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***In Situ* Monitoring of Pb²⁺ Leaching from the Galvanic Joint Surface in a Prepared Chlorinated Drinking Water**

Xiangmeng Ma[†], Stephanie M. Armas[§], Mikhael Soliman^{||}, Darren A. Lytle[‡], Karin Chumbimuni-Torres[§], Laurene Tetard^{||}, Woo Hyoung Lee^{*,†}

[†]Department of Civil, Environmental and Construction Engineering, University of Central Florida, Orlando, Florida 32816, United States

[§]Department of Chemistry, University of Central Florida, Orlando, Florida 32816, United States

^{||}NanoScience Technology Center and Physics Department, University of Central Florida, Orlando, Florida 32826, United States

[‡]National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268, United States

Abstract

A novel method using a micro-ion-selective electrode (micro-ISE) technique was developed for *in situ* lead monitoring at the water–metal interface of a brass–lead solder galvanic joint in a prepared chlorinated drinking water environment. The developed lead micro-ISE (100 μm tip diameter) showed excellent performance toward soluble lead (Pb^{2+}) with sensitivity of 22.2 ± 0.5 mV decade⁻¹ and limit of detection (LOD) of 1.22×10^{-6} M (0.25 mg L⁻¹). The response time was less than 10 s with a working pH range of 2.0–7.0. Using the lead micro-ISE, lead concentration microprofiles were measured from the bulk to the metal surface (within 50 μm) over time. Combined with two-dimensional (2D) pH mapping, this work clearly demonstrated that Pb^{2+} ions build-up across the lead anode surface was substantial, nonuniform, and dependent on local

* W. H. Lee. Phone: +1 407 823 5304; Fax: +1 407 823 3315; woohyoung.lee@ucf.edu.

surface pH. A large pH gradient ($\text{pH} = 6.0$) developed across the brass and leaded-tin solder joint coupon. Local pH decreases were observed above the leaded solder to a pH as low as 4.0, indicating it was anodic relative to the brass. The low pH above the leaded solder supported elevated lead levels where even small local pH differences of 0.6 units ($\text{pH} = 0.6$) resulted in about four times higher surface lead concentrations (42.9 vs 11.6 mg L^{-1}) and 5 times higher fluxes (18.5×10^{-6} vs $3.5 \times 10^{-6} \text{ mg cm}^{-2} \text{ s}^{-1}$). Continuous surface lead leaching monitoring was also conducted for 16 h.

Introduction

Due to its durability and flexibility, lead (Pb) has been widely used in drinking water delivery pipelines, premise plumbing systems, and various fittings, and has been added to solder for making pipe connections.(1) However, as a result of corrosion and the dissolution of corrosion byproducts, lead can leach into drinking water, resulting in elevated Pb levels that can impact blood lead levels.(2) Chronic exposure of lead can cause adverse health effects on cognitive ability, academic performance, behavior and growth of children along with reproductive effects and increased blood pressure in adults.(2) After establishing amendments of the Safe Drinking Water Act (SDWA) in 1986, the United States Environmental Protection Agency (USEPA) mandated the use of “lead free” materials (no more than a weighted average of 0.25% lead in the wetted surfaces of pipes, pipe fittings, plumbing fittings, and fixtures; and less than 0.2% in flux and solder) in all pipelines, fittings, and solders, which were designated for conveying water for human consumption under Section 1417.(3, 4) In 1991, the Lead and Copper Rule (LCR) was promulgated by the USEPA to establish action levels for lead and copper in drinking water at consumer taps of 0.015 and 1.3 mg L^{-1} , respectively.(5) Development and implementation of effective corrosion control is necessary to mitigate lead leaching from potential sources in household plumbing systems.

