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Water Systems Impact Statement.

Lead leaching into drinking water from lead water pipes poses a serious health risk to millions of people. We report novel research on a cost-effective electrochemical method that rapidly stops lead leaching into drinking water. This method may lead to technologies for rapid response to lead-leaching water crises, and offer an intermediate solution to millions of people exposed to lead.

Preventing leaching from lead water pipes with electrochemistry: an exploratory study

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Abstract

Toxic levels of lead leaching from ageing water distribution infrastructure affect over 5,000 public drinking water systems in the US. Pipe replacement, the most effective solution to this problem, is prohibitively expensive. Chemical conditioning of drinking water using orthophosphates, although cost-effective, does not quickly stop lead leaching once it has started. We propose a novel approach to stop lead leaching: to rapidly form an insoluble scale within lead pipes using an external power supply. We report on the feasibility of this approach by first anodizing lead coupons and lead pipes reclaimed form a local water distribution using a phosphate electrolyte and different potentials, pH values, and phosphate concentrations. We subsequently exposed these anodized lead coupons and pipes to synthetic tap water to evaluate their lead leaching rates. We found that polarizing lead coupons in the presence of a 0.05 M phosphate solution decreased lead leaching by up to a 100-fold, relative to leaching from polished bare lead. Similarly, polarizing the reclaimed lead pipes (with a preexisting scale) decreased lead leaching from an average of 36 ppb to 7 ppb. These results were observed when applying potentials that favors Pb(IV) formation, which resulted in the buildup of PbO_2 and $Pb_5(PO_4)_3OH$ in both lead coupons and pipes. Our findings indicate that this novel technology has the potential to rapidly decrease equilibrium lead levels in tap water below the EPA action limit of 15 ppb, and thus deserves further exploration.

1. Introduction

Water distribution systems in many US houses built before 1986 likely have Pb-based service pipes[1]. Over many years of use, Pb water pipes slowly develop a layer of protective scale consisting of Pb corrosion products that limit Pb solubility, including PbO_2 and Pb(II) minerals, such as hydroxylpyromorphite and hydrocerussite, among others[2]. However, this scale is sensitive to water
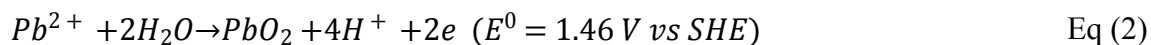
oxidizing conditions and thus, changes in water quality may lead to an increase in Pb solubility, resulting in toxic levels of Pb being released into the drinking water[3–5]. Chronic exposure to Pb has serious adverse health effects, particularly in children, including irreversible damage to the central nervous system[6].

The Pb leaching incident in Flint, MI, illustrates the severity of the situation, in which errors in water quality management led to one of the largest (and most dramatically publicized) recent lead-water crises in the US, putting over 100,000 people at risk[7]. However, this problem is not unique to Flint, MI, as shown by the more recent Pb water crisis in Newark, NJ[8]. It is estimated that there are 6.1 million lead service lines in the US[9]. According to the National Resource Defense Council, more than 5,000 public water systems in the US are in violation of lead standards for drinking water, thus putting at risk over 18 million people[10]. In Europe, an estimated 25% of homes rely on lead-based water distribution pipes, potentially putting over 100 million people at risk[8]. Toxic lead levels also exist in developing world cities – only less publicized[11].

Solutions to the Pb leaching problem do exist but come with their own drawbacks. The most effective solution is to replace the Pb pipes with those of other materials. At a cost between $150 and $300 per meter in the US, this is not a feasible solution for everyone[12]. Moreover, partial lead service line replacement has been associated to the long-term release of particulate Pb into the drinking water[13]. Another approach, chemical conditioning of the water using orthophosphates, is a cost-effective method used to prevent Pb leaching[14]. Orthophosphates form insoluble Pb(II) phosphates in the presence of dissolved Pb(II) ions, binding to the existing scale within the pipes, and preventing Pb leaching. Adding orthophosphates to a city's water supply costs about 0.0016 cents per liter of water and is highly affordable. However, once Pb leaching starts due to the destabilization of PbO_2 scales, stopping it with chemical conditioning may take from months to years[15]. Thus, chemical conditioning is only a protective measure in systems that have already developed an insoluble scale[16]. Currently no rapid and effective solutions exist to stop lead pipes from leaching once leaching has started, putting vulnerable communities at great risk.

Electrochemical systems could provide a rapid resolution to the Pb leaching problem. In principle, it is possible to accelerate the formation of an insoluble scale on the inside surfaces of Pb pipes by temporarily transforming them into electrochemical cells. In such a system, the Pb pipes would be (in-situ) isolated from the rest of the network, and their inside surfaces anodized with an externally

supplied voltage to promote the rapid formation and buildup of insoluble corrosion products on the pipe's inner surface. Depending on the applied potential, one or both of the following reactions will occur on the Pb surface[17]:

$$Pb \rightarrow Pb^{2+} + 2e \ (E^0 = -0.13 \ V \ vs \ SHE) \qquad\qquad \text{Eq (1)}$$

$$Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e \ (E^0 = 1.46 \ V \ vs \ SHE) \qquad \text{Eq (2)}$$

Where a Pb(II) salt or PbO_2 will form when applying a potential that favors Eq.(1) or Eq.(2), respectively. The applied potential for producing the desired corrosion product under different electrolyte conditions may be estimated using the Nernst Equation or Pourbaix diagrams (for further discussion and details of these, see S.I.), while the solubility of the produced Pb(II) salt will depend on the composition of the electrolyte.

Thus, we conjecture that a suitable and freshly formed insoluble scale could be produced in a few hours using this process, and it would protect against further leaching of Pb from a previously-leaching lead pipe. This could be achieved by using the setup depicted in Figure 1. As shown, such a system would require inserting a conductive wire with non-conducting (e.g., plastic) spacers within the pipe and temporarily replacing the tap water in the pipe with a non-toxic supporting electrolyte. The pipe and the wire would then be connected to an external voltage source, which would supply the potential needed to promote the formation of desirable Pb corrosion products. Particularly, Pb(II) phosphates and Pb(IV) oxides would be the most desirable corrosion products to electrogenerate, given their low solubility in water[18,19]. However, to the best of our knowledge, such a system has never been documented in the literature.

We report here the first (and preliminary) results from an experimental investigation to explore the feasibility of lead pipe anodization to prevent Pb leaching into drinking water supply. Implementing this approach also will require overcoming several practical challenges, including the feasibility of inserting a wire and a supporting electrolyte into the pipes. Preliminary discussions with plumbing experts indicate that this approach is feasible and that it would cost about $10-$15 per meter of treated pipe in unbranching lead service lines. Treating branching pipes is also possible if a flexible wire is used and if each branch is treated independently. However, these practical aspects will not be expanded upon in this study. We focus here exclusively on understanding whether a system like this could prevent Pb leaching into the drinking water from a lead plumbing system, studied in a controlled environment.

It is important to clarify that by using the word "prevent" we mean achieving Pb levels below those considered acceptable by the EPA's Lead and Copper Rule. In practical terms, it means Pb levels below 15 ppb, but ideally below 5 ppb. Unless the pipes are replaced, it is unrealistic to expect zero Pb leaching from Pb pipes.

2. Materials and methods

2.1. Choice of the supporting electrolyte

A phosphate solution is a suitable supporting electrolyte for the system described in Figure 1, as it not only provides conductivity, but it also promotes the formation of Pb(II) phosphates and PbO_2[20] depending on the applied potential. Most Pb electrochemical cell studies in the published literature focus on battery applications rather than drinking water. Thus, the published literature is unclear on the values of phosphate concentration and electrolyte pH that would provide the most favorable conditions for preventing Pb leaching into the drinking water. Based on prior literature and our preliminary experiments, we explored four phosphate concentrations (0.5, 0.05, 0.005 and 0.0005 M), and four pH levels (1, 4, 10 and 13), for a total of 16 different compositions for the electrolyte. The phosphate concentrations were chosen based on published literature[20–24], while the pH values were chosen to ensure that only one species of phosphate was present at a time. Thus, the chosen pH values lie roughly midway between the different phosphate pKa values of 2.16, 7.21 and 12.32[25].

