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

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ABSTRACT

This study evaluated the effects of orthophosphate (OP) inhibitor addition on copper corrosion on coupons exposed to different blends of groundwater (GW), surface water (SW), and desalinated seawater. The effectiveness of OP inhibitor addition on copper release was analyzed by statistical comparison between OP treated and untreated pilot distribution systems (PDSs). Four different doses of OP inhibitor, ranging from 0 (control) to 2 mg/L as P, were investigated and non-linear empirical models were developed to predict copper release from the water quality and OP doses. Surface characterization evaluations were conducted using X-ray photoelectron spectroscopy (XPS) analyses for each copper coupon tested. A theoretical thermodynamic model was developed and used to validate the controlling solid phases determined by XPS. OP inhibitor addition was found to reduce copper release for the OP dosages evaluated and the water blends evaluated compared to pH adjustment alone. Empirical models showed increased total phosphorus, silica and pH reduced copper release while increased alkalinity and chloride contributed to copper release. Thermodynamic modeling suggested that $Cu_3(PO_4)_2{\cdot}2H_2O$ is the controlling solid that forms on copper surfaces, regardless of blend, when OP inhibitor is added for corrosion control.

Keywords: Copper 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 (GW) 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 further evaluates the addition of orthophosphate (OP) corrosion inhibitor to the blended source waters and the effects on copper corrosion.

Copper levels in drinking water are regulated through the lead and copper rule (LCR) and limited to an action level of 1.3 mg/L at the 90th percentile of household kitchen taps sampled by voluntary participant homeowners [2]. The source of copper in drinking water comes primarily from corrosion of copper plumbing and is influenced by water quality parameters like pH, alkalinity, chloride, nitrate, sulfate, sodium, calcium, and magnesium [3]. Addition of OPs is believed to reduce copper release by forming $Cu_3(PO_4)_2$ or a similar scale on the surface of the pipe

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[4,5]. However, the benefits of using OP are thought to be limited to cases of pH less than 8 [4,6,7] (Schock, Lytle, and Clement, 1995).

Zhang et al. [8] tested the corrosion of copper exposed to tap water with monochloramine disinfectant for a period of 30 days. They found at a pH of 8, the copper corrosion increased for 6 days and then became steady for the remaining days. Increasing ionic strength, dissolved inorganic carbon, and temperature promoted corrosion, resulting in thicker oxide films.

Pinto et al. [9] evaluated the addition of phosphates as well as pH and alkalinity adjustment for corrosion control of copper in low hardness, low alkalinity waters. Addition of phosphate corrosion inhibitor was shown to help reduce copper levels. Increasing alkalinity was found to increase copper release. Phosphate addition was recommended because it is effective at low doses.

Indian Hills Water Works in Ohio used elevated pH to treat high copper levels and zinc OP for treatment of lead, but still had copper problems. To treat both, a study showed an increase in OP inhibitor to a dose of 3 mg/L as PO_4. This kept both the lead and copper within the action level and use of the zinc OP was discontinued [10].

A test of copper loops with stagnation and flow conditions similar to household plumbing systems showed phosphate inhibitors to reduce copper concentrations. Stabilization of the copper surface layer by building insoluble compounds of copper ions and phosphates was shown to interfere in the reaction kinetics of the dissolution of the copper surface layer [11].

Dodrill and Edwards [7] conducted a survey of about 360 utilities to examine their strategies in controlling lead and copper release, in response to the LCR of 1991. For copper, the survey showed that at high pH, copper release is reduced with and without inhibitors. At pH less than 7.8, copper release was high at high alkalinity, but inhibitor use mitigated that release. However, at pH greater than 7.8, inhibitors had variable and adverse effects on copper corrosion by-product release.

Edwards et al. [12] compared the benefits of OP vs polyphosphate in controlling copper corrosion by-product release in aged copper pipes, at variable pH and alkalinity values. Polyphosphate appeared to perform less favorably than OP at comparable concentrations of 1 mg/L as P. It was believed that OP reduced copper solubility by forming a cupric phosphate scale. In the absence of any phosphate inhibitors, an insoluble malachite scale formed over a period of years. Polyphosphate, however, increased copper release in comparison to OP because it complexed copper, increasing soluble copper release.