Galvanic corrosion is a result of the interaction of two dissimilar metals that can result in the release of significant levels of lead to drinking water. Galvanic corrosion involving leaded materials is a complicated process and our understanding of the associated mechanism(s) related to lead leaching in chlorinated drinking water has largely been based on theory, bulk water analysis and forensic metal surface characterization. For example, inductively coupled plasma mass spectrometry (ICP-MS) measurements have been commonly used to measure lead concentrations in many galvanic corrosion drinking water studies.(6–10) Although ICP-MS provides accurate and informative lead information, measurements are limited to bulk water lead concentrations. For a better understanding of galvanic corrosion, lead leaching and lead transport from metal surfaces as well as direct lead measurements at the interface, where corrosion occurs, are necessary.

Potentiometric ion-selective electrodes (ISEs) are an attractive, sensitive, and easily miniaturized tool for the analysis of heavy metal ions in aqueous samples.(11) They have been used in a variety of applications including clinical, food, environment, and industrial analyses.(12–15) ISEs are the preferred analytical tool in some applications due to their high degree of sensitivity and selectivity, and are able to reach nanomolar and subnanomolar

limits of detection (LOD), competing with other well-established and sophisticated analytical tools (e.g., ICP-MS and high-performance liquid chromatography mass spectrometry (HPLC-MS)).(11, 16, 17) Particularly, polymeric-based ISEs offer the versatility to analyze a variety of ions by simple manipulation of the polymer membrane composition. A polymeric membrane is typically composed of three compounds: (1) an ionophore, which selectively binds the target ion, (2) an ion-exchanger, which maintains electroneutrality within the matrix and allows for permselectivity of ions, and (3) a polymer matrix, which yields the support and mechanical stability of the membrane.(18) The response mechanism does not require an external input of energy, as the resulting potential, or electromotive force (EMF) response is directly related to the potential difference across the hydrophobic and sample phase boundary of the ISE.(18)

In this study, a microscale needle-type ion-selective electrode (micro-ISE) was developed using lead-selective liquid ion exchange (LIX) membrane for *in situ* monitoring of Pb^{2+} concentrations near the metal surface of galvanic joints in a prepared chlorinated drinking water. The miniaturization of the polymeric-based micro-ISE's tip size to micrometer level (50–100 μm) will not only make *in situ* monitoring possible in a small amount of sample volume, but can also provide real-time dynamic information about liquid–metal interfacial chemistry with high spatiotemporal resolution, which can be further interpreted by determining diffusion boundary layer (DBL), reaction rate, and flux of the ion species of interest. As soluble lead (Pb^{2+}) is pH-dependent, two-dimensional (2D) surface pH mapping was also performed using a pH microelectrode in conjunction with lead measurements. The direct measurement of lead concentrations near metal surfaces at microscale will expand the current fundamental understanding of galvanic corrosion and lead leaching mechanisms in drinking water distribution systems.

Materials and Methods

Reagents and Materials

All chemicals used in this study were in analytical reagent grade. Tert-Butylcalix [4] arene-tetrakis (*N,N*-dimethylthioacetamide) (Pb ionophore IV), sodium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate (NaTFPB), 2-nitrophenyl octyl, high molecular weight polyvinyl chloride (PVC), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (Milwaukee, WI). The Pb^{2+} ISE cocktail was prepared by adding 5 mmol/kg of NaTFPB, 12 mmol/kg of Pb IV, *o*-NPOE (66.6 w%), and PVC (33.3 w%), as previously reported by McGraw et al.,(19) and dissolved in 1 mL of THF and vortexed for 1 h. Chlorinated drinking water solutions were prepared in distilled (DI) water with serial dilutions from the stock solution containing dissolved inorganic carbon (DIC), chloride (Cl^-), sulfate (SO_4^{2-}), and free chlorine (Cl_2) (see Supporting Information (SI) for details).