2.2. Electrochemical cell setup

Polarization experiments were performed on pristine Pb coupons and on aged (used, salvaged) Pb pipes collected from the local water distribution system. Given that used Pb pipes have pre-existing scales with diverse compositions, we first used polished and cleaned Pb coupons to understand the basic electrochemistry of the system and to find the operating conditions (pH, phosphate concentration and voltage) that minimize Pb leaching from a simple substrate (pure Pb). We then applied the selected treatment to a more complex substrate (Pb pipe with a preexisting scale) to determine whether the treatment protects against Pb leaching in a more realistic setting. These

experiments, to attempt to develop a scale on a lead substrate using electrochemically accelerated reactions, are referenced in the following text as "polarization experiments".

All polarization experiments used a three-electrode setup, with a Pb working electrode (coupon or pipe), a graphite counter electrode and a Ag/AgCl reference electrode. In all polarization experiments an area of 15 cm^2 was exposed to the supporting electrolyte. Prior to the polarization experiment, each Pb coupon was successively polished with 800, 1000 and 2000 grit sandpaper, etched in a 1.1 M HCl solution and then rinsed with DI water to remove any existing Pb corrosion products. On the other hand, the Pb pipes were preconditioned for a month by filling them with synthetic tap water (1mM NaCl, 0.7 mM $CaCO_3$, 0.02 mM Na_2HPO_4 and a disinfection residual of 1.5 mg L^{-1} as Cl_2 at pH 8 [19]) and replacing the water daily.

2.3. Pb coupon polarization

Under different conditions, the potentials at which Pb(II) and Pb(IV) corrosion products form were estimated with Cyclic Voltammetry (CV), by identifying the potentials at which Pb(0) is oxidized to Pb(II), and Pb(II) is oxidized to Pb(IV). In the following text we refer to these, for brevity, as Pb$^{0/2+}$ and Pb$^{2+/4+}$ potentials, respectively. These potentials were obtained by identifying the different peaks in the voltammograms and then comparing those values to thermodynamic estimations. Ten cycles were performed on each Pb coupon using a scan rate of 10 mV s^{-1} with potentials ranging from -1 to 2 V vs Standard Hydrogen Electrode (SHE). Once the Pb$^{0/2+}$ and Pb$^{2+/4+}$ potentials were identified, the Pb coupons were again polished, etched in a 1.1 M HCl solution and rinsed with DI water to remove any corrosion products, after which they were anodized potentiostatially at the corresponding potential for 2 h. The Pb coupons were separately polarized using the 16 electrolyte combinations described in section 2.1, at either the Pb$^{0/2+}$ or the Pb$^{2+/4+}$ potential, resulting in a total of 32 unique combinations. A control experiment was also conducted in which the Pb coupon was not polarized. Each experiment was performed in triplicate.

2.4. Pb coupon scale and water quality analysis

Immediately after two hours of treatment polarizing the Pb coupons, the anodized surface of each coupon was placed in contact with synthetic tap water, made with DI water and 1mM NaCl, 0.7

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mM $CaCO_3$, 0.02 mM Na_2HPO_4 and a disinfection residual of 1.5 mg L^{-1} as Cl_2 at pH 8. Linear Polarization Resistance (LPR) and Tafel plot experiments were performed to estimate the corrosion current of the generated scale using the Stern Geary equation:

$$I_{corr} = \frac{b_a \cdot b_c}{2.3R_p(b_a + b_c)}$$

Eq (3)

Where I_{corr} is the corrosion current (A cm^{-2}), R_p is the linear polarization resistance (Ω cm^2) and b_a and b_c are the anodic and cathodic slopes of the Tafel plot. The LPR and Tafel analyses were performed using a scan rate of 0.125 mV s^{-1}. We used I_{corr} as an indicator of corrosion rate because Faraday's law allows converting I_{corr} to corrosion rates and vice versa.

A subgroup of electrochemically generated scales was analyzed using a Bruker AXS D8 Discover GADDS X-Ray Diffractometer using a Co Kα source and the PDF-4+ ICDD database to identify the crystalline structures that formed during polarization. These coupons were also analyzed using a Horiba LabRAM Aramis Raman microscope with a 532 nm laser wavelength to identify non-crystalline structures. The American Mineralogist crystal structure database[26], as well as data from the literature were used as reference[27–30]. The Pb coupons in this same subgroup were then placed in contact with 40 mL of synthetic tap water and left to equilibrate for 10 days (free chlorine levels were adjusted daily and maintained at 1.5 mg L^{-1} as Cl_2). The water was tested for dissolved Pb, and total Pb, using a Perkin Elmer 5300 ICP-OES with a detection limit of 5 ppb for Pb. A 0.2 μm filter was used to separate dissolved Pb from particulate Pb. During the 10-day equilibration period, the water was recirculated continuously to prevent stratification of lead concentrations, which would have slowed down the leaching rate by an unknown amount.

2.5. Pb pipe polarization and analysis

The water quality analysis performed on the Pb coupons allowed us to identify the operating conditions (phosphate concentration, pH, duration, and voltage) that very substantially decrease Pb leaching into synthetic tap water starting with pure Pb as a substrate. These conditions were used to polarize the preconditioned (aged, salvaged) Pb pipes and to test whether the treatment provides protection against Pb leaching in a more realistic setting. To that end the pipes were anodized potentiostatially using the $Pb^{0/2+}$ and the $Pb^{2+/4+}$ potentials for 2 h and placed in contact with synthetic tap water for 10 days (the disinfection residual was adjusted daily). The tap water was circulated within the pipes to mimic a simplified residential use cycle, with a flow rate of 0.5

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L min^{-1} for 16 h and no flow for 8 h per day. The scale composition was analyzed before and after the treatment using XRD and Raman spectroscopy. Both dissolved and particulate Pb water levels were measured after the 10th day using ICP-OES. In addition, a control experiment was conducted in which the Pb pipe was not polarized. Each experiment was performed in triplicate.

3. Results and discussion

We discovered that the only feasible treatment (within the explored parameters) that prevents Pb leaching from pure Pb coupons and Pb pipes with a preexisting scale, is to polarize them using the Pb$^{2+/4+}$ potential. In the case of the Pb coupons, this potential promotes the formation of insoluble PbO$_2$, which provides protection against Pb leaching in oxidizing environments (tap water with free chlorine). In the case of the Pb pipes, the Pb$^{2+/4+}$ potential promotes the formation of insoluble Pb$_5$(PO$_4$)$_3$OH and PbO$_2$ and significantly decreases Pb leaching into the drinking water. In contrast, polarizing the Pb coupons with the Pb$^{0/2+}$ potential resulted in the release of particulate Pb into the synthetic tap water. In experiments with aged (salvaged) Pb pipes, this potential was not enough to overcome the electric resistance of the preexisting scale, making the current drop to almost zero throughout the treatment. Further details that lead to this finding are provided below.

3.1. Identifying the Pb oxidation potentials

The CV results obtained for four different values of electrolyte pH and a phosphate concentration of 0.05 M are shown in Figure 2. The Pb$^{0/2+}$ and Pb$^{2+/4+}$ potentials at pH 1, 4, 10 and 13 are represented by the points A$_1$, A$_4$, A$_{10}$ and A$_{13}$, and B$_1$, B$_4$, B$_{10}$ and B$_{13}$, respectively. These values are presented in Table 1 along similar potentials for phosphate concentrations ranging from 0.5 to 0.005 M, as well as the theoretical potential values obtained using the Nernst equation. As seen, there is good agreement between the experimental measurements and the theoretical oxidation potentials, particularly at high phosphate concentrations. However, as the phosphate concentrations decrease, the differences between theoretical and experimental potentials increase, particularly for the Pb$^{2+/4+}$ oxidation reaction at pH 13. We attribute this to the lower conductivity of the electrolyte, which results in larger ohmic losses. Furthermore, at a phosphate concentration

of 0.0005 M it becomes impossible to identify the $Pb^{0/2+}$ and $Pb^{2+/4+}$ potentials because the reactions become diffusion-controlled, and thus the voltammograms do not show any peaks.

