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Electrochemical deposition of amorphous aluminum oxides on lead pipes to prevent lead leaching into the drinking water

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ABSTRACT

Over 5000 public drinking water systems in the US are out of compliance with the Lead and Copper Rule. Lead leaching from lead pipes is limited by the solubility of a naturally occurring scale. Changes in water quality may cause this scale to become more soluble, releasing lead into the drinking water. We propose a novel electrochemical method to prevent lead leaching from lead pipes. In this method, an aluminum wire and an alkaline phosphate electrolyte are inserted into the pipes. The pipes are then anodized for 2 h by using an external power supply, resulting in the electrodeposition of an insoluble aluminum oxide layer on top of the preexisting scale. This technology was tested on lead pipes from the EBMUD water distribution systems located in Berkeley, CA, using recirculating synthetic and actual tap water for 120 days. The untreated pipes leached an average of 23 ppb and 38 ppb of lead respectively, when using free chlorine and monochloramine as disinfection residuals. In contrast, the treated pipes leached 3 ppb and 5 ppb respectively. These results suggest that the proposed treatment has the potential to prevent lead leaching regardless of the disinfection residual and thus should be further explored in a field trial.

1. Introduction

Over 6 million lead service lines currently provide drinking water to more than 15 million people across the US (Cornwell et al., 2016). Even though corrosion control strategies have been successful at decreasing Pb levels in drinking water from Pb water pipes (Tam and Elefsiniotis, 2009; Cardew, 2009; Roy and Edwards, 2019), it is estimated that over 5000 public drinking water systems are out of compliance with the Lead and Copper Rule (LCR) (Olson and Fedinick, 2016). As many as 1100 of these water systems have their 90th percentile Pb levels (from multiple samples collected by the water utility) exceeding the LCR Action Limit of 15 ppb, indicating that at least 10% of their customers are exposed to lead levels that exceed this 15-ppb threshold. Young children are particularly at risk: elevated lead blood levels resulting from environmental lead exposure have been linked to permanent and irreversible brain damage (Cecil et al., 2008). There is no safe level of lead in drinking water (Brown and Margolis, 2012). Thus, mitigation strategies to prevent lead leaching from lead water pipes are paramount to protect children from lead exposure until all lead pipes can be replaced by safer alternatives.

Lead leaching rates are controlled by an insoluble scale that builds up in contact with water, and the solubility of such scale is dictated by the chemical composition of the surrounding water. When free chlorine is used as a disinfection residual, Pb(II) minerals within the pipes' scale are oxidized to Pb(IV), as the oxide, PbO_2. PbO_2 scales are practically insoluble and protective against Pb leaching (Triantafyllidou et al., 2015). However, PbO_2 is only stable under high Oxidation Reduction Potentials (ORP). Thus, changes in water quality that result in a lower ORP may lead to the reductive dissolution of PbO_2, resulting in elevated dissolved lead concentrations (Masters et al., 2016; Wang et al., 2013; Desantis et al., 2020). Changes in ORP may result from a variety of conditions, including the depletion of free chlorine (Triantafyllidou et al., 2015; Guo et al., 2014), the presence of reducing Natural Organic Matter (NOM) (Lin and Valentine, 2008; Dryer and Korshin, 2007), and changes in pH (Kim et al., 2011). Switching disinfectants from free chlorine to chloramines may also result in Pb dissolution (Edwards and Dudi, 2004). However, phosphorous-containing solids from the addition of orthophosphates can help preserve the preexisting PbO_2 scale and act as physical barriers that prevents Pb release (Desantis et al., 2020; Bae et al., 2020a). In contrast, the use of chloramines as a disinfection residual generally results in the formation of Pb(II) scales (Switzer et al., 2006). Minerals typically found in such systems include Pb(II)

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carbonates and Pb(II) phosphates (Tully et al., 2019), with the latter usually occurring in water systems that use orthophosphates as a corrosion control strategy (Stone et al., 2010; Bae et al., 2020b; Wasserstrom et al., 2017). Pb(II) phosphate minerals are highly insoluble; however, their presence may result in toxic levels of particulate Pb being released into the drinking water (Xie and Giammar, 2011). In contrast, Pb(II) carbonate minerals are more soluble and may result in the release of dissolved lead at toxic levels. Other factors also influence lead release into the drinking water, such as physical disturbances and galvanic corrosion resulting from partial lead service line replacement (Cartier et al., 2013; Doré et al., 2019; Triantafyllidou and Edwards, 2011; Wang et al., 2012), among others.

There is no rapid and cost-effective solution to stop lead leaching once it starts. While corrosion control strategies using orthophosphates can help decrease lead levels in systems out of compliance with the LCR, they may take months to years to consistently decrease lead levels, especially the particulate component, to safe drinking water standards (Cardew, 2009). Moreover, recent studies suggest that particulate Pb(II) phosphates may pass through activated carbon water filters under certain conditions due to their small sizes and negative surface charge (Pan et al., 2021).

Lead avoidance strategies, such as pipe replacement, the use of water filters, flushing the water prior to consumption or consuming bottled water also each have their own major drawbacks. Lead service line replacement, at an average cost of $4700 per household (EPA, 2019), is not an affordable solution to many communities living at or below the poverty line. This is particularly true when customers must pay for Pb pipe replacement within their households. Partial pipe replacement (as a result of the customer's inability or unwillingness to pay for internal plumbing replacement) been found to be ineffective at decreasing the risk for elevated blood lead levels in children (Brown and Margolis, 2012). Water filters rely heavily on behavioral change, on the assumption that people will pay $70 every 6 months to replace the filters (Mulhern and Gibson, 2020) and on the availability of such filters in stores. Other water avoidance strategies can be equally problematic in the long term (Pieper et al., 2019). Access to safe drinking water is a basic human right (United Nations, 2010), and the burden should not be on the consumers to adopt protective behaviors because water utilities fail to supply them with lead-free water.

Coating technologies using epoxy have also been proposed to prevent lead leaching (Boyd et al., 2001). Even though these technologies can be effective, their cost, difficulty to implement and potential leaching of harmful contaminants have made them difficult to adopt (Rajasärkkä et al., 2016).

This work build on and improves our previous work (Lobo and Gadgil, 2021), where we proposed an electrochemical method to prevent lead leaching from lead water pipes. In that method, a conductive wire and a phosphate solution are introduced into the lead pipes (the wire has plastic spacers to avoid contact with the pipes). The wire and the pipes are then connected to an external power supply to rapidly drive the electrochemical formation of PbO_2 and $Pb_5(PO_4)_3OH$ on top of the pipe's preexisting scale. Once an electrogenerated scale is formed, the wire is removed, and the phosphate solution is flushed. The advantage of this method over epoxy coatings is that it is less invasive, as the pipes do not need to be pretreated in any way. This treatment was successful at preventing old and leaching lead pipes with a preexisting scale, from leaching into drinking water with a free chlorine disinfection residual. However, a major drawback is that the electrogenerated PbO_2 might reduce to more soluble forms of Pb(II) as a result of changes in ORP. This risk is particularly concerning when significant NOM intrusion in the water causes the reductive dissolution of PbO_2 (Masters et al., 2016), or when monochloramines are used as a disinfection residual (Switzer et al., 2006).