Fabrication, Preparation and Calibration of a Lead Micro-ISE

The fabrication procedures of the lead micro-ISE are similar to a conventional liquid ion exchange (LIX) membrane microelectrode fabrication which can be found elsewhere.(20) A flaming/brown micropipette puller (Model P-1000, Sutter Instrument Co., Novato, CA) was used to pull the glass micropipette (640815, O.D.: 1.5 mm, I.D.: 1.1 mm, 10 cm length,

Warner Instruments, Hamden, CT). After opening the tip with a surgical grade tweezer (Sigma-Aldrich, Milwaukee, WI), the tip was silanized with *N,N*-dimethyltrimethylsilylamine (Sigma-Aldrich, Milwaukee, WI) and the micropipettes were stationed at the glass micropipette holder (custom-made) and baked in the oven (Quincy Lab, Chicago, IL) at 180 °C for 4 h. After they were removed from the oven, the micropipettes were kept in the dark in a desiccator for 1.5–2 h. The silanized micropipette was then backfilled with an internal solution (1 mM Pb(NO₃)₂ and 1 mM KCl) using fine injection needles (World Precision Instruments, MF28G-5) and the lead cocktail was inserted into the front tip by capillary force (2 min). An internal Ag/AgCl coated wire was prepared (see SI for details) and inserted from the electrode back and immersed in the internal solution with 1 cm distance between LIX membrane and the internal reference electrode. The fully assembled lead micro-ISE was then pretreated in 1.0×10^{-3} M Pb(NO₃)₂ solution at 25 °C for overnight to achieve the equilibrium of the sensor. A commercial Ag/AgCl millielectrode was used as an external reference electrode. During profiling, the order of the lead micro-ISE assembly was:

Internal Ag/AgCl | internal solution (1 mM Pb(NO₃)₂ and 1 mM KCl) | PVC membrane | test solution | 3.0 M KCl | external Ag/AgCl.(21–23)

Finally, the finished Pb²⁺ micro-ISE was calibrated in the lead standard solution (Pb(NO₃)₂) with different lead concentrations (1.0×10^{-7} – 1.0×10^{-2} M). Interference of potential ions(21) such as sodium ion (Na⁺) was also evaluated during the calibration. The calibrations for the characterization of the developed Pb²⁺ micro-ISE were carried out at pH 4.8 to ensure full availability of Pb²⁺ ions due to speciation (Figure S2) and 23 °C.

Microprofiling of Lead Concentrations Using a Lead Micro-ISE

A fresh brass–lead galvanic joint coupon imbedded with cold epoxy specimen mounting technique (Figure S1) was prepared (see SI for details) and immersed in the prepared chlorinated drinking water solution (150 mL, pH 7, free chlorine 2 mg Cl₂ L⁻¹, 100 mg L⁻¹ of Cl⁻ and SO₄²⁻, and DIC 10 mg C L⁻¹) for 1 h before lead concentration microprofiling using the fabricated lead micro-ISE. 2 mg Cl₂ L⁻¹ of free chlorine was selected as a reference purpose to compare with the previous studies in drinking water distribution systems.(24–27) All microprofiles were measured during stagnation, where local pH changes were expected to be more apparent compared to the flow conditions based on previous work(24) and thus greater local lead levels were anticipated. During lead concentration microprofiling, the Pb²⁺ micro-ISE tip was positioned at 2,000 μm above the lead joint surface in the prepared chlorinated drinking water (Figure S3). After a steady electric signal (mV vs Ag/AgCl) was obtained, the tip of the micro-ISE was positioned perpendicular to the metal surface area of interest using a three-dimensional (3D) manipulator (UNISENSE A/S, Denmark) and electronic signals were recorded at 50 μm interval from the bulk (2,000 μm) to the metal surface with every 15 s of electrode signal stabilization (total 10 min of duration for one profile). All profile measurements were duplicated to investigate whether the measured profile was reproducible and representable. Two consecutive profiles were measured at 1 and 2 h after the coupon was immersed in the prepared chlorinated drinking water. After lead microprofilings, surface pH at 50 μm above the metal's surface was measured at a total of 96 points (8 × 12) across the galvanic coupon