The experimentally obtained $Pb^{0/2+}$ and $Pb^{2+/4+}$ potentials, shown in Table 1, were used to polarize the Pb coupons to promote the formation of Pb(II) and Pb(IV) corrosion products, respectively, for phosphate concentrations ranging from 0.5 to 0.005 M. In the case of the 0.0005 M phosphate electrolytes, the theoretical potentials shown in in Table 1 with 0.2 V added were used (the additional potential compensates for the increased ohmic losses resulting from lower conductivity).

3.2. Pb coupon polarization curve analysis

The Pb polarization curves obtained using different phosphate solutions at pH 10 and different polarizing potentials are shown in Figure 3 (the figures for other pH values may be found in the S.I.). As expected, when the $Pb^{0/2+}$ potentials were used for polarization, there was a sharp decrease in current caused by the development of a passivating layer consisting of Pb(II) corrosion products. At 120 min the maximum current obtained using any phosphate concentration at pH 10 was 0.03 mA cm^{-2}. These slow oxidation rates indicate that there is little benefit from extending the duration of the treatment beyond 120 min. A similar trend is observed for the other pH values, as shown in the S.I. In contrast, when the $Pb^{2+/4+}$ potentials were used, a higher current was observed at all times, indicating that electrochemical reactions continued to occur. As with the $Pb^{0/2+}$ potentials, there was a sharp decrease in current resulting from the buildup of a passivating layer; however, the currents observed even after this decline were higher than those observed when using the $Pb^{0/2+}$ potentials. Nevertheless, this does not necessarily mean that all the current is caused by the buildup of PbO_2, as O_2 evolution occurred concurrently with Pb(II) oxidation at all of the analyzed potentials[17]. This is supported by the observation that dissolved oxygen (DO) level in the electrolyte increased when using the $Pb^{2+/4+}$ potentials, from an initial value of 8, to about 12 mg L^{-1} across all experiments (see Figure S4 in the S.I.). Oxygen evolution occurs only after a thin PbO_2 film builds up on the Pb surface. After the buildup of this film, PbO_2 formation rates decline in favor of O_2 evolution[15]. This suggests that the thickness of the PbO_2 layer during the electrochemical treatment of Pb pipes is limited by O_2 evolution.

3.3. Testing the Pb corrosion rates of the treated Pb coupons

Immediately after polarization, the Pb coupons were placed in contact with synthetic tap water and the linear polarization resistance, Tafel slopes and corrosion currents were measured. The estimated corrosion currents in synthetic tap water under all the tested conditions are shown in Figure 4. The results indicate that when the treatment was performed at pH 4 and 10, corrosion currents decreased significantly compared to those of bare Pb, regardless of the treatment potential and electrolyte phosphate concentration. The lowest values of corrosion currents were consistently reached when using a phosphate concentration of 0.05 M, for all values of treatment pH and potential. This indicates that, of all the conditions tested, a phosphate concentration of 0.05 M performed the best for decreasing Pb corrosion rates. Polarizing the Pb coupons using a phosphate concentration of 0.05 M decreased corrosion rates between 3 to 76 times compared to those of bare Pb, with the lowest corrosion currents observed when the Pb coupons were polarized at pH 4 and 10.

Notably, polarizing Pb coupons with electrolytes having high phosphate concentrations did not result in the best protection against corrosion, particularly when using the $Pb^{0/2+}$ potential. This happened despite the high electrolyte conductivity (resulting from high phosphate concentration) that should have facilitated redox reactions and thus, the formation of Pb corrosion products. Highly concentrated phosphate solutions, particularly those over 0.1 M at a pH between 9.4 and 12.9 have proven to inhibit Pb oxidation[22]. This is explained by the adsorption of phosphate ions onto the Pb surface[24], which passivates the Pb electrode. Thus, polarizing Pb surfaces under these conditions using the $Pb^{0/2+}$ resulted in low currents because the potential provided was not enough to overcome the passivity provided by the phosphate layer. This interpretation is supported by the polarization curves in Figure 3a, which show that the polarization current when using the $Pb^{0/2+}$ potential and a phosphate concentration of 0.05 M was greater than the polarization current when using a concentration of 0.5 M. This indicates a decrease in electrochemical activity at high phosphate concentrations and thus, a lower rate of Pb(II) scale formation.

When Pb was polarized using the $Pb^{2+/4+}$ potential in an electrolyte with a phosphate concentration of 0.5 M at pH 1, the corrosion current under synthetic tap-water conditions was higher than that obtained with synthetic tap water and bare Pb. We hypothesize that this is because the PbO_2 film dissolves readily in highly concentrated phosphoric acid solutions. Thus, once the polarization

stops, the short exposure time to the acid while the cell is being disassembled resulted in some scale dissolution, revealing the underlying Pb(0) with an increased surface area due to corrosion. A similar mechanism could explain why the corrosion rates of the Pb coupons treated at pH 1 tend to be higher than those for Pb coupons treated under higher pHs, as scale dissolution tends to happen at low pH values.

When using electrolytes with low phosphate concentrations for polarization, the subsequent corrosion currents with tap water remained comparable to the rates observed for bare Pb, which may be explained by the low conductivity of the electrolyte. Lower conductivities resulted in a decrease in polarization current, as shown in Figure 3, and thus, in less buildup of insoluble corrosion products. Therefore, electrolytes with high phosphate levels might not be effective for the buildup of scale on Pb pipes because phosphates tend to inhibit corrosion. In contrast, electrolytes with low phosphate levels might not provide enough conductivity for electrochemical reactions to take place. Thus, our results suggest that an electrochemical treatment to build up a scale within Pb pipes using the $Pb^{0/2+}$ potential should use a phosphate solution of about 0.05 M, as it provides enough conductivity for reactions to take place, while minimizing the passivating effect of the phosphate ions on bare Pb. If the $Pb^{2+/4+}$ potential is used, a 0.05 or a 0.5 M phosphate solution may be used to decrease corrosion rates.

3.4. XRD and Raman analysis of Pb coupons

The smallest corrosion current (signaling the best resistance against corrosion) during exposure to synthetic tap water was achieved by polarizing the Pb coupons in a 0.05 M phosphate solution (Figure 4). However, at this concentration, significant differences were observed among the different pH values and polarization potentials (Figure 4). Thus, XRD was used to test whether differences in scale composition can help explain the differences in corrosion resistance among the scales polarized using a 0.05 M phosphate solution.

The XRD spectra for the eight Pb coupons before and after polarization using a 0.05 M phosphate electrolyte at various pH values are shown in Figures 5a and 5b. When the Pb coupons were polarized using the $Pb^{0/2+}$ potential, a crystalline $Pb_5(PO_4)_3OH$ and PbO mixed film formed only at pH 1 and pH 13. These results are consistent with other studies[23,24,31] , that report the formation of a passivating lead phosphate film at low pH values when polarizing a Pb electrode at the $Pb^{0/2+}$

potential, and the formation of a PbO/Pb(OH)$_2$ film at higher pH values[20]. However, our results at pH 4 and 10 appear to contradict the published literature, as PbO was the only crystalline Pb corrosion product found in our experiments at these pH values when polarizing the Pb coupons at the Pb$^{0/2+}$ potential. This is despite the fact that Pb(II) phosphates are thermodynamically favorable under these conditions. Given that XRD can only detect crystalline structures, it is possible that amorphous Pb(II) phosphates were formed. This was confirmed using Raman, as shown in Figure 6a. In this figure, the characteristic ν_1 and ν_2 P-O stretching modes[29] located at 944 and 918 cm^{-1}, respectively, are clearly visible for every pH and potential used during polarization. The characteristic ν_1 C-O stretching mode[27] located at 1054 cm^{-1} is also visible for almost every spectra. This indicates that PbCO$_3$ formed during Pb polarization likely because of the dissolution of atmospheric CO$_2$ into the polarization electrolyte.