In the present work we propose an improvement to the aforementioned electrochemical method to prevent lead leaching. In this new method, schematically shown in Fig. 1, an alkaline phosphate electrolyte and an Al wire are introduced into the pipe. The pH of the phosphate electrolyte is within the active dissolution range of Al (pH > 11) so that $Al(OH)_4^-$ ions are spontaneously released into solution. A power supply is then used to drive the electrodeposition of an Al oxide layer on top of the preexisting scale, which acts as a barrier between the Pb pipe scale and the drinking water.

In this study we demonstrate that the electrodeposited Al oxide layer protects old Pb pipes with a preexisting scale against Pb leaching when either free chlorine or monochloramines are used as a disinfection residual in drinking water. Implementing this approach requires overcoming several practical challenges, including the feasibility of inserting a wire and a supporting electrolyte into the pipes; however, these aspects will be discussed elsewhere. The focus of this work is to understand whether a system like this could prevent Pb leaching into the drinking water from Pb-based plumbing systems in a controlled environment.

It is important to clarify that by using the word "prevent" we mean achieving Pb levels below the maximum considered acceptable by the EPA's Lead and Copper Rule Action Limit. 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. Lead pipe conditioning

A 2 m continuous segment of an old used lead pipe with an inner and

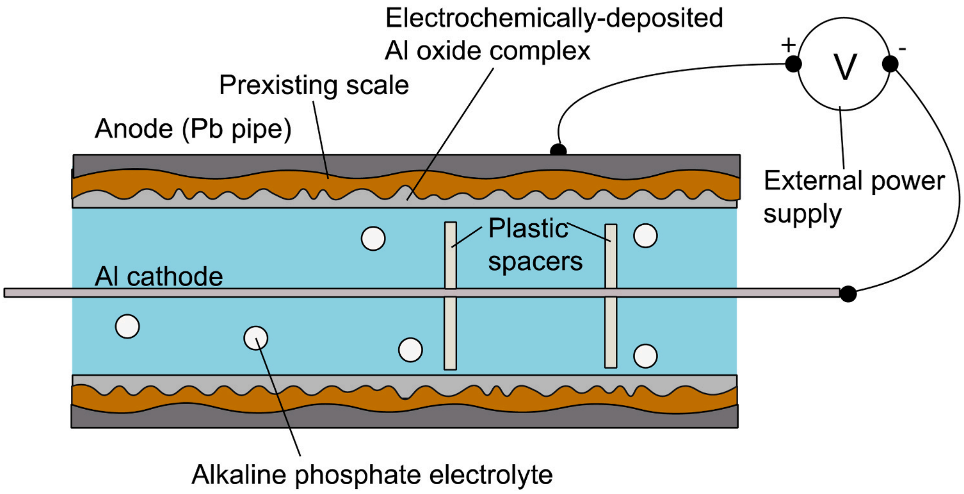

Fig. 1. Schematic cross section of a lead pipe during the operation of a system to deposit an Al oxide layer on the interior of lead pipes that protects against Pb leaching. In this system, the lead pipe is first temporarily isolated from rest of the pipe network. An Al wire (as cathode) is inserted in the pipe, and an alkaline phosphate electrolyte fills the pipe's interior. The central wire and the pipe are then connected to an external power supply that provides the potential to anodize the lead pipe. Insulating spacers keep the wire from touching the pipe and prevent short-circuiting.

outer diameter of 3.8 and 5.1 cm, respectively, was salvaged from the EBMUD water distribution system in Berkeley, CA. This pipe had a uniform lead corrosion scale with thickness of approximately 0.4 mm, which formed over the course of at least 50 years (the exact number of years is unknown). Select water quality parameters of the EBMUD water delivered to our lab are shown in Table 1. The pipe was carefully cut into ten segments (20 cm each) to avoid damaging the preexisting lead corrosion scale. Eight segments were filled with synthetic tap water resembling the inorganic phase of the 2016 Flint, MI tap water quality (referred to as "synthetic Flint water" from now onwards). The composition of the synthetic Flint water, shown in Table 2, was based on published literature (Pieper et al., 2017; Masten et al., 2017). We chose this water matrix to simulate lead leaching in Flint, MI and to provide insights into how the proposed treatment could have helped prevent it. No disinfection residual was added to simulate a worst-case scenario in which the residual is consumed before reaching the Pb pipes. The remaining two segments were filled with tap water from our lab, which is served by the same water system from where the pipes were salvaged.

The water within all ten pipe segments remained stagnant for 24 h and was replaced daily (also referred to as "dump-and-fill" conditioning (Wang et al., 2012)). Lead concentrations were tested three times a week by digesting the water-samples taken from the pipe loop system for 24 h using a 1.1 M HCl solution and a 1:5 ratio of acid to water-sample and then using a Perkin Elmer 5300 ICP-OES with a detection limit for Pb = 1 ppb (limit of quantification = 5 ppb). The pipe conditioning ended once the lead levels became stable (less than 5 ppb difference between six consecutive measurements), which occurred after 3 months. It is worth noting that Pb levels above the LCR action limit were measured in the water within all Pb pipes during the conditioning phase.

2.2. Pipe loop setup before the electrochemical treatment

With the objective to simulate the release of lead from water pipes, each of the ten pipe segments described above were connected to a different but identically constructed PVC pipe loop. All pipe segments had a Pb(II) corrosion scale prior to the electrochemical treatment (for more information on the scale composition, see Section 3.2. and Fig. 3). In each loop, 5 L of water with no disinfection residual were continuously recirculated for 16 h daily at a flow rate of 3.8 L min^{-1}. The water was stagnant for the remaining 8 h per day. These flow conditions were meant to simulate field conditions in which the water flows during the day and is stagnant at night. The water in each pipe loop had the same composition as in the conditioning step described above (eight loops contained synthetic Flint water with no disinfection residual, while two loops contained tap water from our lab). The water in all 10 pipe loops was replaced weekly. Two 50 mL water samples were taken weekly and tested for total and dissolved Pb. 0.2 μm PTFE syringe filters were used to separate particulate from dissolved Pb. The water was tested daily for pH, Dissolved Oxygen (DO) and conductivity. The pipe loops were operated as described above for 60 days.

2.3. Electrochemical treatment

After 60 days of recirculation, five of the ten pipe segments were removed from their respective pipe loops: four segments from the loops with synthetic Flint water and one from the loops with our lab's tap water. These five pipe segments were then treated using the setup described in Fig. 1. The electrolyte used consisted of a 0.05 M PO_4 solution at pH 12 and the polarization was performed using a three-electrode setup with a Ag/AgCl reference electrode, the Pb pipe as the working electrode and the Al wire as the counter electrode. The pipe segments were filled with the electrolyte and were subsequently polarized for 2 h using a current density of 1 mA cm^{-2} (the electrolyte remained stagnant during polarization). Once the polarization was over, the Pb pipe segments were flushed with their corresponding tap water (synthetic Flint water or our lab's tap water) and were then reconnected to their corresponding pipe loops.