When inhibitors are not considered, copper release can be controlled best by raising pH [13]. It was demonstrated that bicarbonates adversely affected copper release, and that a pH increase (7.0–8.0) showed significant reduction in copper release. CO_2 stripping was the recommended method for raising the pH without raising alkalinity.

This study evaluated the effects of OP inhibitor addition to blended treated surface, ground, and seawater sources of varying percentages. The effects of water quality were evaluated and a model predicting total copper release using water quality and total phosphorus concentrations was developed. XPS analysis of copper coupons was evaluated for solid phase surfaces present on the coupon, and thermodynamic modeling was performed to gain insight into inhibitor control of copper 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 distribution systems (Hillsborough County, FL; Pasco County, FL; Pinellas County, FL; City of New Port Richey, FL; City of St. Petersburg, FL; and City of Tampa, FL). Details regarding the PDS and prior study results are reported elsewhere [1]. Each PDS runs in parallel with segments of 20 feet of 6 in PVC, 20 feet of 6 in lined cast iron, 12 feet of 6 in unlined cast iron, and 40 feet of 2 in galvanized steel pipes that were placed sequentially to simulate actual distribution systems. Each PDS was fed blends of GW, surface water (SW), and desalinated seawater by reverse osmosis (RO) along with different types and doses of corrosion inhibitor.

The GW unit used raw well water from the Cypress Creek well field 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 in after 6 months of operation to reduce free ammonia.

SW was treated at the TBW Regional Surface Water Treatment Facility by enhanced coagulation,

Table 1
Blend percentages and average water quality for each phase

Phase	I	II	III	IV
Quarter	February–May 2006	May–August 2006	August–November 2006	November 2006–February 2007
% GW	62	27	62	40
% SW	27	62	27	40
% RO	11	11	11	20
pH	8.0	7.9	8.0	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

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 GW 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 Desalination Facility. RO pretreatment consisted of 2.7 mg/L antiscalant addition (Hypersperse MDC700TM, GE Water, Minnetonka, Minn.) followed by 5-μm cartridge filtration. The RO membrane unit was operated at 72–73% recovery, producing 9.3 gpm permeate flow, which was aerated by a 10-in. 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 and the average water quality are shown below in Table 1. The effects of season are seen in the temperature as well as rainy and dry season effects on the SW between Phases I and III. The blends with a high percentage of GW in Phases I and III are characterized by high alkalinity and pH. Phase II had the highest percentage of SW 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 2-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. 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, 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 copper release control.

2.2. OP Inhibitor

The OP inhibitor used in this study is Inhibit-All WSF-36 (SPER Chemical Corporation, Clearwater, FL). It is made of monosodium OP blended into 17 MΩ purified water at a concentration of 36%. It is a clear, slightly viscous liquid with a bulk density of 11.25 lbs/gal. The specific gravity is 1.35 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 feet of 5/8 in. 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.

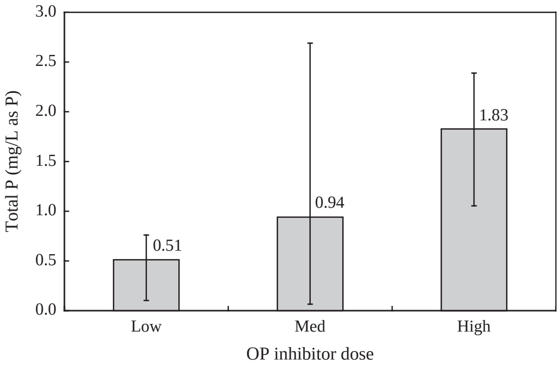

Fig. 1. OP inhibitor dosing.

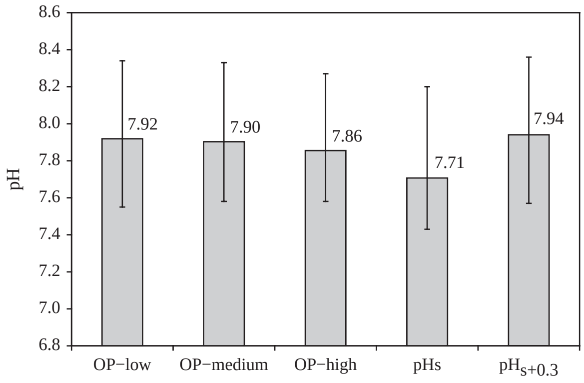

Fig. 2. pH for OP and control PDSs.