(Figure S3a) and a 2D pH spatial map was constructed to investigate the correlation between pH and lead concentrations. The details on microprofile measurements using a microelectrode and the construction of 2D pH spatial map were described elsewhere.(24) Continuous monitoring of Pb^{2+} leaching from the galvanic joint for 16 h was also performed using the lead micro-ISE to evaluate long-term sensor performance. MINEQL+ (Environmental Research Software, Hallowell, ME) chemical equilibrium modeling system software was used to identify soluble lead ions depending on pH in various aqueous solutions. Bulk monitoring including free chlorine and Pb^{2+} concentrations, and pH was also performed over time. Lead (Pb^{2+}) concentrations in the prepared water were validated using an Atomic Absorption Spectrometer (AAS) (PerkinElmer AAnalyst 400 Flame, Waltham, MA). During the experiment, precalibration and postcalibration were performed to ensure accuracy of extrapolated Pb^{2+} measurements. After completion of Pb^{2+} microprofiling, the coupon was sacrificed for surface characterization using Raman spectroscopy (Renishaw RM 1000B Micro-Raman Spectrometer) to identify corrosion byproducts.

Results and Discussions

Characterization of the Developed Lead Micro-ISE Performance

Figure 1 shows the finished lead micro-ISE with a tip diameter of 100 μm . After the Pb^{2+} cocktail was successfully applied to the hydrophobic silanized microelectrode tip, a noticeable dark LIX membrane with a length of 200 μm was observed (Figure 1). The selectivity and sensitivity of the Pb^{2+} ISE can greatly be influenced by the ratio (w/w) between ionophore and ion-exchanger as well as the ration of PVC and plasticizer.(22, 23) In this fabrication, the ratio of ionophore to ion-exchanger was adjusted based on stoichiometric binding to ensure a buffer system is maintained between organic and aqueous phases.(28) PVC content was adjusted to 33% to optimize the sensitivity of electrode toward soluble Pb^{2+} and sensor lifetime of 1 week. A tip diameter less than 50 μm was found to be difficult to fabricate, due to challenges of producing sufficient length of LIX membrane at the sensor tip for lead detection, especially when the density of PVC (33%) in the cocktail is relatively high.

The developed Pb^{2+} micro-ISE exhibited excellent linear relationship with various Pb^{2+} concentrations up to $10^{-3.0}$ M with a near Nernstian slope of 22.2 ± 0.5 mV decade $^{-1}$. The Pb^{2+} micro-ISE showed improved working linear dynamic range (LDR) of lead concentrations from 10^{-6} to 10^{-3} M (0.21 to 210 mg L $^{-1}$), compared to the previous Pb^{2+} ISEs fabricated using a similar configuration of the LIX membrane where the Pb^{2+} LDR was $1.0 \times 10^{-4.1}$ to 1.0×10^{-2} M.(23) It was also found that the performance of the developed Pb^{2+} micro-ISE was comparable to AAS (Table S1). The LOD of the Pb^{2+} micro-ISE was 1.22×10^{-6} M (0.25 mg L $^{-1}$) and the response time of the sensor was less than 10 s. It is expected that the solubility of lead would be changed by the presence of other ions (e.g., CO_3^{2-} , Cl^- , and SO_4^{2-}). In the range of pH 2–10 (DI water containing 10^{-5} M of Pb^{2+}), a MINEQL+ simulation showed that there was no Pb^{2+} concentration change below pH 6.0 and the soluble lead species were changed to all insoluble lead above pH 7.5 (Figure S2a). It was clearly shown that the developed Pb^{2+} micro-ISE followed the trend of the soluble Pb^{2+} concentrations, confirming that the micro-ISE measures the soluble Pb^{2+} ions in a solution

(Figure S2b). Thus, the optimal working pH range for lead detection in DI water using Pb^{2+} micro-ISE is 2.0–7.0.(21, 22)

