Effects of orthophosphate corrosion inhibitor on lead in blended water quality environments

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ABSTRACT

This study evaluated the effects of orthophosphate (OP) inhibitor addition on corrosion of lead/tin coupons exposed to different blends of groundwater, surface water, and desalinated seawater. Four different doses of OP inhibitor, from zero (control) to 2 mg/L as P, were investigated and non-linear empirical models were developed to predict lead release from water quality and OP doses. Surface characterization evaluations were conducted using X-ray Photoelectron Spectroscopy (XPS) for each lead coupon tested. A theoretical thermodynamic model was developed to predict lead. OP inhibitor addition was found to reduce lead release for the OP dosages evaluated and water blends evaluated compared to pH adjustment alone. Empirical models showed increased phosphorus and pH reduced lead release while increased alkalinity, chloride, and temperature contributed to lead release. Thermodynamic modeling suggested that hydroxypyromorphite is the controlling solid that forms on lead surfaces, regardless of blend, when OP inhibitor is added for corrosion control.

Keywords: Lead release; Orthophosphate corrosion inhibitor; Blended source water; Distribution system water quality

1. Introduction

With increasing water demands and more stringent drinking water regulations, many utilities are turning to desalinated sources to supplement their surface and groundwater supplies. Tampa Bay Water (TBW) and the University of Central Florida (UCF) studied the effects of blending multiple alternative source waters on distribution system water quality [1]. This study evaluated the addition of orthophosphate (OP) corrosion inhibitor to differing blended source waters in order to study the effects on lead corrosion.

Lead levels in drinking water are regulated through the Lead and Copper Rule (LCR) provisions of the Safe Drinking Water Act (SDWA) and that defined an action level of 0.015 mg/L at the 90th percentile of household kitchen taps sampled by voluntary participant homeowners [2]. Lead in household tap water originates from several sources including lead service lines, lead-tin solder, brass fixtures and faucets in bathrooms and kitchens [3–5]. Lead levels are a function of water quality, plumbing materials, contact time, pipe geometry, water temperature, and age of materials [6,7]. Chemical treatment for control of lead corrosion includes pH adjustment, carbonate addition, calcium carbonate deposition and inhibitors [6].

Numerous studies have found that orthophosphate inhibitor addition can reduce lead concentrations in water under the ideal pH conditions [8–13]. Orthophosphate chemicals form passivating films on metallic surface

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anodic sites to suppress electrochemical reactions. Zinc, lead, calcium or iron deposition can further enhance the protection by forming films over cathodic sites [14]. Orthophosphate can react with lead plumbing materials to form compounds that do not have a strong tendency to dissolve into water, so lead concentrations tend to remain low in drinking water [14,15].

Edwards and McNeill [16] found that dosing orthophosphate inhibitor reduced lead release by 70%, with exception to new pipes. New pipes had increased lead, suggested to be a result of a lower increase in pH during stagnation. Particulate lead was the dominant corrosion product form observed. Total lead levels decreased with pipeline aging.

Pinto, McAnally and Flora [17] showed addition of orthophosphate corrosion inhibitor reduced lead levels as compared with zinc or blended orthophosphate inhibitors. Inhibitor and alkalinity addition in low alkalinity waters reduced lead levels further than alkalinity adjustment alone. Phosphate addition was recommended because of its effectiveness at low doses. Alkalinity and pH adjustments are viewed as an alternative, but may have adverse secondary affects on water system scaling.

Washington D.C.'s conversion to monochloromines corresponded with increased lead release in the distribution system [18]. A study was done with orthophosphate addition and the scale formed on lead service lines was monitored. It was found that prior to orthophosphate treatment, lead(IV) oxide was dissolving due to the lower ORP experienced with the monochloramine residual compared with the free chlorine. Use of orthophosphate was found to be the optimal inhibitor choice and took eight months to form a passivating scale and reduce lead levels of 150 ppb down below the action level in the distribution system.

Dodrill and Edwards [19] conducted a survey of about 360 utilities to examine their strategies in controlling lead and copper release in response to the LCR. It was observed that without phosphate inhibitors, higher alkalinity resulted in lower lead release. (This is contrary to observations in the system used in this study [1]). At low alkalinity, using inhibitors reduced lead release compared to no inhibitors. The survey revealed that utilities with the low alkalinity and pH below 7.4 benefited from using orthophosphate but not polyphosphate. Moreover, polyphosphate increased lead release at higher alkalinity levels.