Copper 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 reveals the presence of elements, whereas a high resolution scan of those elements found on the outer layer shows the chemical states, providing detailed surface characterization information.

3. Results and discussion

3.1. Dose maintenance

Three of the PDSs were treated with OP 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 OP 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 OP 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 OP inhibitor is added as phosphoric acid, so it has an effect of lowering the pH is 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 OP dosed PDS being the same as the elevated pH PDS at $\mathrm{pH}_{s+0.3}$.

3.2. Empirical modeling

An empirical model for predicting total copper release was developed using the water quality data collected from the PDSs with OP inhibitor addition as well as the pH control PDSs. The range of the data used in development of this model is presented in Table 2. The inclusion of water quality parameters was based on ANOVA procedures for parameters that were statistically significant. Non-linear least squares regression was performed and independent parameters not significant at a 95% confidence level were eliminated. The resulting model is presented in Eq. (1). All parameters shown in the model retained p-values less than 0.05.

$$\text{Total Cu} = 1.446 \times \mathrm{TP}^{-0.280} \times \mathrm{SiO}_2^{-0.281} \times \mathrm{pH}^{-4.591} \times \mathrm{Alk}^{1.459} \times \mathrm{Cl}^{0.408} \tag{1}$$

where Total Cu is the total copper, mg/L; TP is the total phosphorus, mg/L as P; SiO_2 is the silica, mg/L as SiO_2; pH is the $-\log[H^+]$; Alk is the alkalinity, mg/L as $CaCO_3$; and Cl is the chloride, mg/L.

This model suggests the addition of the OP inhibitor, as measured by the total phosphorus concentration, mitigates copper release. This is shown by the negative exponent on the total phosphorus term. Similarly, higher silica and pH reduce copper levels in the corrosion loops. The pH term suggests the elevated pH treatment to $\mathrm{pH}_{s+0.3}$ is a valuable treatment. However, increased alkalinity and chloride contribute to copper release.

The fit of the model to the data has an R^2 value of 0.71 and is shown graphically in Fig. 3. The

Table 2
Range of water quality in model development

Parameter	Minimum	Maximum
Total phosphorus, mg/L as P	0.01	2.69
Silica, mg/L as SiO_2	3.8	13.6
pH	7.4	8.4
Alkalinity, mg/L as $CaCO_3$	84	170
Chloride	38	123

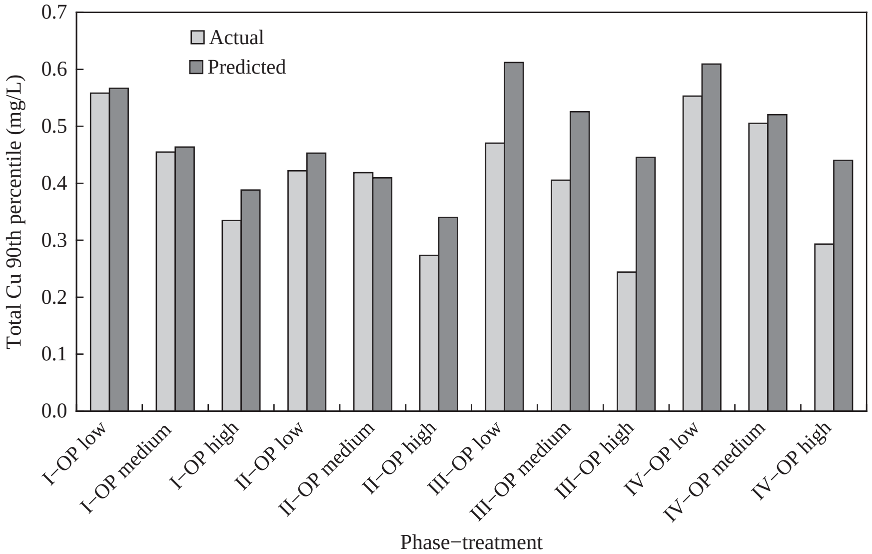

Fig. 3. Actual vs. predicted for empirical model by phase and PDS, 90th percentile.

performance of each corrosion control treatment can also be seen in Fig. 3. The highest dose of OP inhibitor has the lowest copper concentration followed by the medium and low doses, respectively. The elevated pH treatment at pH$_{s+0.3}$ is next followed by no treatment at pH$_s$ with the highest observed copper release. This agrees with the pH effect discussed previously.