When polarizing the Pb coupons using the Pb$^{2+/4+}$ potential, our XRD and Raman results agree consistently and well with the published literature[20,23,32]. We observed the formation of PbO$_2$ in all experiments, as shown in Figure 5b, including the formation of α-PbO$_2$ and β-PbO$_2$ at high and low pH values, respectively. This was also confirmed with Raman, as shown in Figure 6b. These results could explain why the corrosion rates observed in Figure 4 for the Pb coupons polarized at the Pb$^{2+/4+}$ potential were lower than those obtained using the Pb$^{0/2+}$ potential for pH 1, 4, 10 and 13. Since PbO$_2$ is significantly less soluble and less porous than PbO[20], the former would provide better protection against corrosion.

3.5. Implications of scale composition on equilibrium dissolved lead levels in tap water

The type of Pb corrosion product developed on surfaces of Pb pipes with the proposed electrochemical treatment had a large impact on subsequent Pb levels in drinking water. Polarizing at the Pb$^{0/2+}$ potential at pH 1 and 13 mainly produces Pb$_5$(PO$_4$)$_3$OH, which leads to very low predicted Pb concentration for the synthetic tap water used in this study, namely only 0.01 ppb (calculations based on thermodynamic K_{sp} values and stability constants). Conversely, polarizing at the Pb$^{0/2+}$ potential at pH 4 and 10 mainly produced PbO, which leads to very high predicted Pb concentration in the synthetic tap water, namely 233.13 ppb. This suggests that for a polarizing potential of Pb$^{0/2+}$, only the treatments performed at pH 1 or 13 would subsequently provide Pb levels below the 15-ppb action limit of the Lead and Copper rule.

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In sharp contrast, for lead pipes polarized at the $Pb^{2+/4+}$ potential regardless of the electrolyte pH, the subsequent predicted Pb concentration in tap water at pH 8 is below-detection-limit due to the consistent formation of PbO_2, which is insoluble at circumneutral pH. Thus, this treatment appears fail-safe (insensitive to the pH of the electrolyte during polarization) and could theoretically be used to decrease Pb levels in drinking water to below the action limit. However, because PbO_2 is redox-active, it is stable only in highly oxidizing environments where free chlorine is present as a disinfection residual. The presence of orthophosphates in the water (commonly introduced by the water utilities) might help in case the free chlorine is depleted by the time the water reaches the end-user with lead pipes[16]. There is recent evidence that in the absence of free chlorine, orthophosphates may lead to only small levels of dissolved Pb, by limiting Pb dissolution rates[33]; however, that remains to be tested in our system. Scales consisting of PbO_2 may be reduced to Pb(II) in the presence of organic matter[34], or when switching disinfection residual from free chlorine to moderate disinfectants such as chloramines[35], or under other conditions that result in a decrease in the water oxidation-reduction potential[36]. Thus, even though the proposed treatment has the potential to decrease Pb leaching, further research on the long-term stability of electrochemically formed PbO_2 scales in drinking water systems with different disinfection regimes is necessary to understand the practical applicability of this approach.

3.6. Implications of scale composition on measured levels of total lead in tap water

The equilibrium Pb concentrations described above are based only on thermodynamics and exclude kinetics considerations. Thus, they are only an estimate of dissolved Pb levels that would eventually be reached in water "in thermodynamic equilibrium with the scale". Furthermore, these concentrations are only for dissolved Pb, and do not predict the particulate Pb levels that might result from the proposed treatment. We investigated this matter using Pb coupons polarized under a 0.05 M phosphate solution at various pH values and at the two polarization voltages. After scale formation, each coupon was submerged in recirculating synthetic tap water for 10 days (free chlorine levels were adjusted daily), and the dissolved and particulate Pb levels were measured. The results are shown in Figures 7a and 7b.

As seen, the measured values of dissolved Pb agree with the predicted values only for Pb(IV), but not Pb(II) corrosion products. When Pb(IV) corrosion products were formed, the dissolved Pb

levels were consistently below the ICP-OES detection limit of 5 ppb, consistent with predictions from theory. However, the picture is more complicated for Pb(II) corrosion products.   When the main Pb(II) corrosion product was $Pb_5(PO_4)_3OH$ (polarized at pH 1 and 13), the measured dissolved Pb values were higher than the predicted values (but still below the action limit of 15 ppb). In contrast, when the main Pb(II) corrosion product was PbO (polarized at pH 4 and 10), the measured dissolved Pb values were lower than the predicted values (but nevertheless above the action limit). The inconsistencies between measured and predicted dissolved Pb values for the Pb(II) scales are likely owing to the heterogeneous nature of the electrochemically-generated Pb(II) corrosion films, with mixed PbO and $Pb_5(PO_4)_3OH$ crystalline and amorphous structures.

The picture about which polarization strategy might actually work, becomes clearer when we consider the particulate Pb values released in tap water from various coupons (also shown in Figures 7a and 7b). Even though submerging the $Pb_5(PO_4)_3OH$ scales in synthetic tap water did not result in high levels of dissolved Pb, high levels of particulate Pb were observed. This result is likely due to the formation process of $Pb_5(PO_4)_3OH$. In this process, Pb^{2+} ions are solubilized into water, reacting with phosphate ions and then forming a solid that precipitates onto the Pb surface[37]. This dissolution-precipitation mechanism likely generates a scale that is loosely bound to the Pb substrate, resulting in the release of particulate $Pb_5(PO_4)_3OH$. Particulate Pb(II) phosphate minerals have been shown to be problematic for drinking water systems, particularly because of their ability to pass through Point-of-use water filters[38]. In contrast, formation of PbO and PbO_2 are surface phenomena. These start with the adsorption of OH^- ions on the Pb surface, forming a tightly bound scale[12]. This is likely why the electrochemically generated PbO and PbO_2 scales did not generate high particulate Pb levels in this study.

Considering both the dissolved and particulate levels of Pb in tap water subsequent to the polarization treatment, our findings suggest that electrochemically generated PbO_2 scales are the most promising for further investigation. They generated acceptably low levels of both dissolved and particulate Pb in the synthetic tap water tested in this study. This suggests that the electrochemical formation of Pb(IV) corrosion products on Pb pipes using a 0.05 M phosphate electrolyte, could provide protection against Pb leaching. Conversely, the formation of Pb(II) corrosion products should be avoided – they likely will not provide enough protection against Pb leaching.

3.7. Applying the treatment to lead pipes with preexisting scale

The preconditioned aged (old, salvaged) lead pipes were polarized using a 0.05M phosphate solution at pH 8 and the $Pb^{2+/4+}$ potential for 120 min. As discussed, freshly polished and cleaned Pb coupons polarized under these operating conditions, produced negligible leaching of Pb into synthetic tap water. In addition, experiments were also undertaken with the $Pb^{0/2+}$ potential to explore whether the smaller potential can help decrease Pb leaching in Pb pipes with a preexisting scale.

The average polarization current with application of the $Pb^{2+/4+}$ potential in the used lead pipes was 0.4 mA cm^{-2}. This current is smaller than that observed for the Pb coupons, which is attributed to the presence of a passivating preexisting scale. In contrast, when the smaller $Pb^{0/2+}$ potential was applied, the average observed current was far smaller, at 0.001 mA cm^{-2}. This suggests that the $Pb^{0/2+}$ potential might be too small to overcome the insulating properties of Pb pipe scales existing in water distribution systems. Moreover, this current is likely inadequate to generate significant changes to the scale composition, and therefore is not expected to affect subsequent rates of Pb leaching into the drinking water.