Table 1
Mean and standard deviation values of select water quality parameters from our lab's tap water. These parameters were measured once weekly for 10 weeks.

	Mean	Standard deviation
pH	8.2	0.4
Monochloramine residual (mg L^{-1} as Cl_2)	0.5	0.6
Orthophosphates (mg L^{-1} as PO_4)	0.5	0.3
Alkalinity (mg L^{-1} as $CaCO_3$)	35.1	12.2
Total dissolved solids (mg L^{-1})	42.3	7.6
Dissolved Organic Carbon (mg L^{-1})	1.9	0.8

Table 2
Composition of the Synthetic Flint Water before and after the treatment date.

	Before treatment date	After treatment date
pH	7.4	8.5
Disinfection residual (mg L^{-1} as Cl_2)	–	2.00
Orthophosphates (mg L^{-1} as PO_4)	–	3.00
NaCl (mM)	1.10	1.10
MgCl2 (mM)	1.00	1.00
Na2SO4 (mM)	2.86	2.86
NaHCO3	0.75	0.75

2.4. Pipe loop setup after treatment

After the treatment of five pipe segments, the water quality in each of the pipe loops with synthetic Flint water was modified to reflect corrosion control strategies typically implemented in water systems out of compliance with the LCR. To that end, the synthetic Flint water was supplemented with 2 mg L^{-1} of orthophosphates and the pH was raised from 7.4 to 8.5 using a 2 M NaOH stock solution. Moreover, the water was dosed with a disinfection residual: four of the eight pipes with Flint synthetic tap water were dosed with 2 mg L^{-1} as Cl_2 of free chlorine, while the remaining four were dosed with 2 mg L^{-1} as Cl_2 of monochloramines. The monochloramine stock solution was prepared following the procedure described by Korich et al. (1990) and the concentration was determined using the Indophenol method (Hach method number 10171). Free chlorine was measured using the USEPA DPD method (Hach method number 8021). Both disinfection residual types were measured using a Hach DR6000 UV–VIS spectrophotometer The disinfection residuals were adjusted daily, and the water was completely replaced weekly. In the case of the pipe loops with our lab's tap water, we adjusted its orthophosphates levels to 2 mg L^{-1} once per week and its monochloramine residual to 2 mg L^{-1} as Cl_2 daily. The lab's tap water came with a variable level of monochloramine residual and orthophosphate level from the water treatment process at the EBMUD water treatment plant serving Berkeley, CA. This water was also completely replaced weekly. Moreover, a 30 s flush sample was taken and tested for total Pb prior to placing the lab's tap water in the corresponding pipe loops each week.

We tested both the synthetic Flint water and our lab's tap water within the pipe loops daily for pH, DO, conductivity and disinfection residual. We also tested total and dissolved Pb, Al and orthophosphates by taking 50 mL samples twice a week. Pb and Al concentrations were measured using ICP-OES and the procedures described in Section 2.1, while orthophosphate concentrations were measured using the USEPA ascorbic acid method (Hach method number 8048). We were particularly interested in measuring total Al because high levels would point to the dissolution of the electrogenerated Al oxide layer. Moreover, we continuously monitored the Open Circuit Potential (OCP) of the pipe loops by inserting a reference electrode near the inlet of the lead pipes at an approximate distance of 2 mm from the corrosion scale. The pipe loops were operated under these conditions for an additional 60 days (the flow conditions remained the same as those described in Section

2.2.).

To summarize, we explored the efficacy of the electrochemical treatment under three different scenarios and each scenario was applied to a treated and an untreated pipe: (1) Synthetic Flint water with a free chlorine disinfectant, (2) Synthetic Flint water with a monochloramine disinfectant, (3) Our lab's tap water with a monochloramine disinfectant. Scenarios 1 and 2 were performed in duplicates, while scenario 3 consisted of a single treated and untreated pipe. We did not perform duplicate experiments in scenario 3 because of the low reproducibility of the results, owing to the high variability of our lab's tap water quality.

2.5. Lead pipe scale analysis

Segments of the Pb pipes before and after the electrochemical treatment were analyzed using a Bruker AXS D8 Discover GADDS X-Ray Diffractometer (XRD) using a Co Kα source and the PDF-4+ ICDD database to identify the main crystalline structures before and after polarization. Moreover, we analyzed segments of all Pb pipes 60 days after polarization using XRD to test whether changes in structure resulted from interactions between the pipes' scale and the water within the pipe loops. We also used a Fei Fenom tabletop Scanning Electron Microscope with Energy Dispersion X-Ray analysis (SEM EDX) to study the morphology of the pipes and the elemental composition of the scales before and after the treatment, and after 60 days since the treatment date. Additionally, we used a Horiba LabRAM Aramis Raman microscope with a 532 nm laser wavelength to identify non-crystalline structures within all the aforementioned Pb pipe segments. The American Mineralogist crystal structure database (Downs and Hall-Wallace, 2003) was used as a reference.

3. Results and discussion

3.1. Effect of the treatment on Pb leaching

3.1.1. Free chlorine residual

The treatment was successful at decreasing total Pb concentrations below the action limit of the LCR of 15 ppb for the duration of the experiment, as shown in Fig. 2. When free chlorine was used as a disinfection residual in the synthetic Flint water, the treatment immediately decreased total Pb levels below the LCR action level (Fig. 2a). Over 95% of the measured Pb concentrations after the treatment day correspond to particulate Pb, as we did not detect any dissolved Pb when measuring the filtered samples in the case of the treated pipe with synthetic Flint water and a free chlorine residual (see S.I.).