Hozalski, Esbri-Amador and Chen [20] studied the benefit of inhibitors in controlling lead release from lead pipe. They used orthophosphate, polyphosphate, blended ortho-polyphosphate (BOP), and stannous chloride ($SnCl_2$). The evaluated inhibitors performed better than the no-action alternative at reducing lead release with various degrees. The ranking of inhibitors based on total lead concentrations, from lowest to highest, in the tested pipe loops was as follows: ortho-P < $SnCl_2$ < BOP < poly-P

< control. The authors also observed that phosphate-based inhibitors resulted in increased biological growth compared to the stannous chloride and control pipes.

This study evaluated the effects of orthophosphate inhibitor on lead release when added to blended treated surface, ground, and seawater sources of varying blend percentages. The effects of water quality were evaluated and a model predicting total lead release using water quality and total phosphorus concentrations was developed. XPS analysis of 50/50 lead/tin coupons was evaluated for solid phase surfaces present on the coupon, and thermodynamic modeling was performed using collected experimental information to gain insight into the mechanism of inhibitor control of lead release.

2. Experimental methods

2.1. Experimental design

Experimentation was conducted with the use of pilot distribution systems (PDSs) built from actual pipelines extracted from TBW member governments' (Hillsborough County, Fla.; Pasco County, Fla.; Pinellas County, Fla.; City of New Port Richey, Fla.; City of St. Petersburg, Fla.; and City of Tampa, Fla.) distribution systems. Details regarding prior study results on variable water supplies are reported elsewhere [1]. Each PDS was operated in parallel with segments of 20 ft (6.1 m) of 6 in (0.15 m) PVC, 20 ft (6.1 m) of 6 in (0.15 m) lined cast iron, 12 ft (3.66 m) of 6 in (0.15 m) unlined cast iron, and 40 ft (12.19 m) of 2 in (0.05 m) galvanized steel pipes that were placed sequentially to simulate actual distribution systems. Each PDS was fed blends of groundwater (GW), surface water (SW), and desalinated seawater by reverse osmosis (RO) along with different types and doses of corrosion inhibitor. This same PDS configuration was used for this study.

The GW unit used raw well water from the Cypress Creek well field, which is owned by TBW. The GW was treated with aeration, disinfection, and pH stabilization. Aeration was achieved in the GW by pumping the raw water to the top of the finished water tank through a spray nozzle. Sodium hypochlorite was used for primary disinfection and was dosed to provide a 5 mg/L residual after a 5 min contact time. Afterwards, ammonium chloride was added to produce a 5 mg/L monochloramine residual. Ammonia was added in the form of NH_4Cl at a 5:1 ratio. The Cl_2:NH_3 ratio was initially 4:1 to protect against DBP formation. This ratio was increased to 5:1 after 6 months of operation to reduce free ammonia.

SW was treated at the TBW Regional Surface Water Treatment Facility by enhanced coagulation, ozonation, biologically activated carbon (BAC) filtration, aeration, and chloramination. The SW was hauled weekly to the field facility for use and temporarily stored in two 7000 gallon storage tanks before being transferred to the SW

finished water tank. In the SW finished tank, the chloramine residual was adjusted to 5 mg/L as Cl_2.

The RO pilot plant was housed in a trailer at the testing facility and utilized raw groundwater for the feed stream. The RO treatment pilot system required the addition of TDS, calcium and alkalinity to the RO permeate to represent the finished water produced by the TBW Regional Seawater Desalination Facility. RO pretreatment consisted of 2.7 mg/L antiscalant addition (Hypersperse MDC700TM, GE Water, Minnetonka, Minn.) followed by 5-micron cartridge filtration. The RO membrane unit was operated at 72–73% recovery, producing 9.3 gpm (35.2 L/min) permeate flow, which was aerated by a 10 in (0.25 m) diameter aeration tower filled with tripack plastic packing. After aeration, 50 mg/L of sea salt was added to the aerated permeate stream to simulate the TBW desalination process. Calcium chloride and sodium bicarbonate were also added to meet the calcium and alkalinity specifications. The finished was stabilized with sodium hydroxide to 0.1–0.3 pH units above pH_s.

