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Impact of water quality on chlorine demand of corroding copper

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ABSTRACT

Copper is widely used in drinking water premise plumbing system materials. In buildings such as hospitals, large and complicated plumbing networks make it difficult to maintain good water quality. Sustaining safe disinfectant residuals throughout a building to protect against waterborne pathogens such as Legionella is particularly challenging since copper and other reactive distribution system materials can exert considerable demands. The objective of this work was to evaluate the impact of pH and orthophosphate on the consumption of free chlorine associated with corroding copper pipes over time. A copper test-loop pilot system was used to control test conditions and systematically meet the study objectives. Chlorine consumption trends attributed to abiotic reactions with copper over time were different for each pH condition tested, and the total amount of chlorine consumed over the test runs increased with increasing pH. Orthophosphate eliminated chlorine consumption trends with elapsed time (i.e., chlorine demand was consistent across entire test runs). Orthophosphate also greatly reduced the total amount of chlorine consumed over the test runs. Interestingly, the total amount of chlorine consumed and the consumption rate were not pH dependent when orthophosphate was present. The findings reflect the complex and competing reactions at the copper pipe wall including corrosion, oxidation of Cu(I) minerals and ions, and possible oxidation of Cu(II) minerals, and the change in chlorine species all as a function of pH. The work has practical applications for maintaining chlorine residuals in premise plumbing drinking water systems including large buildings such as hospitals.

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1. Introduction

Copper is the most widely used material in premise plumbing drinking water systems. Copper, however, is subject to problems including corrosion-related issues such as excessive copper leaching (leading to elevated levels in the water) (Grace et al., 2012; Turek et al., 2011; Schock, Lytle and Clement, 1995a), "blue" water (Boulay and Edwards 2011) and pinhole leaks (Lytle and White, 2014; Lytle and Schock, 2008; Sarver et al., 2011). Copper levels at the tap are regulated under the United States Environmental Protection Agency's (EPA's) Lead and Copper Rule (Federal Register, 1992; Federal Register 1991a; Federal Register, 1991b) at an action level of 1.3 mg/L, and as a result, many drinking water utilities practice corrosion control (e.g., phosphate addition, pH adjustment). In drinking water premise plumbing systems, oxygen and disinfectants used to destroy microorganisms and control biofilms

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http://dx.doi.org/10.1016/j.watres.2016.01.032 0043-1354/Published by Elsevier Ltd. in drinking water such as free chlorine, monochloramine and chlorine-dioxide, decay as they interact with bulk water constituents, drive copper corrosion and react with other materials on the pipe wall including biofilm. The corrosion of copper and associated consumption of disinfectants is of great interest in building water supplies, particularly in hospitals and nursing care facilities where sensitive populations reside. In particular, biofilm propagation and the harboring of pathogens including *Legionella* and *Mycobacterium* in premise building plumbing has gained a great deal of recent negative attention and concern. The greatest barrier against exposure to pathogenic microorganisms beyond the drinking water treatment facility is disinfection.

The challenge in large premise plumbing systems is to provide good drinking water quality, both biologically and chemically. This includes maintaining protective disinfectant residuals particularly when copper is the plumbing material of choice. Building plumbing networks can be complicated and extensive, include storage and hot water recirculation loops, serve sensitive populations (e.g., hospitals, schools, nursing homes, etc.) and may not require or







practice drinking water quality monitoring, all of which add to the challenge. Some building operators choose to add corrosion inhibitors such as orthophosphate to reduce corrosivity and metal levels, and others boost disinfection to address internal plumbing demands and minimize biological pathogen exposure risks. Another option building operators choose is to add point-of-use (POU) treatment devices to protect and/or improve tap water quality.

Given the important connection between copper corrosion, disinfectant residual and public health in premise plumbing systems, there is a need to better understand the role of water quality on the disinfectant demand associated with corroding copper and copper release. The objective of this work was to evaluate the impact of water quality (pH and orthophosphate) and copper pipe surface age on the demand of free chlorine associated with corroding copper. Furthermore, the impact of pH, orthophosphate and free chlorine on copper release was evaluated. The results provide useful insight on strategies to better maintain free chlorine residual in premise plumbing, including large buildings such as hospitals.