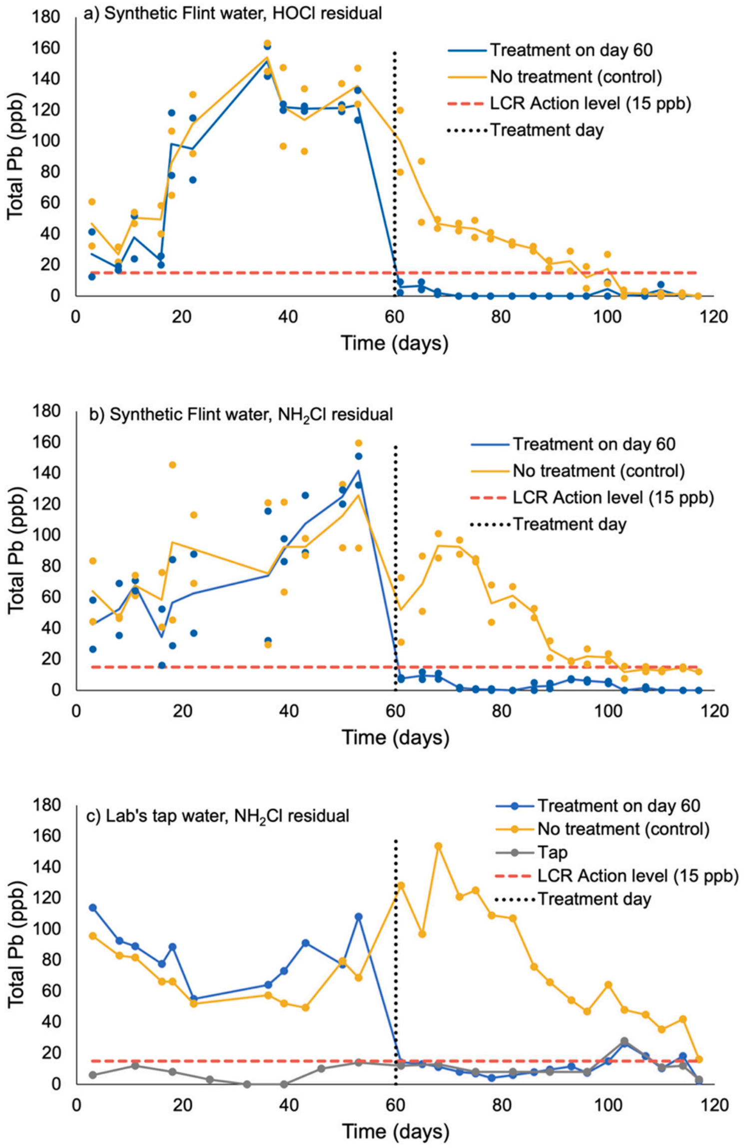

Fig. 2. Total Pb levels before and after the electrochemical treatment when using the synthetic Flint water with (a) a free chlorine disinfectant, (b) a monochloramine disinfectant, and (c) tap water from our lab with a monochloramine disinfectant. Before the treatment, no corrosion control measures were taken, while after the treatment, the pH was raised in (a) and (b), while disinfection residuals and orthophosphates were adjusted daily and weekly, respectively in (a), (b), and (c). In (a) and (b) the dots represent individual Pb measurements of each duplicate, while the lines represent the average Pb concentrations.

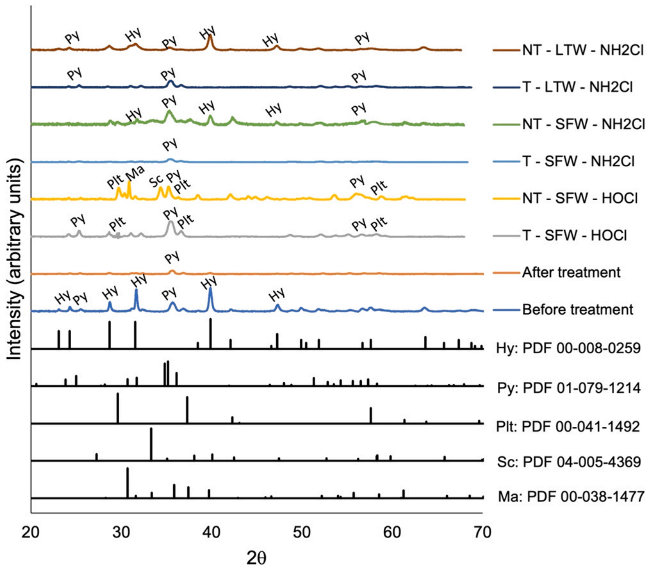

Fig. 3. XRD patterns for the treated and untreated Pb pipes immediately before and after the treatment, and after 60 days since the treatment date. As shown, the treatment generates an amorphous scale that is undetectable with XRD when treating a pipe with a Pb(II) corrosion scale. The following abbreviations are used: T: treated pipe after 60 days since treatment date, NT: untreated pipe after 60 days since treatment date, SFT: Synthetic Flint Water, LTW: Lab's Tap Water, Hy: Hydrocerussite, Py: Pyromorphite, Plt: Plattnerite, Sc: Scrutinyite, Ma: Massicot.

In contrast, when the treatment was not applied, total Pb concentrations remained above the action limit of the LCR for over 40 days. During this period Pb was present in both dissolved and particulate forms (compare Figs. 2 and S1 in the S.I.). This is likely a result of Pb(II) dissolution from the hydrocerussite mineral scale of the untreated pipe (see Fig. 3) and the formation of Pb(II) phosphates in the bulk solution due to the presence of orthophosphates. Pb concentrations gradually decreased during these 40 days as the Pb pipe slowly developed an insoluble PbO_2 scale that protected against Pb leaching. This timeline is consistent with a study in which Pb(II) was oxidized to Pb(IV) after 28 days in contact with synthetic tap water with 20 mg L^{-1} of dissolved inorganic carbon and 3 mg L^{-1} of free chlorine (Wang et al., 2010). We confirmed the presence of Pb(IV) minerals, scrutinyite and plattnerite, 60 days after the treatment in the untreated Pb pipe with synthetic Flint water, as shown in Fig. 3.

In terms of the monitored water quality parameters, the treatment did not significantly affect the system's demand for free chlorine, or the pH or conductivity of the Flint synthetic water with a free chlorine residual, as shown in Figs. 4a, c and d, respectively (for statistical significance, see Table S1 in the S.I.). However, the treated pipes consistently consumed less orthophosphates than their untreated counterparts (Fig. 4b). This is explained by the low Pb levels detected in the synthetic Flint water with a free chlorine residual within the treated Pb pipes (Fig. 2a). Given that orthophosphates react with dissolved Pb(II), it is likely that the low Pb concentrations due to the treatment caused orthophosphate concentrations to remain higher than those observed in the water within the untreated pipes.

The treated pipes released significantly more Al into the water when free chlorine was used as a disinfection residual compared to their untreated counterparts. The largest amount of Al detected throughout the experiment was 70 ppb, which is lower than the 200-ppb secondary standard established by the EPA. The release of Al into the synthetic Flint water might be a result of interactions between free chlorine and the underlying Pb scale. Free chlorine has been proven to permeate passive Al_2O_3 layers and promote Al corrosion (Subba Rao and Bera, 2021). Thus, it is likely that it can also permeate the electrogenerated Al-based layer (see Section 3.2. for details on the composition of the electrogenerated layer) via its pores and cracks. Redox reactions between free chlorine and the underlying Pb(II) might have caused small-scale detachment of the electrogenerated Al oxide layer. This might explain our observation that free chlorine consumption within the treated and untreated pipes were similar, as in both cases Pb(II) minerals within the pipe scales were oxidized by free chlorine (see detailed free chlorine consumption data in Fig. S2 in the S.I.). Further research is needed to fully understand the mechanism by which free chlorine may degrade the electrogenerated Al oxide layer and whether this degradation affects the long-term performance of the treatment. Moreover, Al in drinking water resulting from this degradation may influence Pb concentrations in drinking water in the presence of orthophosphates (Li et al., 2020). However, the release of Al into the water did not have any adverse effects on the drinking water quality throughout the duration of our experiment.