The XRD results revealed that, before the treatment, the preexisting scale consisted mainly of hydrocerussite and hydroxylpyromorphite, as shown in Figure 5c. After the treatment using the $Pb^{2+/4+}$ potential, the predominant crystalline structures became β-PbO_2, hydroxylpyromorphite and hydrocerussite, indicating that the treatment was successful at modifying the surface of the Pb pipes. However, the presence of hydroxylpyromorphite and hydrocerussite in the electrogenerated scale, both of which were part of the original scale, indicate that not all the surface was affected by the electrochemical treatment. This suggests that the particular composition of the prior (i.e. preexisting) scale, which is itself determined by the water matrix to which the lead pipe was exposed over the years, might impact the replicability of our results. However, that analysis is outside the scope of this study. We do note that, as expected due to the low polarization currents, the treatment using the $Pb^{0/2+}$ did not produce any changes to the pipe surface, as shown in Figure 5c.

In terms of Pb solubility, the treated Pb pipes leached significantly less Pb into synthetic tap water after 10 days than the untreated pipes, as shown in Figure 7c. This is likely because the crystalline

structures on the surface of the treated pipes, namely β-PbO_2 and hydroxylpyromorphite, are all highly insoluble, which allowed Pb leaching levels to fall below the 15-ppb threshold for both dissolved and total Pb. On the other hand, the untreated pipe leached over 35 ppb of Pb, thus being above the action limit of the Lead and Copper Rule. This was also the case for the pipe treated using the $Pb^{0/2+}$ potential, which, as discussed earlier, did not experience any surface changes after the treatment.

It must be noted that in every case most of the Pb in solution was in dissolved and not particulate form. This was true even for the pipe treated using the $Pb^{2+/4+}$ potential, in which $Pb_5(PO_4)_3OH$ was generated. As noted earlier, the $Pb_5(PO_4)_3OH$ when generated on surfaces of clean Pb coupons tends to detach from the Pb substrate into the solution. However, this was not the case when polarizing Pb pipes with a preexisting scale. This might be because of the roughness of the preexisting scale, which increases the surface area and allows the $Pb_5(PO_4)_3OH$ particles to attach more firmly to the pipe surface. In contrast, the Pb coupons have a smooth surface and a low surface area that might prevent $Pb_5(PO_4)_3OH$ particles from attaching.

These findings suggest that lead pipe anodization could be a feasible technique to prevent Pb leaching into the drinking water supply, even when pipes with a preexisting scale are being anodized. The treatment was successful at modifying the inner surface of the old (salvaged) Pb pipes used in this study when using the $Pb^{2+/4+}$ potential. We note that further study is warranted: our findings may not be universally replicable. The proposed treatment may not work, or may work differently, with other kinds of pre-existing scales, than the kind we encountered in the local (SF Bay Area) water distribution system. Scales with low conductivity might hinder the application of the anodizing treatment; however, the scale we tested was not particularly conductive (mostly Pb(II) minerals) and thus we speculate that scale conductivity will be unlikely to be a barrier in other situations.

Conclusions

Accelerating the formation of an insoluble scale within Pb pipes by using an external voltage source is a novel idea that could prevent Pb leaching into the drinking water. This exploratory study found that the technical approach appears feasible in the short-term, when tested in a controlled laboratory environment, even on old, salvaged lead pipes with a preexisting scale.

However, prior to any real-world applications, the long-term performance and chemical and mechanical stability of electrochemically generated scales should be monitored, as changes in the water oxidation reduction potential could result in the reduction of PbO_2 to more soluble forms of Pb(II). Moreover, the effect of the disinfection residual and corrosion control strategies should be studied and monitored, as it is unclear whether the electrogenerated scale will be stable in the presence of chloramines and orthophosphates.

If the treatment is successful at providing long-term protection against Pb leaching, a field test seems warranted, in which we will explore other challenges not addressed in this study. These include inserting a conductive wire inside the Pb pipes, determining the number of electrical connections needed for a uniform treatment, dealing with the buildup of O_2 and H_2 (we may need to flush the pipes throughout the treatment to avoid gas buildup), and studying the effect of galvanic couples typically found in water distribution systems, among others.

Pb leaching into the drinking water is a very serious risk that will persist as long as Pb pipes are used for water distribution. Technologies such as the one presented in this study could provide a tool for substantially and rapidly decreasing Pb levels in water until the Pb pipes can be replaced, preventing millions of people from toxic levels of lead in their tap water, or having to rely on bottled water or expensive water filters.

Acknowledgements

Table 1. Comparison between theoretical and experimental oxidation potentials for the $Pb^{0/2+}$ and $Pb^{2+/4+}$ oxidation reactions at different pH and phosphate concentrations. As shown, the experimental and theoretical values are generally in good agreement; however their differences increase with decreasing phosphate concentrations possibly because of the decreasing conductivity of the electrolyte.

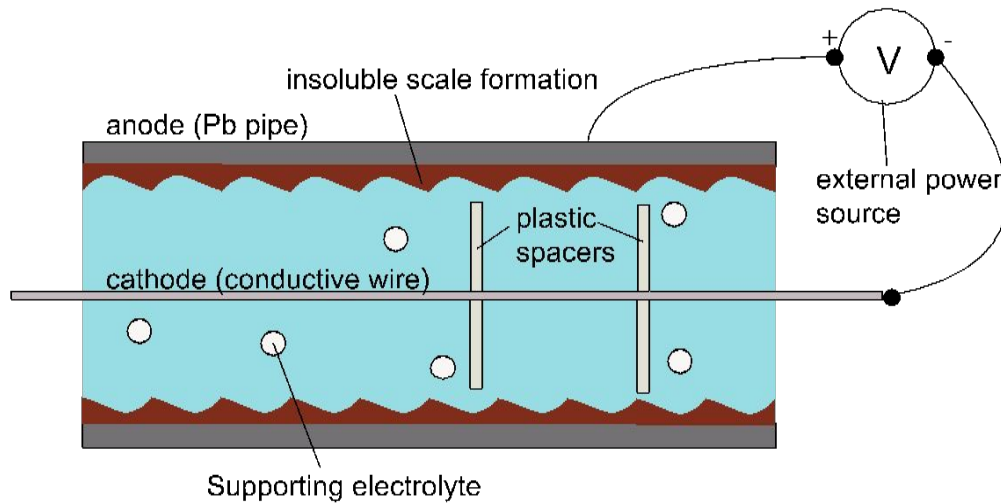| $[PO_4^{3-}]$ (M)	pH	$Pb^{0/2+}$ potential (V vs SHE)		$Pb^{2+/4+}$ potential (V vs SHE)	
		theoretical	experimental	theoretical	experimental
0.5	1	-0.13	-0.01	1.52	1.72
	4	-0.35	-0.32	1.21	1.32
	10	-0.48	-0.44	0.63	0.86
	13	-0.65	-0.44	0.45	0.71
0.05	1	-0.13	0.04	1.52	1.64
	4	-0.33	-0.31	1.19	1.37
	10	-0.48	-0.46	0.63	1.09
	13	-0.65	-0.21	0.45	0.91
0.005	1	-0.13	0.91	1.52	1.86
	4	-0.31	-0.28	1.15	1.65
	10	-0.48	-0.4	0.63	1.21
	13	-0.65	-0.38	0.45	1.11

Figure 1: Schematic cross section of a lead pipe treated with a system to anodize the inside of the lead pipe and accelerate the formation of an insoluble scale that protects against Pb leaching. In this system, the lead pipe is first temporarily isolated from the rest of the pipe network. A conductive wire (as cathode) is inserted in the pipe, and a supporting electrolyte fills the pipe's interior. The central wire and the pipe are then connected to an external power source that provides the potential to anodize the lead pipe. Insulating spacers keep the wire from touching the pipe and prevent short-circuiting.