Based on the selectivity coefficient for lead ionophore IV, mercury (Hg) and silver (Ag) have the highest interference with lead due to their soft character and binding affinity to sulfur atoms.(19, 29) Among the other possible ions interference, sodium ion (Na^+) is known as one of the interfering ions for the lead concentration measurements.(22, 23) As the selectivity coefficients of other positively charged ions (Mg^{2+} and Ca^{2+}) are relatively low, only sodium ion interference was evaluated for the sensor performance. In the standard lead solution containing 1 mM Na^+ , the slope of the calibration curve slightly decreased to 18.4 mV decade⁻¹ from the original slope of 22.2 mV decade⁻¹ without Na^+ (Figure 2) due to the increased ionic strength. Given that sodium concentration in typical drinking water is approximately 20 mg L⁻¹ (1 mM),(30) the sensitivity change was only about 82.9% with a good linear relationship with different Pb^{2+} concentrations, indicating that the presence of the sodium would not affect the sensor performance significantly. The ion interference is based on the lead ionophore IV used for Pb^{2+} micro-ISE fabrication and thus it is important to test ion interferences in every real environment. Therefore, in this study, a pre- and postcalibration was performed in the same solution of microprofiling for accurate Pb^{2+} measurements (Figure S5).

Pb^{2+} Microprofiles in a Galvanic Joint

After the sensor characterization, the developed Pb^{2+} micro-ISE was deployed to measure soluble Pb^{2+} concentrations in the prepared drinking water (pH 7, free chlorine 2 mg Cl_2 L⁻¹, 100 mg L⁻¹ of Cl^- and SO_4^{2-} , and DIC 10 mg C L⁻¹). Figure 3 shows Pb^{2+} concentration microprofiles from 2,000 μm above to the metal surface at three different locations of the galvanic joint coupon after one and 2 h of stagnation. After 1 h, Pb^{2+} concentration in the solution between 600 μm and 2,000 μm directly above the surface of location 1 was 9.89×10^{-6} M (2.05 mg L⁻¹). From the microprofiling (Figure 3b), the bulk water concentration was relatively constant until 600 μm above the lead joint surface and, after 600 μm , the concentration of Pb^{2+} dramatically increased as the micro-ISE moved closer to the lead joint surface, indicating the buildup of Pb^{2+} ions from the corroding lead joint surface. DBL was approximately 380 μm . The soluble Pb^{2+} concentration at 50 μm above the lead joint surface (location 1) was 5.31×10^{-5} M (11.0 mg L⁻¹), which is 5.4 times greater than the bulk lead concentration. The increase of Pb^{2+} concentration was associated with a corresponding local decrease in pH (Figure 4), increasing the solubility of Pb^{2+} . Although not measured simultaneously with lead, pH microelectrode measurements at the coupon surface were very informative. The pH at location 1 was as low as 6.4 at a distance of 50 μm from the lead joint. The Pb^{2+} microprofile at location 3 (3,000 μm downward from location 1) over the brass surface showed that lead levels were consistent throughout the distance from the bulk to the brass surface, indicating that there is no detectable lead leaching from the brass surface (Figure 3b). The relatively low Pb^{2+} in this region was attributed to the minor amount of lead (0.07%) associated with the brass and the negligible change in pH at the metal surface (Figure S2) from the bulk (e.g., pH 7.0). The 2D pH mapping of the coupon surface (Figure 4) also shows that the pH near the cross section of 7,000 μm (Y-axis) and 4,000 μm (X-axis) was approximately 7.6 which was