For the data, but for the pH$_s$ PDS, the model under-predicts the copper concentration in some cases. With respect to the action level of 1.3 mg/L of total copper, the model describes the data below the action level better than above the action level. If exceeded, then the model under-predicts very high concentrations. Therefore, the model is useful as a predictor of copper release with OP inhibitor addition. All of the PDSs operating with OP inhibitor addition are maintained below the action level.

Fig. 3 shows the model predictions of the total copper release for each PDS by phase. The bars represent the 90th percentile total copper concentrations observed or predicted for comparison to the action level of 1.3 mg/L for the 90th percentile of samples. The trend of decreasing concentration with increasing inhibitor dose is well defined by the model. It is also shown that actual and predicted total copper concentration for all PDSs receiving the OP inhibitor were maintained below the action level of 1.3 mg/L.

3.3. *OP inhibitor performance*

Fig. 4 shows a summary of the copper release in each of the OP treated and pH control PDSs. As shown with the predictive model presented previously, Fig. 4 shows copper concentration to decrease with increasing dose of OP inhibitor. Also shown in Fig. 4 is the total copper concentration was consistently 80–90% in the dissolved form. These values are also shown graphically in Fig. 4 with the action level of 1.3 mg/L noted. The error bars represent the 90th percentile observations for the action level and the average values are displayed. Again it can be seen that no observation in the PDSs treated with OP inhibitor exceeded the action level. This figure also shows higher copper concentrations were observed in the pH$_s$ PDS than the pH$_{s+0.3}$ PDS.

The elevated pH treated PDS had observations exceeding the standard in all but Phase III, but the 90th percentile was only exceeded for Phase IV. However, the pH$_s$ PDS had observations exceeding the standard in every phase and exceeded at the 90th percentile in all but Phase I.

The average water quality observed in each PDS in each phase is presented in Table 3. The water quality parameters presented here are those that were significant in the empirical model presented previously. As seen with the model, the total phosphorus concentration has mitigating effects on copper release. Increased phosphorus concentration decreases copper concentration. Also consistent with the model, the elevated pH treatment consistently has lower copper concentrations than the PDS at pH$_s$. The additional phosphate in the OP PDSs reduced copper levels further than elevated pH treatment alone.

The effect of silica was shown to be beneficial for copper release in the empirical model presented previously. This was also observed and significant in the

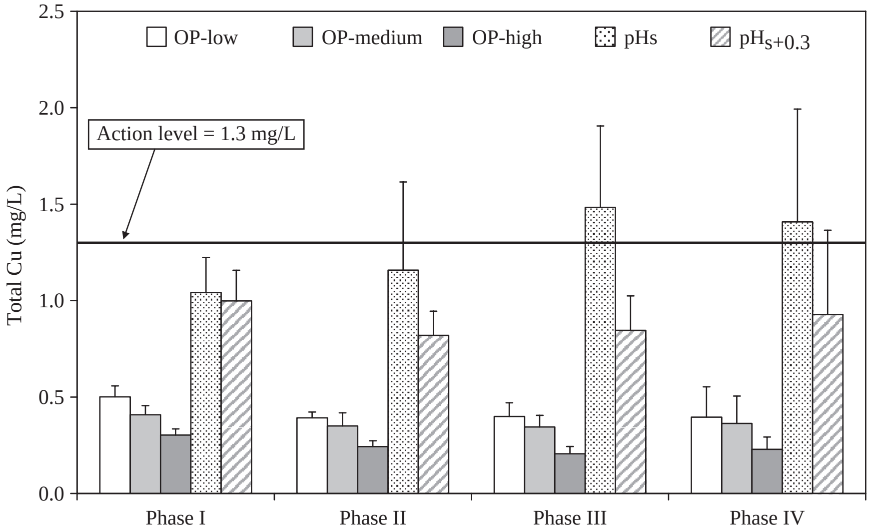

Fig. 4. Comparison of total Cu by phase and treatment.

empirical model developed in the previous study without inhibitor addition shown in Eq. (2) [1].

$$\begin{aligned} \mathrm{Cu} = 0.28 + \ & \mathrm{Temp}^{0.72} \times \mathrm{Alk}^{0.73} \times \mathrm{pH}^{-2.86} \\ & \times (\mathrm{SO}_4^{2-})^{0.10} \times \mathrm{SiO}_2^{-0.22} \end{aligned} \quad (2)$$

where Cu is the total copper concentration, mg/L; Temp is the temperature, °C; Alkalinity is the mg/L as $CaCO_3$; pH is the $-\log\,[H^+]$; and sulfate is the mg/L; silica is the mg/L as SiO_2.