The effects of water quality were evaluated by varying the blend quarterly, while seasonal effects were evaluated by maintaining the same blend in the summer and winter. The quarterly phases and percentages of the blends are shown in Table 1 with the average water quality of each of the source waters in each phase. The effects of season are seen in the temperature as well as rainy and dry season effects on the surface water between Phases I and III. The blends with a high percentage of groundwater in Phases I and III are characterized by higher alkalinity and pH. Phase II had the highest percentage of surface water and is characterized by high sulfate concentrations. Phase IV has average water quality parameters due to the equal percentage of GW and SW.

The feed rate of the blend into each PDS was maintained to achieve a two-day hydraulic residence time (HRT). Pumps maintained the blend flow as well as the inhibitor addition into each PDS. The PDSs each were fed different inhibitor types and doses. The inhibitors were dosed to the PDSs at three different levels, categorized as low dose, medium dose, and high dose. Orthophosphate (OP) was maintained at a target dose of 0.5 mg/L as P for the low dose, 1.0 mg/L as P for the medium dose, and 2.0 mg/L as P for the high dose. Control PDSs were not fed any chemical inhibitor; one was maintained at pH_s and a second was treated with elevated pH at an LSI of 0.3, maintained at $pH_{s+0.3}$. The PDS at $pH_{s+0.3}$ was maintained at a positive LSI to assess the affect of elevated pH treatment as a means of lead release control.

2.2. Orthophosphate inhibitor

The orthophosphate inhibitor used in this study is Inhibit-All WSF-36 (SPER Chemical Corporation, Clearwater, Fla.). It is made of monosodium orthophosphate blended into 17 megohm purified water at a concentration of 36%. It is a clear, slightly viscous liquid with a bulk density of 11.25 lbs/gal (1.35 kg/L). The specific gravity is 1.35 and the pH of 1% solution is 5.1–5.4.

2.3. Data collection

Portions of the flow from each PDS were fed to a corrosion loop consisting of 30 ft (9.14 m) of 5/8 in (0.02 m) copper tubing with one lead/tin coupon to represent solder. Each loop holds approximately 1.8 L of water. The copper tubes were flushed every morning with 2 gallons of the PDS water. Weekly samples were collected after a 6-h stagnation period in order to simulate tap monitoring as described in the LCR.

50/50 lead-tin coupons were placed in cradles that received flow in parallel with each PDS. The coupons were evaluated for surface characteristics after incubation during each phase. X-ray Photoelectron Spectroscopy (XPS) analysis was then performed on each type of coupon to identify chemical components on the outer layer of the corrosion surface. A survey scan can reveal the presence of elements providing detailed surface characterization information.

Table 1
Blend percentages and average water quality for each phase

Phase	I	II	III	IV
Quarter	Feb–May 2006	May–Aug 2006	Aug–Nov 2006	Nov 2006–Feb 2007
% GW	62	27	62	40
% SW	27	62	27	40
% RO	11	11	11	20
pH	8	7.9	8	7.9
Alkalinity, mg/L $CaCO_3$	161	104	150	123
Chloride, mg/L	45	67	68	59
Sulfate, mg/L	62	103	66	76
Temperature, °C	21	26	26	21

3. Results and discussion

3.1. Dose maintenance

Three of the PDSs were treated with orthophosphate corrosion inhibitor at a low, medium, and high dose. These doses were targeted to maintain at 0.5 mg/L as P, 1.0 mg/L as P, and 2.0 mg/L as P, respectively. The average orthophosphate inhibitor dose for the course of the study in each PDS is shown in Fig. 1. Error bars represent the minimum and maximum observations. The low dose of orthophosphate averaged 0.51 mg/L as P, the medium dose averaged 0.94 mg/L as P, and the high dose averaged 1.83 mg/L as P.

The orthophosphate inhibitor is added as phosphoric acid, so it has an effect of lowering the pH in those PDSs treated with inhibitor. The pH maintained in each of these PDS is shown in Fig. 2 with the error bars representing the minimum and maximum observations. The difference in pH maintained in each of the PDSs is significantly different with the exception of the low orthophosphate dosed PDS being the same as the elevated pH PDS at $pH_{s+0.3}$.

