - brass - lead	1	Yes	compression	~1915 (1994) ⁴	2006	~91 (12) ⁴
E	E1	brass - lead	3	No	wiped	?	?	?
	E2	brass - lead	3	No	wiped	?	?	?
F	F1	brass - lead	1	No	flare	?	2004	?
	F2	brass - lead	2	Yes	flare	1923	2010	87
	F3	brass - lead	2	Yes	wiped	?	?	?
	F4	brass - lead	1	No	wiped	1912	2010	98
	F5	brass - lead	2	Yes	wiped	1912	2010	98
G	G1	brass - lead	1	No	wiped	?	2005	?
H	H1	brass - lead	3	No	wiped	?	?	?

¹ **Red** indicates anode of galvanic couple at time of sampling, based on corrosion deposits

² Galvanic corrosion pattern observed: 1 = no evident galvanic corrosion, 2 = Pb cathodic, 3 = Pb anodic

³ Wiped and cup joints are constructed with lead-tin solder. Flare and compression joints are mechanically connected.

⁴ Partial service line replacement. Utility portion replaced with copper in 1994.

? = unknown chronology of pipe installation and/or extraction

Bold = pipe sample presented in this paper

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Table 2.

Water quality parameters obtained from the water utilities (average and/or range). Conditions highlighted in bold reflect the three samples representing the three galvanic corrosion patterns

Utility	pH	Total alkalinity	Total hardness	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Disinfectant	Residual
(mg/L as CaCO ₃)										
A	7.7	83 (60 – 102)	139 (112 – 139)	42 (34 – 47)	8 (6 – 11)	28 (22 – 34)	48 (39 – 56)	2.46 (2.23 – 3.11)	Mono chloramine^a	3.7 (3.7 – 3.8)
B	8.6 (8.1 – 8.9)	70 (50 – 91)	125 (100 – 155)	36 (31 – 40)	8 (4 – 11)	27 (18 – 34)	66 (40 – 77)	0.18	Chlorine	1.17 (0.95 – 1.48)
C	8.1, 9.3 ^b (7.8 – 8.5)	19.9 (14 – 24)	35.3 (20 – 44)	--	--	--	--	NA	Chlorine	0.62 (0.40 – 0.86)
D	7.6	300	--	69	--	15	17	NA	Chlorine	0.2 – 0.4
E	7.4 (4.4 – 8.2)	30.2 (12 – 75)	--	--	--	50	9	NA	Chlorine	1.4 (0.17 – 3.05)
F	7.4 – 7.8	65 – 85	--	--	--	24 – 32	15 – 29	NA	Chlorine	0.4 – 0.9
G	9.4 (9.2 – 9.8)	35 (25 – 60)	90 (85 – 100)	20 (16 – 24)	10 (7 – 10)	46 (10 – 100)	70 (40 – 150)	0.8 (0.2 – 1.0)	Mono chloramine	2.0 (1.0 – 3.5)
H	8.77 (8.2 – 9.6)	35.78 (24 – 80)	109.87 (75 – 177)	28.18 (23.8 – 37.9)	6.87 (4.5 – 11.9)	30.56 (41.2 – 18.8)	56.67 (38.59 – 76.49)	NA	Mono chloramine	1.43

-- = Not analyzed.

NA = Not applicable. Utility did not add phosphate chemical

Conditions shown are typical of 5 years preceding pipe sample collection.

^aUtility A previously used free chlorine disinfectant at ~2.5 – 4 mg/L residual until November 2000.

^bUtility C raised pH to ~9.3 in March 2006. From June 2006 to December 2008, pH in the distribution system ranged between 8.9 and 9.7.

Table 3.

Lead solids, copper solids, tin solids and zinc solids, as identified by PXRD in galvanic (Galv) and/or background (Bkgd) zones of three joints. Each joint represents one of the three galvanic corrosion patterns. Question marks (?) indicate possible presence.

	Mineralogy		Galvanic Pattern (Sample Zone(s))				
			Pattern 1: No Galvanic (D1)	Pattern 2: Pb Cathodic (A2)		Pattern 3: Pb Anodic (E1)	
	<i>Solid (abbrev.)</i>	<i>Formula</i>	Bkgd	Bkgd	Galv	Bkgd	Galv
Lead Pipe	Litharge (<i>L</i>)	PbO	X	X	X	X	
	Plattnerite (<i>P</i>)	PbO ₂	X	X			
	Scrutinyite (<i>S</i>)	PbO ₂	?	X			
	Cerussite (<i>C</i>)	PbCO ₃	X			X	
	Hydocerussite (<i>Hc</i>)	Pb ₃ (CO ₃) ₂ (OH) ₂	X	X		X	X
	Plumbonacrite (<i>Pn</i>)	Pb ₁₀ (CO ₃) ₆ (OH) ₆ O	X				
	Calcium lead phosphate (<i>Clp</i>)	Pb _{5-x} Ca _x (PO ₄) ₃ OH		X			
	Lanarkite (<i>Ln</i>)	Pb ₂ (SO ₄)O				X	
	Leadhillite/Susannite (<i>Lh/Su</i>)	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂				X	X
	Anglesite (<i>An</i>)	PbSO ₄			X		X
	Laurionite (<i>Lr</i>)	Pb(OH)Cl					X
Brass or Copper Pipe	Cuprite (<i>Cp</i>)	Cu ₂ O	X		X	X	
	Malachite (<i>M</i>)	Cu ₂ CO ₃ (OH) ₂	X		X		
	Nakaurite (<i>N</i>)	Cu ₈ (SO ₄) ₄ (CO ₃)(OH) ₆ ·48H ₂ O			X		
	Brochantite (<i>B</i>)	Cu ₄ SO ₄ (OH) ₆			X	X	
	Posnjakite (<i>Po</i>)	Cu ₄ SO ₄ (OH) ₆ · H ₂ O			X		
	Antlerite (<i>At</i>)	Cu ₃ SO ₄ (OH) ₄			X		
	Mushistonite (<i>Mu</i>)	CuSn(OH) ₆		X		X	
	Cassiterite (<i>Cs</i>)	SnO ₂				X	
	Hopeite (<i>Ho</i>)	Zn ₃ (PO ₄) ₂ · 4H ₂ O		?			
	Smithsonite (<i>Sm</i>)	ZnCO ₃		?			