3.1.2. *Monochloramine residual*

When monochloramine was used as a disinfection residual, the treatment also decreased total Pb levels below the LCR action level of 15 ppb for the duration of the experiment, as shown in Fig. 2b. Like in the free chlorine case, Pb was mostly in particulate, and not dissolved form (see S.I.). In contrast, when the treatment was not applied to the Pb pipe with synthetic Flint water and a monochloramine residual, Pb concentrations remained above the action level of the LCR throughout the duration of the experiment in both particulate and dissolved forms. This is likely because monochloramine is a moderate disinfectant that does not promote Pb(II) oxidation (Switzer et al., 2006) and because of the formation of Pb(II) phosphate particles in the bulk solution. Total Pb concentrations likely decreased as a result of the corrosion control measures taken on day 60 (adding orthophosphates and increasing the pH). This is supported by the XRD results shown in Fig. 3, in which the treated and untreated Pb pipe with synthetic Flint water and a monochloramine residual only have peaks for crystalline Pb(II) minerals.

In the case of the pipes with our lab's tap water and a monochloramine residual, we observed similar results to those obtained for the treated Pb pipe with synthetic Flint water and a monochloramine residual. The treatment immediately decreased Pb levels below the action limit of the LCR; however, Pb levels remained at around 10 ppb for the duration of the experiment (except for one day where they surpassed the action level of the LCR). This was a result of the Pb concentrations detected in our lab's tap water (average = 9.1 ppb) and not because of the treatment. As shown in Fig. 2c, the lab's tap water that was used in the pipe loops (taken directly from the tap) already had Pb in it. The Pb concentrations in the lab's tap water and those observed for the treated pipe with our lab's tap water are almost identical. This shows that the treated pipe did not contribute to the Pb concentrations observed in Fig. 2c. In contrast, the untreated pipe with our lab's tap water and a monochloramine residual did not achieve Pb concentrations below the action limit of the LCR. Moreover, these Pb concentrations were higher than those observed for the untreated Pb pipes with synthetic Flint water, as shown in Fig. 2. This is likely a result of using a more complex water matrix with variable water quality, lower pH (8 vs 8.5 for our lab's tap water and the synthetic Flint water, respectively) and higher levels of organic matter, all of which contribute to increasing Pb solubility (Lin and Valentine, 2008; Kim et al., 2011). As expected, the XRD pattern for the untreated Pb pipe with our lab's tap water revealed that by the end of the experiment, only Pb(II) crystalline minerals were present. The formation of these Pb(II) minerals did not provide enough protection against Pb leaching, despite the use of corrosion control strategies.

In terms of the monitored water quality parameters, the treatment did not significantly affect the system's demand for monochloramines or the pH, conductivity and Al concentrations when using Flint synthetic water or our lab's tap water with a monochloramine residual (Fig. 4a, c, d, and e, respectively, and Table S1 in the S.I.). As in the case of the synthetic Flint water with a free chlorine residual, the treated pipes

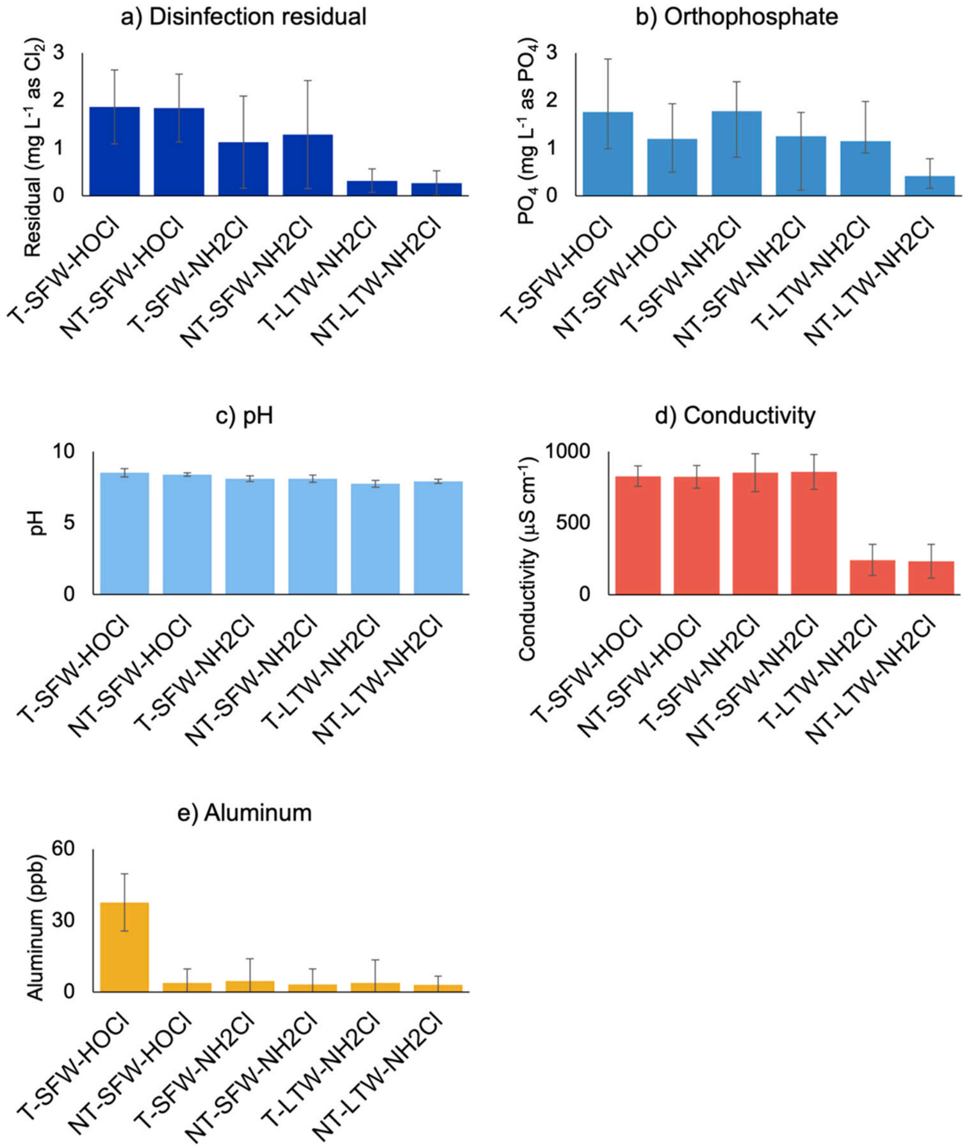

Fig. 4. Average water quality conditions for the 60 days following the treatment date. The monitored water quality conditions are (a) disinfection residual after 24 h of residual adjustment, (b) orthophosphate levels after 7 days of orthophosphate adjustment, (c) daily water pH, (d) daily water conductivity, and (e) Total Al measured twice a week. The following abbreviations are used: T: treated pipe after 60 days since treatment date, NT: untreated pipe after 60 days since treatment date, SFT: Synthetic Flint Water, LTW: Lab's Tap Water.

consumed less orthophosphates than their untreated counterparts. This is likely because the treated pipes released less Pb into the water, decreasing their orthophosphate consumption when compared to the untreated pipes.