The effects of silica tend to be confounded with the negative effects of alkalinity because of the high levels of each associated with the blends enriched with GW. The high alkalinity observed in Phase I tends to have a greater effect on the copper release than the high silica concentration seen in Phase I. This is seen in Table 3 with the higher copper concentrations observed during Phase I. Alkalinity was also high in Phase III due to the same blend as Phase I. However, copper concentrations in Phase III tended to be lower than Phase I. The lowest alkalinity was observed in Phase II with the lowest percentage of GW.

For the low OP dose PDS, Phase I copper release is significantly higher than the other phases. However, Phases II, III, and IV all experienced about the same copper release. This suggests the high alkalinity in Phase I was able to affect the copper release with a low dose of inhibitor, but the copper release was maintained to be very stable in other phases. Even in Phase I, the copper release did not exceed the action level for the low OP dose PDS.

The medium OP dose PDS also saw its highest copper release in Phase I, but not as significant. The copper release was lower for the medium dose than with the low dose and was better able to maintain a consistent copper concentration, regardless of water quality. Similar results were seen with the high OP dose PDS, except even lower copper release was maintained.

The control PDSs had higher concentrations than any of the OP treated PDSs and the PDS at pH_s was higher than the PDS at $pH_{s+0.3}$. The $pH_{s+0.3}$ PDS saw its the highest concentration in Phase I, like was seen with the OP PDSs. The pH_s PDS saw the opposite, with the lowest concentrations seen in Phase I. This is likely due to the lower pH and higher alkalinity observed in Phases III and IV compared with Phase I.

Overall, the copper release was still able to be maintained below the action level with the addition of OP inhibitor, even in the presence of high alkalinity and the slight depression of pH. The elevated pH treatment could not always mitigate the copper concentrations below the action level and in the presence of high alkalinity could lead to decreased carrying capacity of pipes due to calcium carbonate scale build up.

3.4. Surface characterization

Copper coupons were exposed to the OP corrosion inhibitor at the medium dose and the pH_s and $pH_{s+0.3}$ treatment for the duration of each phase. XPS analysis on each of the coupons was completed after incubation to determine the elements and their states that had formed on the surface of the coupon. A survey scan revealed the elements present.

A summary of the elements found on the coupons exposed to OP compared to the pH_s and $pH_{s+0.3}$ exposed coupons is presented in Table 4. Phosphorus

Table 3
Average influent water quality by PDS and phase

Treatment	Phase	Total phosphorus (mg/L as P)	Silica (mg/L as SiO_2)	pH (std. units)	Alkalinity (mg/L as $CaCO_3$)	(mg/L)
OP-low	I	0.49	10.8	8.0	164	43.2
	II	0.55	5.0	7.8	106	67.2
	III	0.54	10.4	8.0	152	63.6
	IV	0.47	6.3	7.8	125	56.6
	Average	0.51	8.2	7.9	143	54.7
OP-med	I	1.04	10.8	8.0	164	43.1
	II	0.90	4.9	7.8	107	67.4
	III	0.99	10.4	8.0	152	62.8
	IV	0.82	6.3	7.8	125	56.4
	Average	0.94	8.2	7.9	143	54.5
OP-high	I	1.84	10.7	8.0	163	43.2
	II	1.91	5.0	7.8	107	67.8
	III	1.87	10.4	7.9	151	65.0
	IV	1.69	6.2	7.8	125	57.9
	Average	1.83	8.2	7.9	142	55.4
pH_s	I	0.11	11.0	7.7	146	64.2
	II	0.03	4.9	7.8	92	82.8
	III	0.04	10.2	7.7	149	88.4
	IV	0.05	6.3	7.6	119	68.1
	Average	0.06	8.2	7.7	130	75.2
$pH_{s+0.3}$	I	0.16	10.8	8.0	164	43.2
	II	0.04	5.2	7.9	106	65.1
	III	0.04	10.5	8.0	151	64.8
	IV	0.06	6.3	7.9	125	57.9
	Average	0.08	8.3	7.9	139	57.2

was detected on three of the four coupons exposed to OP inhibitor. None of the coupons exposed to pH_s or $pH_{s+0.3}$ had phosphorus compounds, suggesting the only source of phosphate is from the inhibitor.