similar to the bulk pH after 1 h of stagnation (Table S2). After 2 h of stagnation, the surface Pb^{2+} concentration (50 μm above the surface) in location 1 increased to $1.13 \times 10^{-4} \text{ M}$ (23.4 mg L^{-1}), which is 12.5 times greater than the bulk lead concentration of $9.04 \times 10^{-6} \text{ M}$ (1.87 mg L^{-1}) (Figure 3c). DBL decreased from 380 to 220 μm , indicating the surface reaction of lead joint with high concentration of Pb^{2+} . In a different location (location 2) of lead joint, the Pb^{2+} concentration was $3.84 \times 10^{-5} \text{ M}$ (7.95 mg L^{-1}), which was lower than the concentration in location 1 which was attributed largely the higher local surface pH (Figure 4) of approximately 7.0. The 2D pH mapping of the coupon surface (Figure 4) showed the dramatic pH differences between lead joint and brass surface. The maximum pH difference (pH) between brass (the highest pH was 10) and lead (the lowest pH was 4) was 6 pH units, while the bulk pH did not change throughout the experiments (Table S2). The pH difference between lead and brass reflected anodic (lead solder) and cathodic (brass) designations in the electrolyte (a prepared chlorinated drinking water) of the galvanic cell, which directly impacted the corrosion and solubility of lead in the respective regions.

The measured lead concentration profiles were further interpreted to determine reaction rates (k) and flux (J) related to the lead leaching process (Table 1). The reaction rates (k) and flux (J) in location 1 after 1 h of reaction was $2.46 \times 10^{-4} \text{ cm s}^{-1}$ and $3.7 \times 10^{-6} \text{ mg cm}^{-2} \text{ s}^{-1}$, respectively. After 2 h, the reaction rates (k) and flux (J) in location 1 increased to $4.31 \times 10^{-4} \text{ cm s}^{-1}$ and $18.5 \times 10^{-6} \text{ mg cm}^{-2} \text{ s}^{-1}$ with decreased DBL, indicating the increased Pb^{2+} leaching from the lead joint over time and accumulation of lead at the metal surface. The predicted surface Pb^{2+} concentration at location 1 increased by 3 times, from 14.0 to 42.9 mg L^{-1} , for 1 h (Table 1). During the profiling, Pb^{2+} concentration in the bulk solution was relatively constant at 2 mg L^{-1} (Table S2). Relatively high Pb^{2+} concentration in the bulk can be possible because of stagnation which can accelerated the galvanic corrosion, increasing Pb^{2+} leaching from the galvanic joint (24, 27) (see the SI for general mechanism of galvanic corrosion in water), a freshly prepared coupon which may be more reactive compared to old coupons, and relatively small volume of test water (150 mL) under stagnation.

The lowest pH (4.0) was found in the left side of the lead joint surface. pH across the Pb/Sn alloy was 3.1 (pH 4.0–7.1). In contrast, the pH values on each brass side increased to a maximum pH of 10 in some locations. However, the initial and final pH in the bulk (before and after the lead and pH microprofile measurements) was 7.0 and 7.2, respectively. It is important to point out that although the pH in the bulk was 7.2 throughout the experiment, over time of the galvanic reaction under stagnation, pH across the brass–lead joint coupon was approximately 6.0, indicating a significant pH difference. The low pH environment at the lead joint that was created by galvanic corrosion along with Pb^{2+} leaching could intensify the corrosion on both lead and brass surface. (27) In this experiment, the measured lead concentrations between location 1 and 2 clearly demonstrated the pH effect on lead leaching processes. From the surface pH variance across the Pb/Sn alloy surface (pH 4.0–7.1), it is predicted that the left side of the lead material would contribute more to the lead leaching to the bulk, indicating that the lead leaching is a nonuniform process. The mechanism of this randomly selective Pb^{2+} leaching is still unclear; however, the 2D map of pH changes and lead concentration microprofiles with two different locations (Figure 4) clearly showed that lead leaching is highly heterogeneous even in the small area of the lead

joint and lower pH resulted in higher lead concentration at the lead surface. Although pH was only 0.6 units between location 1 (pH 6.4) and 2 (pH 7.0), the surface lead concentration was 4 times different between location 1 (42.9 mg L^{-1}) and 2 (11.6 mg L^{-1}) probably due to the lead solubility (Figure S2). The increase in soluble Pb^{2+} concentrations after 2 h showed the continuous oxidation–reduction reaction between the chlorinated bulk water and the galvanic joint, oxidizing pure solid lead to the soluble Pb^{2+} form before forming any possible complexes with background solution.(31)