3.2. Empirical modeling

A non-linear empirical model was developed using the water quality data and phosphorus dose for the three
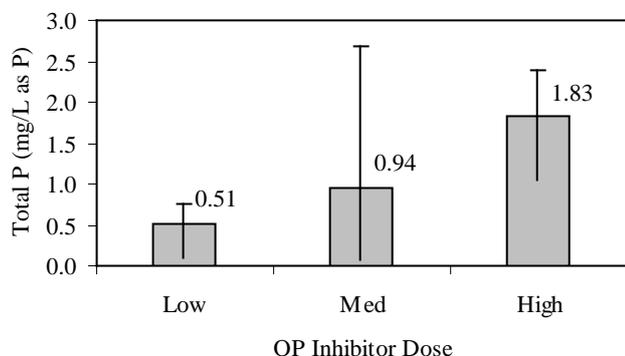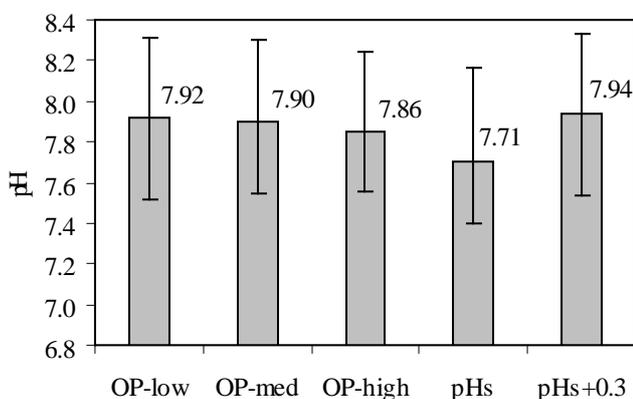
Table 2
Water quality range in model development

Parameter	Minimum	Maximum
Total phosphorus, mg/L as P	0.01	2.69
pH	7.4	8.4
Alkalinity, mg/L as CaCO$_3$	84	170
Chloride	38	123
Temperature, °C	10.4	29.7

PDSs with orthophosphate inhibitor addition and the PDSs maintained at pH_s and $pH_{s+0.3}$. Water quality parameters found to be significant using analysis of variance (ANOVA) procedures at 95% confidence were retained as variables in the model. All variables retained p-values less than 0.05. The range of the water quality parameters included in the model are shown in Table 2.

Eq. (1) presents a non-linear least squares regression model that was developed using results of the study. The water quality parameters pH, alkalinity, chloride, and temperature remained significant as well as the total phosphorus, which represents the inhibitor addition. Total phosphorus and pH mitigated lead release, as shown by the negative exponent on the variable in the model. However, alkalinity, chloride, and temperature are shown to increase lead release for the conditions experienced during this testing.

$$Total\,Pb = TP^{-0.435} \times pH^{-12.064} \times Alk^{2.853} \times Cl^{1.168} \times 1.144^{T-25} \qquad (1)$$

where Total Pb = total lead, mg/L; TP = total phosphorus, mg/L as P; pH = $-\log[H^+]$; Alk = alkalinity, mg/L as CaCO$_3$; Cl = chloride, mg/L; T = temperature, °C.

The model fits the data reasonably well with an R^2 of 0.62. The predicted lead release by the model compared with the total lead release observations is shown graphically in Fig. 3. It can be seen that most observations from the PDSs treated with orthophosphate inhibitor were below the detection limit for lead measurement of 0.001 mg/L. The observations at higher concentrations are from the pH_s and $pH_{s+0.3}$ control PDSs. This further shows the benefits of addition of the corrosion inhibitor to reduce lead release, often to levels below detection.

The model fits the data, but tends to under-predict the very high concentrations. All observations for the OP treated PDSs were below the action level of 0.015 mg/L and are well described with the model. Observations from the pH_s PDS tend to be much higher than the action level and are under-predicted by the model. Therefore the model is best suited for predicting cases where treatment is used to maintain lead release near and below regulated concentrations.

Fig. 3 presents the average lead release at the inhibitor doses evaluated as compared to the average of the model

Fig. 1. Orthophosphate inhibitor dosing.

Fig. 2. pH for OP PDSs and controls.
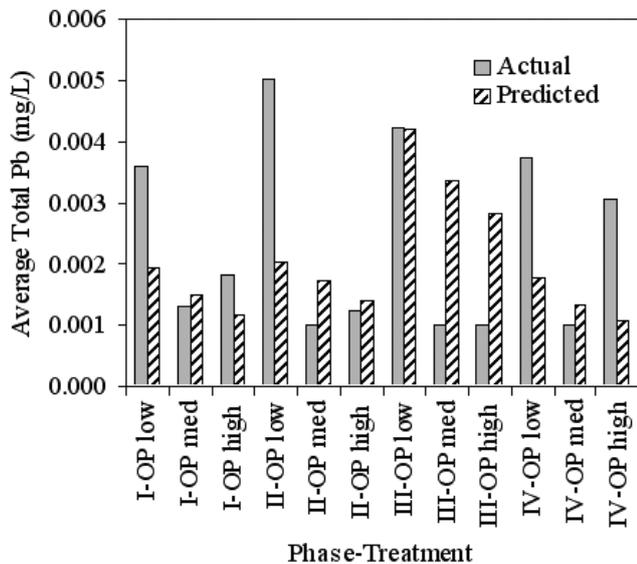
Fig. 3. Actual vs. predicted for empirical model by phase and PDS.