3.5. Thermodynamic modeling

Thermodynamic modeling was done to validate the copper controlling solid phase. As previously discussed, the controlling solid phase for all PDSs appears to be $Cu(OH)_2$ as found from XPS analysis. However, phosphate was present on the coupons exposed to the OP inhibitor. The equilibrium model, assuming copper (II) species developed for TBW I [1], was expanded for phosphate, sulfate, chloride, and ammonia complexes. The model is presented in Eq. (3). This model was used to calculate the total dissolved copper concentration based on the assumption of a controlling solid phase.

Table 4
Elements detected in XPS analysis

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

$$\begin{aligned} Cu_T = {} & [Cu^{2+}] + [CuOH^{+}] + [Cu(OH)_2^0] + [Cu(OH)_3^-] \\ & + [CuHCO_3^+] + \{CuCO_3^0] + [Cu(CO_3)^{2-}] \\ & + [Cu(OH)CO_3^-] + [Cu(OH)_2CO_3^{2-}] \\ & + [CuH_2PO_4^+] + [CuHPO_4^0] + [CuSO_4^0] \\ & + [CuNH_3^{2+}] + [Cu(NH_3)_2^{2+}] + [Cu(NH_3)_3^{2+}] \\ & + [Cu(NH_3)_4^{2+}] + [Cu(NH_3)_5^{2+}] + [CuCl^+] + [CuCl_2^0] \end{aligned} \tag{3}$$

The empirical model developed previously suggests chloride and alkalinity contribute to copper release, while pH and total phosphorus help to mitigate it. The equilibrium model presented here has species to account for changes in pH (OH), alkalinity (CO_3), phosphate (PO_4), sulfate (SO_4), chloramine disinfectant (NH_3), and chloride (Cl) observed in the system.

Table 5
Thermodynamic modeling calculations for OP PDSs

Phase	OP dose	Actual copper release (mg/L)		Modeled copper release (mg/L)			
		Diss Cu	Total Cu	$Cu(OH)_2$	CuO	$Cu_3(PO_4)_2{\cdot}2H_2O$	$Cu_3(PO_4)_2$
I	Low	0.46	0.50	0.51	0.07	0.90	3.96
	Medium	0.38	0.41	0.54	0.08	0.53	2.34
	High	0.26	0.30	0.58	0.09	0.35	1.54
II	Low	0.33	0.39	1.07	0.06	0.62	2.65
	Medium	0.28	0.35	1.15	0.06	0.47	1.99
	High	0.21	0.24	1.40	0.07	0.27	1.16
III	Low	0.36	0.40	1.05	0.06	1.03	4.42
	Medium	0.29	0.35	1.07	0.06	0.68	2.93
	High	0.19	0.21	1.23	0.07	0.44	1.87
IV	Low	0.34	0.40	0.59	0.08	0.64	2.78
	Medium	0.32	0.36	0.61	0.09	0.43	1.86
	High	0.21	0.23	0.68	0.10	0.26	1.14
Average	Low	0.38	0.42	0.74	0.07	0.80	3.48
	Medium	0.32	0.37	0.78	0.07	0.53	2.30
	High	0.21	0.25	0.88	0.08	0.33	1.43

$Cu(OH)_2$ has been identified as a metastable intermediate that forms in young copper pipe, and has been used as the basis for thermodynamic models of copper [5,14]. Cupric hydroxide can age to its dehydrated form, tenorite, CuO, which is less soluble. In the presence of alkalinity, old copper pipe tends to form the more stable, less soluble cupric hydroxycarbonate $Cu_2(OH)_2CO_3$, malachite (5).

For the OP inhibitor PDSs, equilibrium calculations considered cupric hydroxide ($Cu(OH)_2$), tenorite (CuO), cupric phosphate dihydride ($Cu_3(PO_4)_2{\cdot}2H_2O$), and cupric phosphate ($Cu_3(PO_4)_2$) as the controlling solid phase and are presented in Table 5. These compounds are considered because cupric hydroxide and tenorite were the most predominant scales found on the coupon. Additionally, thermodynamic data was available for cupric phosphate dryhydride and cupric phosphate to account for the addition of OP inhibitor corresponding to the reduction in copper release compared with the pH control PDSs.