In contrast to the experiments with synthetic Flint water with a free chlorine residual, the use of monochloramines did not result in significant Al being released into either the synthetic Flint water or our lab's tap water. This finding implies that the monochloramine residual did not impact the integrity of the electrogenerated Al oxide layer throughout the duration of the experiment. Moreover, the stark contrast between the released Al levels of the treated pipes with a free chlorine and a monochloramine residual supports our hypothesis that free chlorine may cause small-scale detachment of the electrogenerated Al oxide layer.

3.2. *Effect of the treatment on the Pb pipe scale*

The treatment was successful at depositing an amorphous Al_2O_3 layer on top of preexisting scales within the Pb pipes. As shown in Fig. 3, the treatment caused most of the peaks present in the XRD analysis of the untreated pipes to disappear, except for a small peak associated to pyromorphite (see XRD patterns before and after the treatment). The lack of peaks indicates the formation of an amorphous layer on top of the preexisting scale. We characterized this amorphous layer using Raman spectroscopy, which revealed the characteristic peaks for α-Al_2O_3 at wavenumbers of 419 and 643 cm^{-1}, as shown in Fig. 5. These peaks were not detected in any of the untreated pipes, indicating that the presence of Al_2O_3 should be attributed to the electrochemical treatment.

The electrogenerated Al_2O_3 layer was clearly visible under the SEM, as shown by the presence of a uniform, but highly cracked layer on the treated pipes (see images for before and after the treatment on Fig. 6). This layer had a thickness of 10 – 25 µm. The EDX analysis, also shown in Fig. 6, revealed that the electrodeposited layer contained large amounts of O and Al (see Fig. S3 for EDX weight percentages), further supporting our hypothesis that the electrodeposited layer is comprised of Al_2O_3. In contrast, the native scale of the untreated pipes did not contain significant amounts of Al, as shown in Fig. 6.

3.2.1. *Effect of the free chlorine residual on the Al oxide layer*

After 60 days in contact with synthetic Flint water and a free chlorine residual, the electrogenerated layer changed both in appearance and elemental composition compared to these attributes right after the treatment (Fig. 6). After 60 days, the surface of the treated Pb pipe consisted mainly of O and Pb, indicating that Pb corrosion products

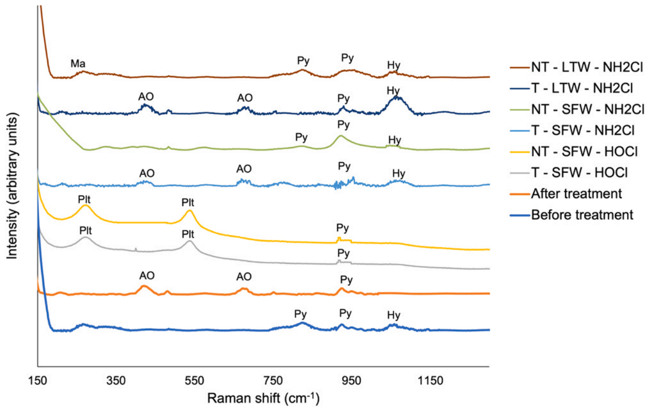

Fig. 5. Raman spectra for the treated and untreated Pb pipes immediately before and after the treatment, and after 60 days since the treatment date. As shown, the treatment generates an amorphous scale that consists mainly of α-Al_2O_3. The following abbreviations are used: T: treated pipe after 60 days since treatment date, NT: untreated pipe after 60 days since treatment date, SFT: Synthetic Flint Water, LTW: Lab's Tap Water, Hy: Hydrocerussite Py: Pyromorphite, Plt: Plattnerite, Sc: Ma: Massicot, AO: Aluminum oxide (α-Al_2O_3).

became the predominant surface solids. This was confirmed using XRD and Raman analysis, which show the formation of plattnerite on the treated pipes after 60 days of exposure to synthetic Flint water with a free chlorine residual (see Figs. 3 and 5, respectively). There are two likely mechanisms that explain this change in surface during the 60 days after the treatment. First, as shown in Fig. 4e, Al was released into the water when free chlorine was used as a residual. This Al was predominantly in dissolved form (we did not detect particulate Al). Thus, it is likely that the electrochemically generated Al oxide layer partially dissolved and revealed some of the underlying scale. Second, PbO_2 may have deposited on top of the Al_2O_3 layer due to the oxidation of Pb(II) minerals, such as cerussite and hydrocerussite, within the cracks of the Al_2O_3 layer by free chlorine (Liu et al., 2008). Given that Pb concentrations within the treated pipes with synthetic Flint water and a free chlorine residual remained consistently low throughout the 60 days after treatment, we hypothesize that the Al_2O_3 layer was the primary defense against Pb leaching until PbO_2 became the predominant scale solid. This is supported by the fact that the untreated pipe with synthetic Flint water and a free chlorine residual leached significant amounts of Pb until PbO_2 became the predominant scale solid. However, this means that if the free chlorine residual is not maintained, it is likely that the PbO_2 layer that formed on top of the Al_2O_3 layer will be reduced to Pb (II), resulting in Pb leaching.

The OCP measurements shown in Fig. 7 also support our hypothesis that the treatment was the primary reason why Pb levels decreased on the treated Pb pipes with synthetic Flint water and a free chlorine residual. The four main electrochemical reactions within the untreated pipes due to the action of free chlorine likely were:

$$Al(OH)_4^- + 3e^- \Longleftrightarrow Al_{(s)} + 4OH^- \quad , \quad E_0 = -2.31 \quad V \quad vs \quad SHE \tag{1}$$

$$PbCO_{3(S)} + 2e^- \Longleftrightarrow \quad Pb_{(s)} + CO_3^{2-}, \quad E_0 = -0.51 \quad V \quad vs \quad SHE \tag{2}$$