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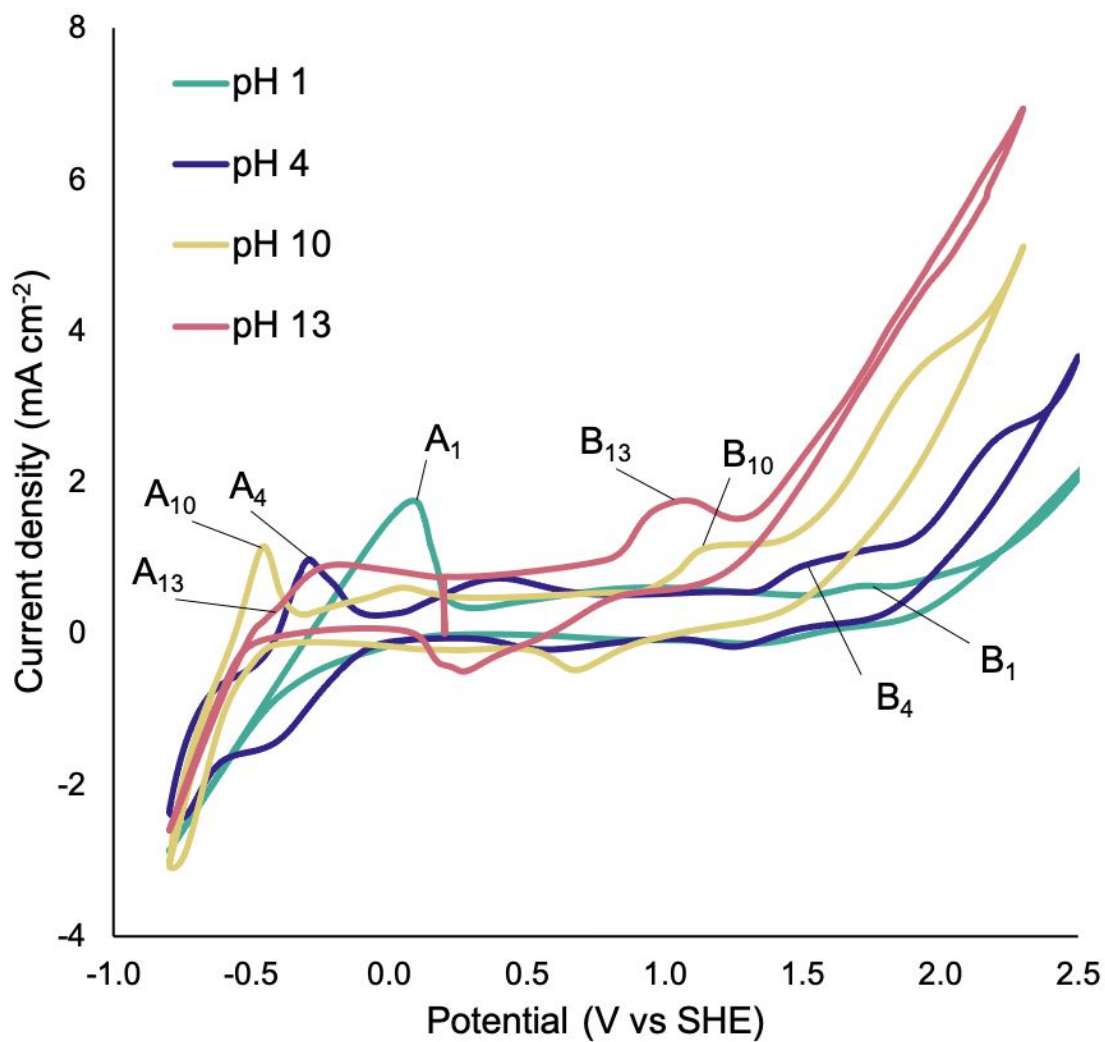
Figure 2. Cyclic voltammetry of a Pb coupon in a 0.05 M phosphate solution at different pH values. The letters A_{XX} and B_{XX} show the potentials at which Pb(0) is oxidized to Pb(II), and Pb(II) is oxidized to Pb(IV), respectively, where XX is the pH of the electrolyte (1, 4, 10 and 13).
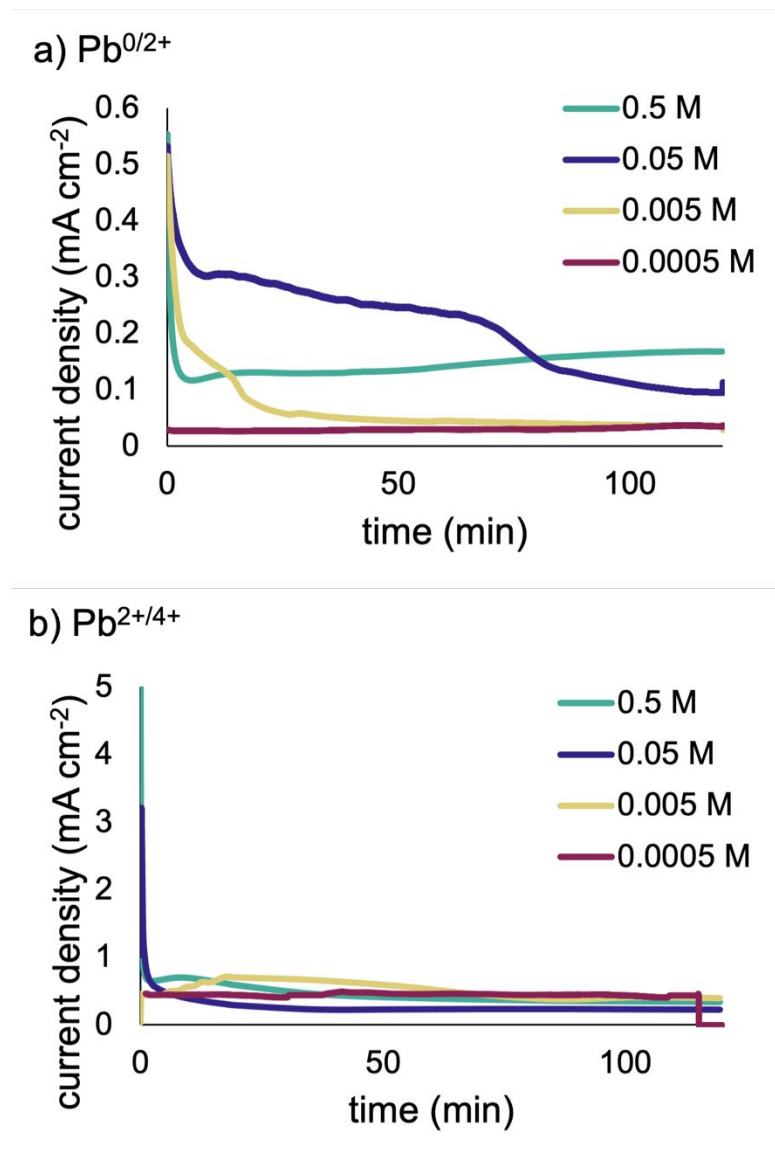
Figure 3. Polarization curves for a Pb anode polarized at the a) $Pb^{0/2+}$ potential and b) at the $Pb^{2+/4+}$ potential using a phosphate solution of varying concentrations at pH 10. The applied potentials depend on the phosphate concentration (see Table 1). As shown, higher phosphate concentrations generally result in higher initial current densities; however, over time the current declines with the formation of a passive film on the Pb electrode
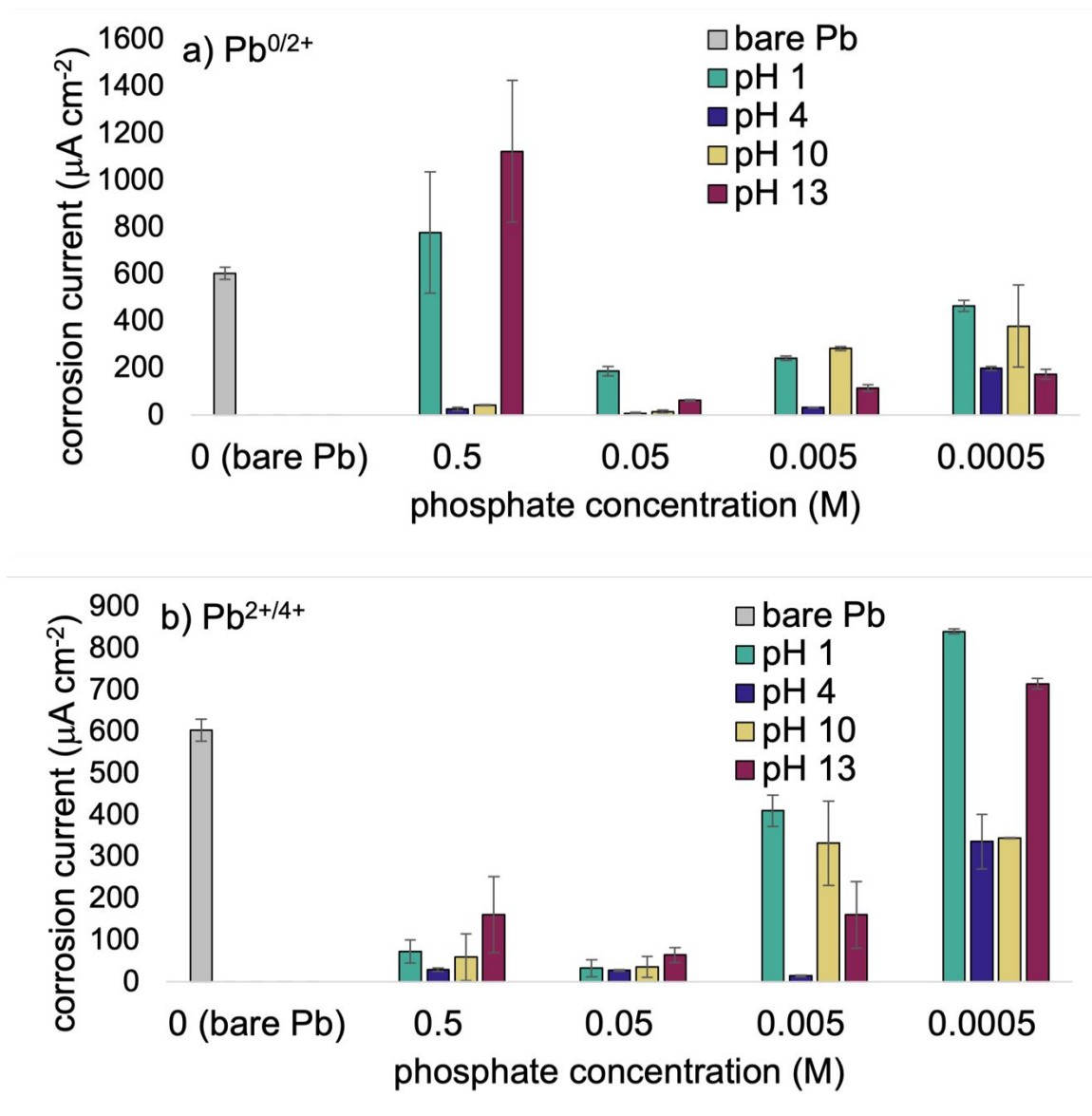