Fig. 4. Comparison of total Pb by phase and treatment.

predictions. The model predicts decreasing lead release with increasing inhibitor dose. The lowest inhibitor dose has the highest lead release, but the highest inhibitor dose appears to have the same lead release as the medium dose, due to so many observations below detection. Paired t-tests show no significant difference between the medium and high dose PDSs lead release at a 95% confidence level. The other PDSs were found to have a significant difference between lead release observations. Also, both the model predictions and actual observations for the lead release are always below the action level of 0.015 mg/L for all OP treated PDSs.

3.3. Orthophosphate inhibitor performance

A summary of the lead release from orthophosphate treated PDSs and pH control PDSs is shown in Fig. 4. The total lead release remained below the action level of 0.015 mg/L for the orthophosphate treated PDSs except one observation for each the low and high dose in Phase IV. The $pH_{s+0.3}$ PDS exceeded 0.015 mg/L at the 90th percentile in Phase II and the pH_s PDS exceeded the action level in Phases II and III. As a result of the low lead release levels observed in this study, the average values calculated are skewed. This is due to many lead observations being below the measurement detection limit of 0.001 mg/L.

The average total lead release is shown in Fig. 4 with the action level of 0.015 mg/L noted. The error bars represent the 90th percentile concentrations. Lead release for the low dose OP PDS is statistically lower in Phase I and IV than in Phase II and III. This is believed to be a result of the increased temperature observed in Phase II and III. The empirical model presented previously also showed this trend of increasing lead release with increas-

ing temperature. The temperature effect is coupled with low chloride in Phases I and IV compared with Phases II and III. The negative effect of increased chlorides was also observed in the empirical model. Trends of increasing lead release with increasing temperature and chloride are consistent with the lead release model developed for the previous study [1] presented in Eq. (2).
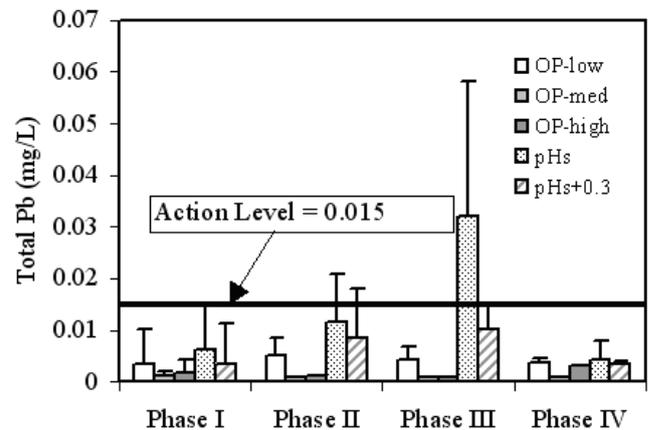
$$Pb = 1.027^{(T-25)} \times Alk^{0.677} \times pH^{-2.726} \times Cl^{1.462} \times S^{-0.228} \qquad (2)$$

where Pb = total lead concentration, µg/L; T = temperature, °C; Alk = alkalinity, mg/L as $CaCO_3$; pH = –log [H^+]; Cl = chloride, mg/L; S = sulfate, mg/L.

The medium dose OP PDS and the high dose OP PDS have consistent lead release between each other and between each phase. As previously discussed, most observations with these two treatments were below detection. Consequently, any water quality effects in either of these two PDSs are dampened and are not shown to have an effect on lead release.

For the pH_s PDS, Phase I and IV had lower lead release than Phase II and III with Phase III having the highest lead release. Again, Phase I and IV had lower temperature and chloride as was seen with the low OP dose PDS discussed previously. The increased alkalinity in Phase III due to the high percentage of groundwater caused higher lead release in Phase III than Phase II. This is consistent with the negative effects of alkalinity described by the empirical model presented previously in Eq. (1) as well as the lead release model developed in the previous study [1] as shown in Eq. (2). This alkalinity effect is not as apparent in the OP treated PDS due to the dampening the inhibitor addition has on the water quality effects on lead release.