Continuous real-time monitoring of lead concentrations was profiled from a location only 50 μm above the lead joint surface (location 1) to the bulk water using the developed Pb^{2+} micro-ISE over 18 h of stagnation (Figure 5). The monitoring result showed that the Pb^{2+} levels built-up rapidly above the lead joint during the first 3 h of stagnation. During this time, white solids deposits formed at the lead joint (Figure S4). After 12 h of stagnation and depletion of free chlorine concentration in the water as measured by the Hach method (Table S2), the soluble Pb^{2+} near the lead joint surface decreased to a level similar to that of the bulk water (1.58 mg L^{-1}). However, when replacing the feed solution with a freshly prepared chlorinated drinking water after 15 h, the Pb^{2+} concentration rapidly increased to $2.28 \times 10^{-5} \text{ M}$ (4.71 mg L^{-1}) within 1 h, suggesting that free chlorine is one of the strong driving forces of lead corrosion and subsequent Pb^{2+} generation. Throughout the measurement period, there was only a slight change of dissolved oxygen (DO) concentrations in the bulk and near the metal surface (e.g., 8.5 to 8.4 $\text{mg O}_2/\text{L}$) based on previously reported DO microsensors measurements.(24)

The galvanic coupon was sacrificed for surface examination and characterization following ISE measurements. Close visual examination of the coupon surface showed the structure of the brass surface remained unchanged suggesting no corrosion attack (i.e., acted as the cathode of the galvanic connection), whereas in lead joint appeared corroded (i.e., anodic surface) with areas of white deposits having defined a crystal structure (Figure 6a and Figure S4). The lead joint surface was scanned using Raman spectroscopy and the resulting spectra showed peaks of PbO , Pb_3O_4 , and PbCO_3 on the surface (Figure 6b).(32–34) The Raman analysis of white deposits on the coupon surface directly showed results of soluble Pb^{2+} into the formation of insoluble Pb complexes. This finding agreed with the previous study(27) and the MINEQL simulation also verified that the solids identified using Raman spectroscopy are the most thermodynamically favorable solids to precipitate (Figure S6 and Table S3).

Three results from these experiments may have environmental implication for better understanding of lead leaching in chlorinated drinking water systems. First, bulk pH and lead concentrations provided no information on localized lead leaching. Using the microelectrode technique, it was clearly demonstrated that galvanic reactions in chlorinated water resulted in dramatic local pH drops at the anode which can be a driving force for lead leaching. This cathodic–anodic reaction may also accelerate localized pitting corrosion on either lead and brass. Second, little oxygen was consumed during the galvanic reaction between brass and lead, indicating that oxygen may not be a significant promoter of this galvanic reaction. Third, free chlorine was consumed along with lead leaching on the lead

surface, showing that free chlorine is a strong oxidant which promotes corrosive environments.

Overall, this study successfully developed and demonstrated an innovative tool for *in situ* monitoring of Pb^{2+} concentrations in microenvironments very near to corroding metal surfaces and may be applicable to potentially other applications with the need to examine high spatial resolution. Specifically, this is the first work to measure lead concentrations directly near (within 50 μm) a metal galvanic joint surface and furthermore in combination with corresponding pH measurements at same resolution. Although the long-term continuous monitoring (i.e., months) may not be possible due to the inherent short life (1–3 days) of Pb^{2+} ISE resulting from evaporation of the liquid membrane,(20) the real-time monitoring of Pb^{2+} for short durations (e.g., 16 h) is sufficient to provide meaningful trends of lead leaching from the galvanic joint under various water/metal conditions as successfully demonstrated.