Figure 4. Estimated corrosion currents (surrogates for estimated corrosion rates) for the lead coupons in synthetic tap water. The lead coupons had been previously polarized using different potentials and electrolyte composition. The coupons were polarized using either (a) the $Pb^{0/2+}$ potential or (b) the $Pb^{2+/4+}$ potential (potentials shown in Table 1). Pb corrosion rates decrease after performing the electrochemical treatment using a 0.05 M phosphate solution at any pH regardless of the potential used. When using other phosphate concentrations, the resulting corrosion rates depend on the potential and the pH of the solution during polarization.
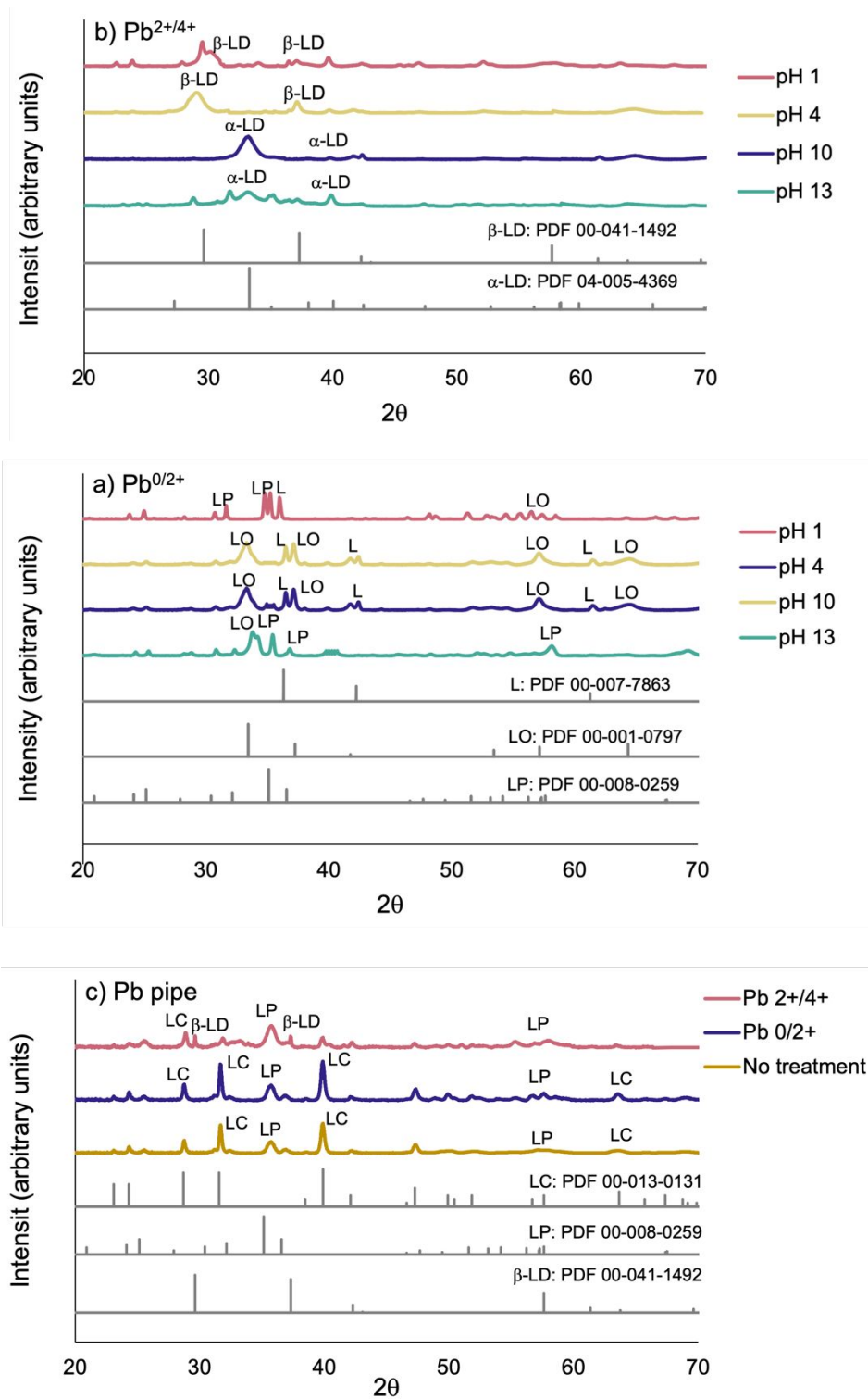
Figure 5. XRD patterns using a Co Kα source for Pb coupons polarized using the a) $Pb^{0/2+}$ and b) $Pb^{2+/4+}$ potentials and c) Pb pipes polarized using the $Pb^{0/2+}$ and $Pb^{2+/4+}$ potentials. A 0.05M phosphate electrolyte with varying pH was used in a) and b), while only a 0.05M phosphate