The $pH_{s+0.3}$ PDS had similar trends as the low OP dose PDS. Lead release was lower in Phases I and IV than in Phases II and III. The effects of water quality are somewhat reduced by the elevated pH treatment as were seen with the low OP dose. This confirms the mitigating effects of increased pH as seen in the empirical model presented

previously as well as the water quality model developed in the previous study shown in Eq. (2) [1]. However, lead concentrations were not reduced as much as with the inhibitor addition and exceeded the action level in Phase II, as seen in Fig. 4.

Overall, the orthophosphate inhibitor treated PDSs were able to maintain lead release below the action level of 0.015 mg/L for the 90th percentile samples at the doses evaluated. The $pH_{s+0.3}$ treatment helped to reduce the lead release and effects of water quality to some extent, yet still exceeded the action level during Phase II.

3.4. Surface characterization

For each phase, lead/tin coupons of 50% lead and 50% tin composition were exposed to the medium inhibitor dose and each of the two pH control PDSs. The coupons were then analyzed by X-ray Photoelectron Spectroscopy (XPS) to identify elements present on the surface in an effort to gain insight to the mechanism of lead control by orthophosphate inhibitor addition. The elements found on the surface of the orthophosphate lead/tin coupons and both pH control coupons are shown in Table 3. There were four coupons (one for each phase) incubated over the course of the study in each of the PDSs.

For the orthophosphate treated coupons, phosphorus was determined to be present in the surface scale on lead/tin coupons for Phases I, II, and IV. For pH_s and $pH_{s+0.3}$ phosphate based compounds were not detected by XPS for pH_s and $pH_{s+0.3}$. The absence of phosphorus from lead/tin coupons taken from the pH PDSs indicates phosphorus scale came from the orthophosphate inhibitor. The phosphate scale is considered to be in the form of hydroxypyromorphite, $Pb_5(PO_4)_3OH$, as discussed in the thermodynamic modeling section below. Other lead corrosion products detected in the XPS analysis include PbO_2, PbO, hydrocerussite ($Pb_3(OH)_2(CO_3)_2$), and cerrussite ($PbCO_3$).

3.5. Thermodynamic modeling

Thermodynamic modeling was performed to validate the lead controlling solid phase. Assuming the presence

Table 3
Elements found in XPS analysis

Element	OP (4 total)	pH_s (4 total)	$pH_{s+0.3}$ (4 total)
Carbon	3	3	3
Calcium	2	2	1
Lead	4	3	4
Oxygen	4	4	4
Phosphorus	3	0	0
Tin	4	3	4

of Pb(II) species, the following dissolved lead ions and complexes were incorporated into the thermodynamic modeling efforts. Equilibrium modeling considered the same dissolved lead species as that of TBW I [1]. Incorporation of any other complexes cited by the literature proved to be redundant. The resulting model is presented in Eq. (3).

$$Pb_T = \left[Pb^{2+}\right] + \left[PbOH^+\right] + \left[Pb(OH)_2^0\right]$$
$$+ \left[Pb(OH)_3^-\right] + \left[Pb(OH)_4^{2-}\right] + \left[PbCO_3^0\right] \quad (3)$$
$$+ \left[Pb(CO_3)_2^{2-}\right] + \left[PbHCO_3^+\right]$$
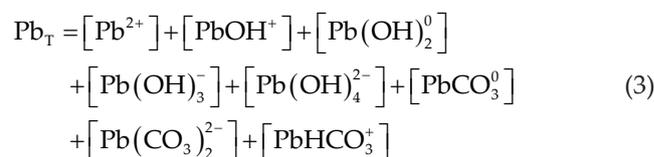
A pe-pH diagram was developed assuming the PbO, $Pb(OH)_2$, $PbCO_3$, and $Pb_3(CO_3)_2(OH)_2$ solid species and dissolved species discussed previously. In addition, this model considered phosphate-based solids to be significant in the corrosion layer and complexes to be a significant fraction of the dissolved lead. The phosphate-based complexes proved to be insignificant with respect to Pb_T, consistently representing less than 1% of Pb_T for PO_{4T} as high as 2 mg/L as P. The basic-lead(II) phosphate, hydroxypyromorphite, is often assumed to be the solid responsible for inhibiting lead release [21]. The reaction used during the analysis is shown in Eq. (4).