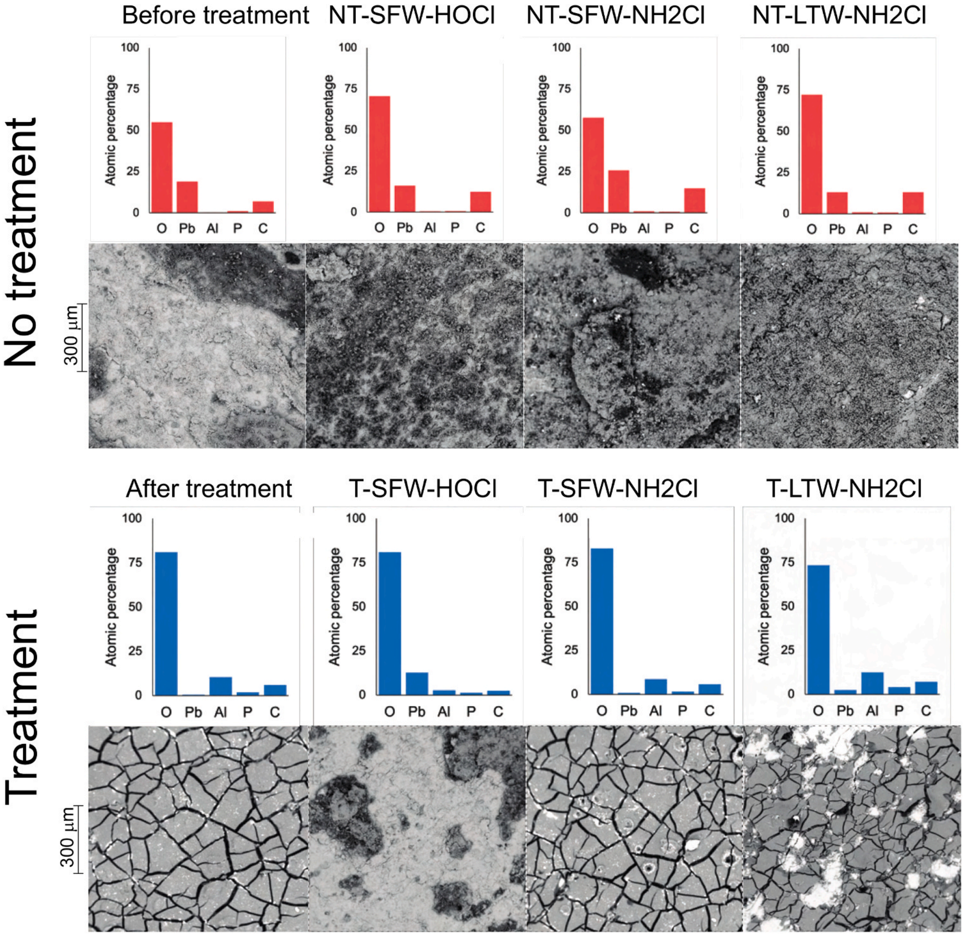

Fig. 6. Scanning Electron Microscope with Energy Dispersive X-ray Analysis (SEM-EDX) of the Pb pipes immediately before and after the treatment, and after 60 days in contact with water from the different pipe loops. The treatment deposits a layer mainly composed of O and Al. The following abbreviations are used: T: treated pipe after 60 days since treatment date; NT: untreated pipe after 60 days since treatment date, SFT: Synthetic Flint Water, LTW: Lab's Tap Water.

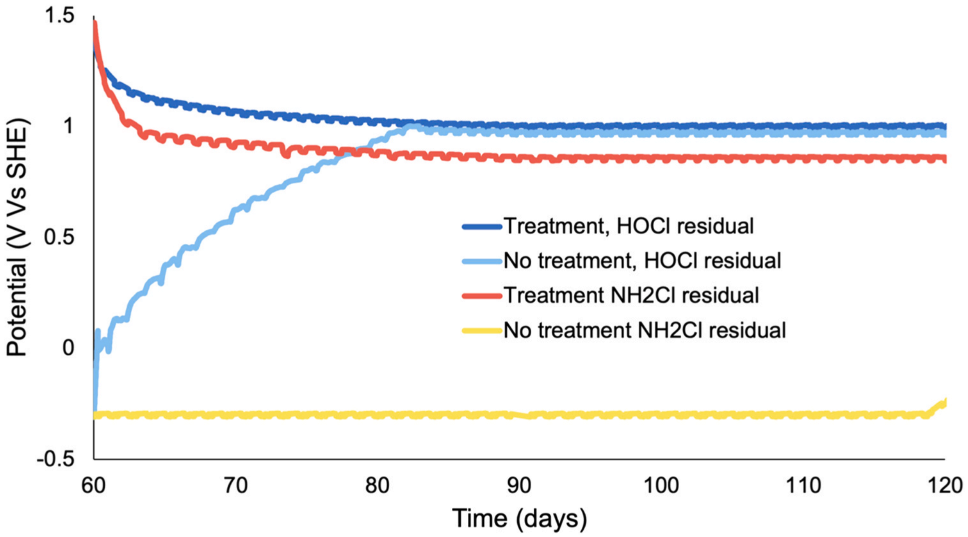

Fig. 7. Open Circuit Potential (OCP) of the pipe loops with synthetic Flint water, with and without the treatment for 60 days after the treatment date. The treated pipe with a monochloramine (NH_2Cl) disinfection residual has a higher OCP than its untreated counterpart. In contrast, the treated pipe with a free chlorine (HOCl) residual starts with a higher OCP, but after 21 days the OCP of the untreated pipe increases to match its treated counterpart. Note that the time starts at 60 days because the treatment was applied on day 60 of the experiment.

$$PbO_{2(s)} + \quad CO_3^{2-} + 4H^+ + 2e^- \Longleftrightarrow \quad PbCO_{3(s)} + 2H_2O, \quad E_0 = +1.84 \quad V \quad vs \quad SHE \tag{3}$$

$$OCl^- + H_2O + 2e^- \Longleftrightarrow \quad Cl^- + 2OH^- \quad , \quad E_0 = +0.88 \quad V \quad vs \quad SHE \tag{4}$$

Where E_0 is the standard electrode potential (V vs SHE). We computed the theoretical reduction potential for the Flint synthetic tap water using the Nernst equation, resulting in −1.99, −0.41, 0.98 and 1.15 V vs SHE for Eqs. (1), (2), (3) and (4), respectively. The OCP values indicate that the predominant electrochemical reaction within the untreated pipe with a free chlorine residual on day 60 was likely Eq. (2) (compare the measured OCP of −0.37 V vs SHE and the estimated reduction potential using Eq.(2) of −0.41 V vs SHE). However, by day 97, the OCP shifted towards the reduction potential of Eq. (4) (compare the measured OCP of 1.03 V vs SHE and the estimated reduction potential using Eq. (4) of 1.15 V vs SHE). Given that the OCP on day 97 is higher than the reduction potential of PbO_2 (0.98 V vs SHE), it is likely that PbO_2 became the dominant scale component after day 97 of the experiment. This is consistent with Fig. 2a, in which dissolved Pb levels decreased below the action limit of the LCR on day 100, likely due to the formation of a PbO_2 layer.

In the case of the treated pipe exposed to synthetic Flint water with a free chlorine residual, the OCP remained above the PbO_2 reduction potential throughout the experiment. This indicates that the predominant equilibrium reaction likely was Eq. (4) (compare the measured OCP of 1.08 V vs SHE and the estimated reduction potential using Eq. (4) of 1.15 V vs SHE). Thus, it is likely that any Pb that existed after the treatment was in the form of PbO_2, which is consistent with the low Pb levels detected throughout the experiment after the treatment (Fig. 2a) and the presence of PbO_2 on top of the electrochemically generated Al oxide layer (Figs. 3 and 5). Note that the oscillating patterns seen in all OCP curves are likely due to the 8 h daily stagnation period in each pipe loop. The local consumption of the disinfection residual and orthophosphates results in a decrease in OCP (Henfy et al., 1990; Rajasekharan et al., 2007). Thus, in stagnant waters where orthophosphates and the residual are locally consumed, measured OCP values are likely to decrease. This causes the OCP to decrease during stagnation and to then increase when the flow restarts.