solution with a pH of 10 was used pin c). The labels above the energy peaks correspond to: L – Lead, LO – Lead Oxide, LP – Lead phosphate Hydroxide (Hydroxylpyromorphite), α−LD – alpha Lead Dioxide, β-LD – beta Lead Dioxide and LC – Lead Carbonate Hydroxide (Hydrocerrusite), These XRD patterns demonstrate that Pb(II) and Pb(IV) corrosion products form at a) and b), respectively, while mixed Pb(II) and Pb(IV) products form at c).
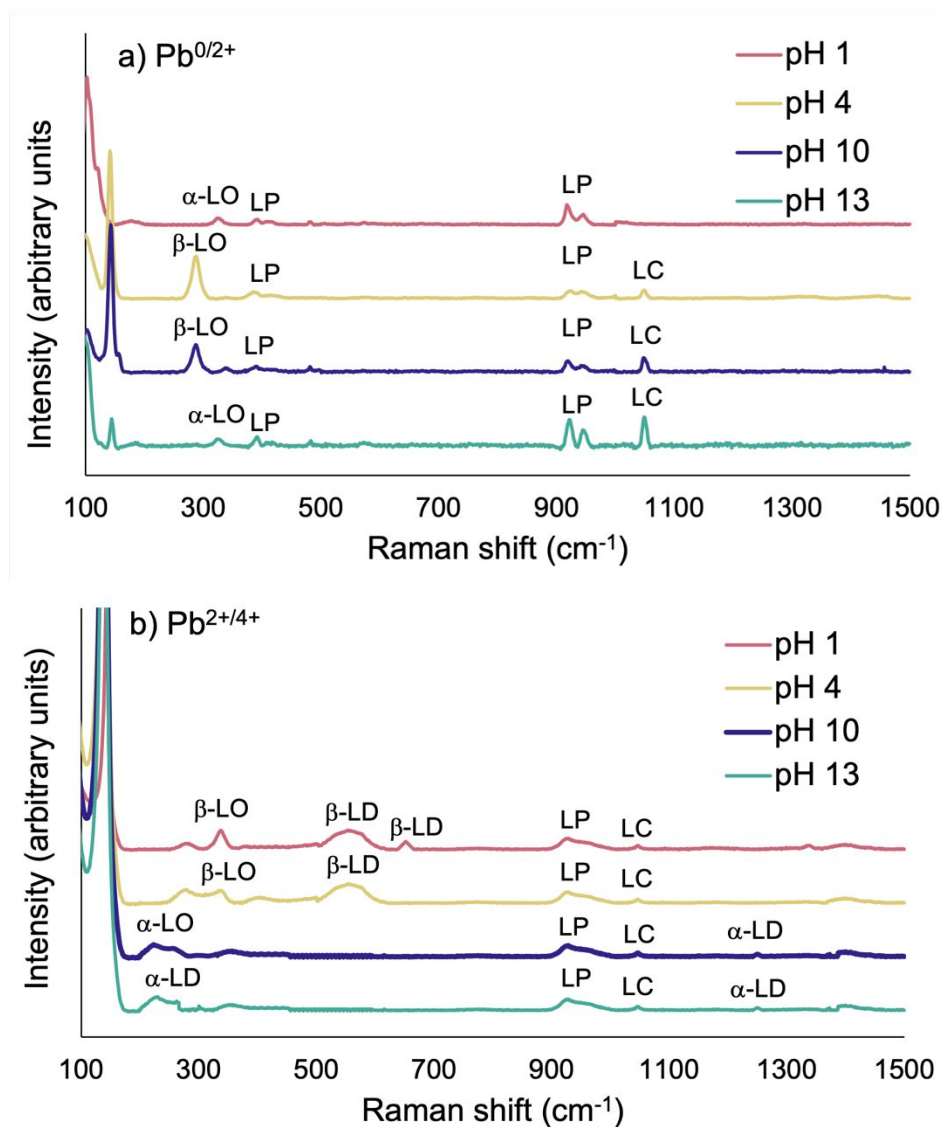
Figure 6. Raman spectra using a laser wavelength of 532 nm for Pb coupons polarized using the a) $Pb^{0/2+}$ and b) $Pb^{2+/4+}$ potentials. A 0.05M phosphate electrolyte with varying pH was used. The labels above the peaks correspond to: α-LO – α-Lead Oxide (litharge), β-LO – β-Lead Oxide (massicot), α–LD – α–Lead Dioxide (scrutinyite), β-LD – β-Lead Dioxide (plattnerite), Lead phosphate Hydroxide (Hydroxylpyromorphite) and LC – Lead Carbonate Hydroxide (Hydrocerrusite). These Raman spectra confirm the presence of the crystalline structures identified using XRD and the presence of amorphous lead phosphate at pH 4 and 10 when using the $Pb^{0/2+}$ potential.
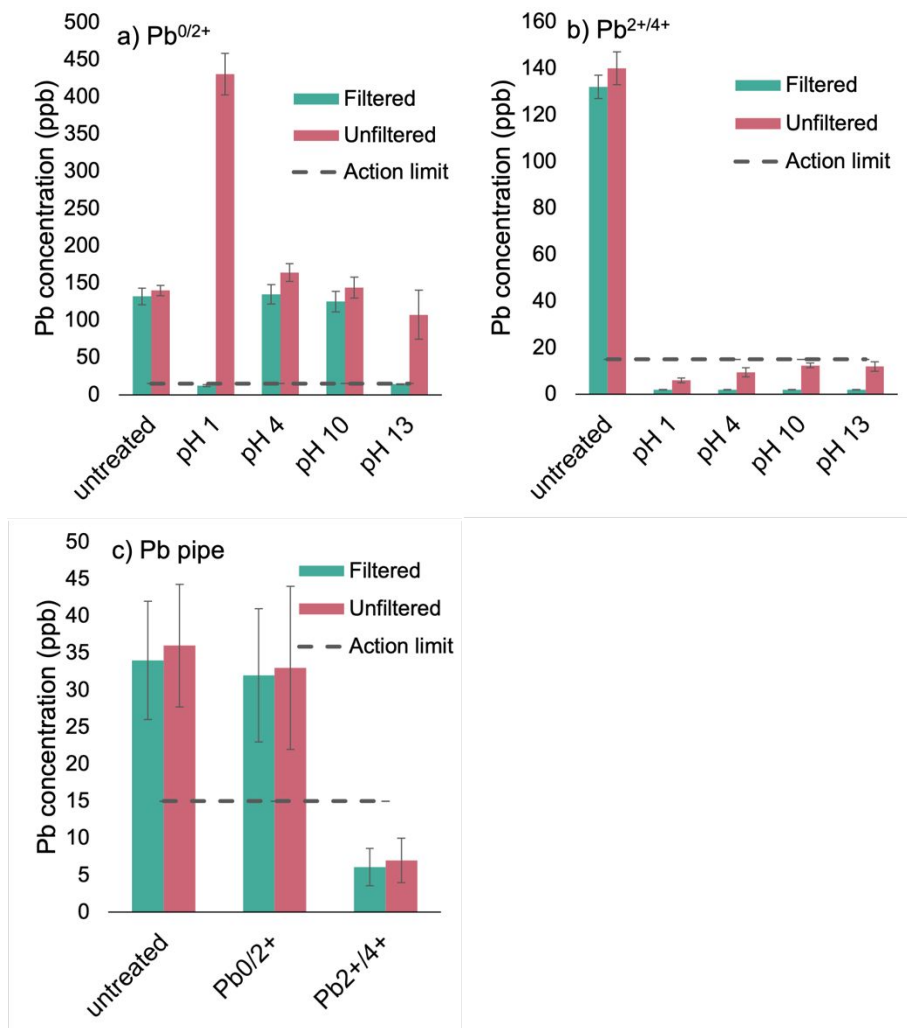
Figure 7: Filtered and unfiltered Pb levels after 10 days of contact between Pb coupons (7a and 7b) and pipes (7c), and recirculating synthetic tap water. Analysis results are shown for each sample as unfiltered (Red), and after filtering it through a 0.2 µm filter (Green). Note the different vertical scales of panels a), b) and c). Only the treatment performed at the $Pb^{2+/4+}$ potential provides enough protection against Pb leaching to comply with the Lead and Copper Rule action limit of 15 ppb for both coupons and pipes.

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