$$Pb_5(PO_4)_3OH(s) + H^+ = 5Pb^{2+} + 3PO_4^{3-} + H_2O \quad (4)$$
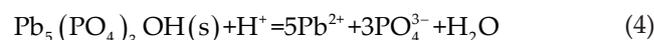
The pe-pH diagram taking into account orthophosphate inhibition of lead, with $Pb_T = 10^{-6} M$ and PO_{4T} = 1 mg/L-P, is shown in Fig. 5. The diagram suggests hydroxypyromorphite to be the predominant form of the corrosion layer, and not hydrocerussite, for domains typical of drinking water conditions, depicted within the shaded cube. The shaded cube represents the region of the diagram that would be typical of drinking water having an alkalinity between 50 and 300 mg/L as $CaCO_3$. The pH spans from 7.5 to 8.5, while the pe spans from 9.0 to 12.5 for a system maintaining a monochloramine residual.

Although increasing Pb_T would widen the predominance boundary of hydroxypyromorphite and hydrocerussite, the coexistence boundary between the two solids would remain the same, provided both solids are favorable. This implies that for a dose of 1 mg/L as P, hydroxypyromorphite formation would be more favorable over hydrocerussite within household plumbing. With respect to the prediction of the solid present, an increase in orthophosphate dose would extend the boundaries of hydroxypyromorphite, including the coexistence boundary, thus further ensuring its favorability over hydrocerussite in household plumbing.

While the pe-pH diagram implies that hydroxypyromorphite is less soluble than hydrocerussite, the pe-pH approach lacks application for determining the extent of inhibition. For this reason a pC-pH diagram was developed while varying C_T to determine the response of

Pb_T. The resulting pC-pH diagram is shown Fig. 6. Fig. 6 assumes that the pe is such that only Pb(II) species exist within the pH range of interest, a valid assumption as demonstrated by the typical drinking water conditions identified by the shaded cube in Fig. 5.

Fig. 6 was developed assuming hydroxypyromorphite as the controlling solid. The log of the Pb^{2+} ion concentration was plotted so the effects of carbonate complexes could be accounted for, but the total phosphorus could remain a variable. The upper plane shows the hydroxypyromorphite model prediction of Pb^{2+} with varying pH and phosphorus concentrations. However, due to the small lead coupon used in the copper loops to represent solder, lead release was diffusion limited in the sampling observations. Therefore, the diffusion equation shown in Eq. (5) was used to calculate a diffusion factor for the lead concentrations that would be expected from such a small quantity of lead.

$$C_x = C_s\left(1 - \mathrm{erf}\,\frac{x}{\sqrt{4D_{\mathrm{eff}}t}}\right) \tag{5}$$

where C_x = concentration at distance x and time t; C_s = equilibrium concentration; x = distance; t = time; D_{eff} = diffusion coefficient; erf = the error function.

The lead coupon was located about 1 ft from the sample port in the copper loops. 1 L samples were taken after a 6 h stagnation time, drawing about 5 m of water from the loops. Using this information and Eq. (5) a diffusion adjustment factor of 0.002 was determined. Therefore $C_{\mathrm{obs}} = 0.002\ C_s$. The thermodynamic model was adjusted for this diffusion limitation and is shown as the lower plane in Fig. 6. Plotted in Fig. 6 are the observations of lead release from each of the OP treated PDSs. These observations agree well with the diffusion limited model.

One coupon from each PDS was also left to incubate for 14 months after removal from the PDSs in a 100 mL container of the PDS water. These three coupons dissolved lead concentrations were measured and are also plotted in Fig. 6 as equilibrated samples. Since they have had time to come to equilibrium, they agree well with the thermodynamic model without adjustment for diffusion. As was seen with the observations during the study, the dissolved lead concentration in the low dose OP PDS was greater than the dissolved lead concentrations from the medium and high dose OP PDSs. These results suggest hydroxypyromorphite model is well suited as the controlling solid phase and formation may be the mechanism for lead release control with orthophosphate corrosion inhibitor addition.