The microscopic analytical tool developed in this study has great potential for use in evaluating lead corrosion, particularly galvanic coupons involving various lead-containing materials. Although the current finding in this study was limited to a fresh lead–brass couple, it provided a clear image of pH dynamics by galvanic reaction and the associated lead leaching during the initiation stage. It is expected that future application of this novel lead measurement microelectrode technique will improve our fundamental understanding of lead corrosion and leaching associated with drinking water distribution plumbing materials and potentially improve lead corrosion control strategies. For example, the time-course investigation of galvanic joints with long periods or microscopic investigation of aged galvanic coupons from real water distribution systems would provide meaningful information. Furthermore, the versatility of this polymeric-based micro-ISE can be expanded to the development of other heavy metal ions detecting micro-ISE sensors (e.g., Zn^{2+} , Cd^{2+} , and Cu^{2+}) and the on-site analysis of sediments or soils that have been contaminated with heavy metals.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Finished Pb^{2+} micro-ISE with a tip size of 100 μm and membrane length of 200 μm .

Figure 2.

Calibration curves of a developed Pb^{2+} micro-ISE with different Pb^{2+} concentrations.

$\text{Pb}(\text{NO}_3)_2$ was used for preparing Pb standard solutions and NaNO_3 was used for testing potential ion interference (pH 4.8 at 23 °C). The lead concentrations on the x-axis are the measured lead concentrations using AAS.

Figure 3.

(a) *In situ* Pb^{2+} concentration microprofiling of a lead–brass galvanic joint coupon with three profiling locations, (b) Pb^{2+} concentration and pH microprofiles on location 1 and location 3 after 1 h of stagnation, and (c) Pb^{2+} concentration microprofiles on location 1 and 2 after 2 h of stagnation (pH 7, 23 °C, 2.0 mg Cl_2 L⁻¹, 100 mg Cl^- L⁻¹, 100 mg SO_4^{2-} L⁻¹, and DIC 10 mg C L⁻¹).

Figure 4.

2D mapping of pH on the galvanic coupon surface (50 μm above the surface) under stagnation (pH 7, 23 °C, stagnation, free chlorine 2 mg L⁻¹, 100 mg L⁻¹ of Cl⁻ and SO₄²⁻, and DIC 10 mg C L⁻¹).

Figure 5.

Continuous real-time monitoring of Pb^{2+} leaching from the lead surface (50 μm above the surface) and comparison of Pb^{2+} concentrations between lead joint surface and bulk.

Another spike of a feed solution after 15 h was performed (pH 7, 23 $^{\circ}\text{C}$, stagnation, free chlorine 2 mg L^{-1} , 100 mg L^{-1} of Cl^{-} and SO_4^{2-} , and DIC 10 mg C L^{-1}).

Figure 6. Metal surface characterization using Raman spectroscopy. (a) Optical images of the brass, lead joint and region made of white deposit characterized with Raman spectroscopy. (b) Average Raman spectra obtained in each region described in (a) with bands corresponding to Pb₃O₄ (125 cm⁻¹), PbO (185 cm⁻¹), PbCO₃ (230 cm⁻¹), SO₄²⁻ (980 cm⁻¹), and CO₃²⁻ (1050 cm⁻¹).

Table 1.

Quantification of Pb Leaching from Microprofiles after 1 and 2 h

Location	Time	DBL (μm)	Reaction rate, k (cm s^{-1})	Flux, J ($\text{mg cm}^{-2} \text{s}^{-1}$)	C_s (ppm) ^a	C_{bulk} (ppm)
1	after 1 h	380	2.46×10^{-4}	3.7×10^{-6}	14.86	2.05
	after 2 h	220	4.31×10^{-4}	18.5×10^{-6}	42.93	1.87
2	after 2 h	320	3.46×10^{-4}	3.5×10^{-6}	11.61	1.87

^a C_S is the predicated surface lead concentration (ppm) at 0 μm based on the measured lead concentration at 50 μm above the metal surface with the assumption of same flux.