It can be seen that cupric hydroxide and cupric phosphate dihydride over-predict the dissolved copper concentration observed in the PDSs. If the equilibrium constant for cupric hydroxide were elevated to match the observed copper release in the $pH_{s+0.3}$ PDS, then the cupric phosphate dihydride model would explain the decrease in copper release with OP inhibitor addition. This trend of decreasing copper with increasing OP dose can be seen in Table 5.

$Cu_3(PO_4)_2{\cdot}2H_2O$ models provided the best prediction of copper release, over predicting by no more than about 0.3 mg/L Cu. The CuO model consistently underpredicted copper release by about 0.25 mg/L Cu. In contrast, the values predicted by a cupric phosphate dihydride, $Cu_3(PO_4)_2{\cdot}2H_2O$ would be a closer match to the data. A review of the literature confirmed the lack of information identifying the form of copper OP solids in water distribution systems. However, the forms $Cu_3(PO_4)_2{\cdot}2H_2O$ and $Cu_3(PO_4)_2$, were modeled since thermodynamic data was available for these copper forms [5].

3.6. Copper coupons

Copper coupons were left to incubate for 14 months after removal from the PDSs in 100 mL of distribution system water. These coupons were from Phase III of operations and shown in Fig. 5. As seen in the picture, a blue-green scale formed on the copper exposed to the medium and high dose OP inhibitor, but not on the $pH_{s+0.3}$ control PDS coupon. The pH_s coupon similarly

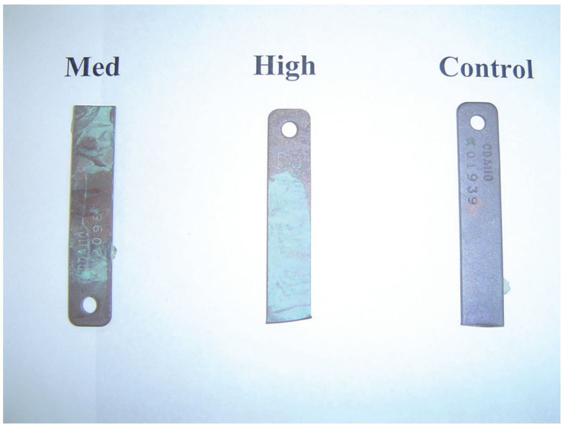

Fig. 5. Scale on coupons incubating for 14 months.

showed no blue green scale. The scale also appears to be thicker on the high dosed coupon.

The dissolved copper concentration was measured in the water these coupons had been incubating in. Measurements showed the low, medium, and high dosed coupons to have dissolved copper concentrations of 0.41, 0.26, and 0.23 mg/L, respectively. These still show decreasing concentration with increasing dose as was observed over the course of the study and were also lower than the controls. The coupon exposed to pH_s had a dissolved copper concentration of 0.76 mg/L and the coupons exposed to $pH_{s+0.3}$ had a concentration of 0.74 mg/L. The OP treated coupons had similar concentrations to those observed during the study and have had time to reach near equilibrium. This suggests the controlling solid for the OP treated coupons is different from the controlling solid that forms when inhibitor is not present.

4. Conclusions

- Empirical modeling of water quality resulted in a model with an R^2 of 0.71. The model showed total phosphorus, silica, and pH to reduce copper release while alkalinity and chloride increase copper release. This suggests addition of OP inhibitor will reduce copper release, as will elevating pH. However, elevating pH could cause scaling problems in the distribution system.
- Addition of OP inhibitor reduced copper release and maintained levels below the action level at the doses evaluated, regardless of blend. This was improvement over pH elevation alone because copper remained low, even in the presence of high alkalinity, compared to the operation at pH_s.
- XPS analysis showed phosphorus forms were detected on the copper coupons exposed to OP inhibitor that were not detected in either of the pH_s or $pH_{s+0.3}$ treatments.
- Thermodynamic modeling suggested $Cu_3(PO_4)_2 \cdot 2H_2O$ as a controlling solid phase and followed the trend of dissolved copper release decreasing with increasing dose. Also, visual inspection of equilibrated coupons showed different scale formation for the OP treated coupons than the pH control coupons, suggesting a different controlling solid for copper surfaces exposed to OP inhibitor.

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