4. Conclusions

- Empirical modeling of water quality to predict total lead release showed that total phosphorus, pH, alkalinity, chloride and temperature were significant pa-
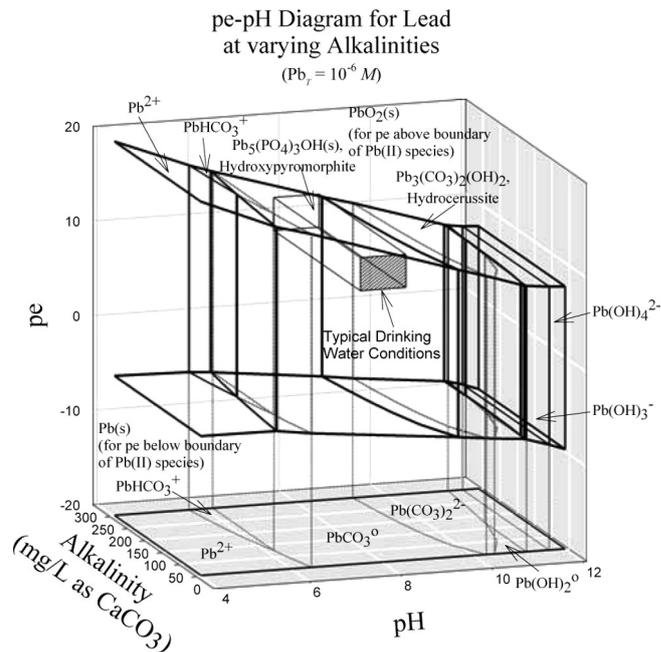
Fig. 5. Pourbaix diagram for lead species with 1 mg/L P inhibitor addition.
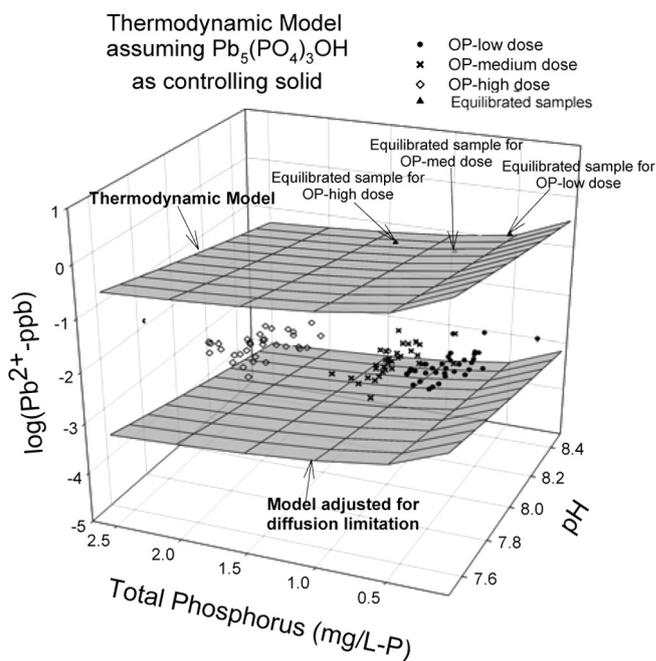
Fig. 6. pC-pH diagram assuming hydroxypyromorphite as the controlling solid.

rameters. The addition of phosphorus and an increase in pH were found to decrease the total lead release while the alkalinity, chloride and temperature were found to contribute to total lead release. The range of

phosphate dosages used in this study was 0 (control) to 2 mg/L as P.

- Observations found all PDSs treated with orthophosphate inhibitor did not exceed the action level of 0.015 mg/L. The low dose of OP had higher lead release than the medium and high dose, both of which had many observations below the measurement detection level for lead of 0.001 mg/L. This shows the ability of the inhibitor to dampen the effects of water quality on lead release. Elevated pH treatment to $pH_{s+0.3}$ also reduced lead release and slightly dampened water quality effects compared to the pH_s PDS, yet was found at times to exceed the action level.
- XPS analysis showed phosphorus forms were found on the orthophosphate coupons that were not identified on the pH control coupons. This suggests a phosphorus solid is responsible for lead release being significantly reduced in the OP treated PDSs.
- Thermodynamic modeling was performed to find the thermodynamically favorable controlling solid responsible for corrosion layer composition. Hydroxypyromorphite, $Pb_5(PO_4)_3OH$, was found to be less soluble in the region of water quality typical of drinking water distribution systems than hydrocerussite. Observations of lead release followed a model assuming hydroxypyromorphite as the controlling solid with diffusion limitations taken into account. Observations from equilibrated samples followed the trends of the equilibrium model. Therefore, the controlling solid was determined to be hydroxypyromorphite. Hydroxypyromorphite forms a solid on the lead surface in the presence of orthophosphate inhibitor to reduce lead release.

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