3.2.2. *Effect of the monochloramine residual on the Al oxide layer*

The electrogenerated Al oxide layer did not change in terms of structure and composition after being exposed to water with a monochloramine residual for 60 days. As shown in Fig. 5, the uniform and cracked layer that was present after the treatment was still present after 60 days of exposure to synthetic Flint water and our lab's tap water with a monochloramine residual. However, small deposits became visible under the SEM (see white precipitates on Fig. 5) after 60 days in contact with water, particularly for the treated pipe with our lab's tap water and a monochloramine residual. These deposits likely comprised lead corrosion products, such as Pb(II) phosphate minerals that formed during the 60 days after the treatment due to the presence of orthophosphates. This is supported by the presence of the pyromorphite and hydrocerussite characteristic peaks in the XRD pattern of the treated pipe with our lab's tap water and a monochloramine residual shown in Fig. 3. We also detected peaks for the characteristic n_1 and n_2 P-O stretching modes (Botto et al., 1997) located at 944 and 918 cm^{-1}, and the n_1 C-O stretching mode (Martens et al., 2004) located at 1054 cm^{-1}, which may also correspond to pyromorphite and hydrocerussite, respectively. It is likely that more deposits formed on the treated pipes exposed to our lab's tap water than on the pipes exposed to the synthetic Flint water because the lab's water matrix had about 10 ppb of Pb (see Fig. 2c). This Pb in the water matrix is likely to have formed Pb(II) phosphate minerals in the presence of orthophosphates.

Another interpretation of the presence of Pb(II) corrosion products on the electrogenerated layer after 60 days in contact with our lab's tap water is that the layer could have partially dissolved during that time, revealing the underlying scale. However, this is unlikely because of the low Al concentrations (< 5 ppb) detected in the water within any of the pipes with a monochloramine residual throughout the experiment (Fig. 4e).

The OCP measurements (Fig. 7) are consistent with our hypothesis that the treatment provides a stable protection against Pb leaching when monochloramines are used as a disinfection residual. In this system, the dominant electrochemical reactions likely are Eqs. (1)–(3) and the following reaction:

$$NH_2Cl + \quad 2H^+ + 2e^- \Longleftrightarrow \quad Cl^- + NH_4^+, \quad E_0 = +1.45 \quad V \quad vs \quad SHE \tag{5}$$

Using the Nernst equation, the reduction potential for monochloramine in the synthetic Flint water is 0.98 V vs SHE. As shown in Fig. 7, the OCP stabilized at a potential close to the reduction potential of monochloramine (0.91 V vs SHE), indicating that the predominant redox equilibrium was likely that of Eq. (5). The measured OCP was also close to the reduction potential of PbO_2 (Eq. (3)). However, it is unlikely that this was the predominant equilibrium reaction given that PbO_2 is unstable in the presence of monochloramines and that we did not detect

Pb(IV) minerals using XRD or Raman spectroscopy. These results suggest that Pb redox reactions are inhibited by the electrogenerated Al_2O_3 layer, which explains why Pb leaching decreased significantly for 60 days after the treatment (Fig. 2b). In contrast, when the treatment was not applied, the OCP remained at around the Pb(II) reduction potential (Eq. (2)) of −0.41 V vs SHE. This is likely a result of Pb(0) from the underlying pipe material being oxidized to Pb(II), which is driven by the dissolution of the more soluble Pb(II) minerals, such as hydrocerussite. By the end of the experiment the OCP started to slowly increase, indicating that the Pb pipe was gradually becoming more passive. We hypothesize that this is a result of the buildup of Pb(II) phosphate minerals due to the presence of orthophosphates. Pb(II) phosphate mineral scales are highly insoluble and passivating (Henfy et al., 1990), thus, the OCP should increase as a more insoluble scale develops within the Pb pipes. This is also consistent with the Pb measurements for the synthetic Flint water with a monochloramine residual within the untreated pipes shown in Fig. 2b. Under these conditions, Pb levels remained above the action limit of the LCR until the end of the experiment. However, they decreased as a function of time, particularly at the end of the experiment, which is when the OCP started to increase.

Note that we did not measure the OCP of the Pb pipes exposed to our lab's tap water with a monochloramine residual because we had no control over the water quality. Thus, monitoring the OCP in this system would not have provided meaningful results because the OCP is a function of all the possible redox reactions given a specific water composition.

3.3. Advantages and limitations

The proposed electrochemical treatment was successful at preventing total Pb concentrations from exceeding the action level of the LCR for 60 days in synthetic tap water with a free chlorine residual and in synthetic and actual drinking water with a monochloramine residual. However, full deployment of this technology demands rigorous research into multiple field conditions that were not explored in this study. First, it is unclear whether the treatment will work on every type of scale within Pb pipes because we only tested Pb pipes reclaimed from the EBMUD water distribution system located in Berkeley, CA. However, given that the tested pipes had an electrically nonconductive Pb(II) mineral preexisting scale, it is likely that the treatment will work on most Pb(II) scales regardless of scale conductivity. In the case of Pb pipes with a preexisting Pb(IV) scale, the treatment is also likely to work given the high electrical conductivity of PbO_2.

Even if the treatment works on every type of preexisting scale within Pb pipes, it is unclear from this study for how long it will provide protection against Pb leaching, particularly under field conditions. Moreover, there are multiple factors that could affect the deposition and stability of the electrogenerated Al_2O_3 layer, including galvanic coupling, variable water quality and long stagnation periods and the presence of biofilm. All these factors must be studied in a field trial to assess whether the proposed treatment is flexible enough to protect against Pb leaching under most circumstances. Nevertheless, the results so far appear promising, and further investigation seems worthwhile.

Finally, there are multiple practical limitations that remain unexplored, including the insertion of an Al wire and a phosphate electrolyte into the Pb pipes. We recognize that these factors could render the implementation of the proposed technology cumbersome; however, these matters remain to be tested out on the field in consultation with knowledgeable experts. By deploying the technology with the help of plumbing experts, we hope to improve the existing design to make it as practical and economically feasible as possible.

4. Conclusions

The electrochemical deposition of an Al_2O_3 coating within Pb pipes is a novel approach that may help provide long-term protection against Pb leaching into the drinking water from Pb water pipes. Pipe replacement will always be the best solution to the Pb leaching problem. However, the proposed technology could provide a non-invasive, rapid, and cost-effective temporary solution until all Pb pipes can be replaced. Moreover, this technology may even provide protection against Pb leaching during the pipe replacement process and in cases when only partial Pb pipe replacement is possible. Thus, further research in needed to better understand the limitations of this technology under field conditions so that it can be effectively used to provide safe drinking water until all Pb pipes can be replaced.

CRediT authorship contribution statement

Gabriel P. Lobo: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition. **Bavisha Kalyan:** Methodology, Validation, Investigation, Data curation, Writing – review & editing. **Ashok J. Gadgil:** Conceptualization, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.127195.

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