1.1. Background

In drinking water distribution systems, there are several pathways that result in the loss of oxidants, including oxygen (O₂), and disinfectants such as free chlorine (Cl₂), monochloramine (NH₂Cl) and chlorine-dioxide (ClO₂). At the surface of premise plumbing pipe walls, sources of oxidant demand include metal corrosion, solid metal oxides, metal ions, biofilm and natural organic material.

In copper premise plumbing, copper surfaces can go through electron transfer reactions. Copper metal (Cu⁰) is readily oxidized in contact with most drinking waters. Copper may exist in water as either the monovalent copper (I) (cuprous) or divalent copper (II) (cupric) valence states. The copper(III) and copper(IV) valence states are known to exist, however, they occur at high temperatures and usually in the presence of high oxygen concentrations (Cotton and Wilkinson, 1988), and are not expected in drinking water. In potable waters, copper metal may undergo the following two electrochemical reactions:

$$Cu(s) \leftrightarrow Cu^+ + e^- \tag{1}$$

$$Cu^+ \leftrightarrow Cu^{2+} + e^- \tag{2}$$

Because of the positive cell potentials for copper metal oxidation, copper pipe in water containing dissolved oxygen will continue to corrode until all of the oxygen is depleted, or until precipitated oxide films arrest the rate of corrosion (Obrecht et al., 1972). There is some evidence that the overall transformation from Cu^+ to Cu^{2+} is essentially the rate-limiting factor, with Cu^+ existing essentially in reversible equilibrium with the Cu metal at the pipe surface (Mattsson, 1980).

In drinking water, oxidizing agents (electron acceptors) that will cause the corrosion of metallic copper are predominantly dissolved oxygen and aqueous chlorine species (Cruse and von Franqué, 1985; Atlas et al., 1982; Reiber, 1989), or other disinfectants such as monochloramine and chlorine. The following equations are possible net reactions for the corrosion of copper in drinking waters, and may be composed of several intermediate steps, any of which can be rate-controlling (Stumm and Champlin, 1967):

$$HOCl^{o} + H^{+} + Cu(s) \leftrightarrow Cu^{2+} + Cl^{-} + H_2O$$
 (3)

$$OCl^{-} + 2H^{+} + Cu(s) \leftrightarrow Cu^{2+} + Cl^{-} + H_2O$$
 (4)

$$Cu(s) + 12O_2 + 2H^+ \leftrightarrow Cu^{2+} + H_2O$$
(5)

The overall driving force of corrosion potential for any of equation (3) through (5) may be computed through the Nernst equation (Snoeyink and Jenkins, 1980; Stumm and Morgan, 1981; de Zoubov et al., 1974; Schock, 1990; Pankow, 1991).

Many papers and texts have documented the impact of dissolved oxygen on copper oxidation and dissolution rates. Several studies have also proven aqueous chlorine species have a significant impact on the copper oxidation and corrosion rates (Atlas et al., 1982; Reiber, 1989; Suzuki et al., 1983; Reiber et al., 1987; Pisigan and Singley, 1987). Free chlorine species (i.e., HOCl°, OCl⁻ and Cl2) have not been conclusively shown to affect the equilibrium solubility of copper other than by influencing the valence state of the copper by its presence or absence. Oxidants may have several other potential impacts on the observed copper levels in the water and the nature of the passivating solids on the pipe. The effect of chlorine on the oxidation rate of the copper metal might be the alteration of the crystalline characteristics and porosity of the oxide corrosion product film produced at the pipe surface by 1) reducing the formation of a protective Cu2O(s) underlayer by producing a high EH level, or 2) indirectly influencing scale structure and conductivity through chloride formation as the chlorine is reduced (Adeloju and Hughes, 1986). However, many of the apparent effects of chlorine on copper solubility may merely result from accelerated corrosion kinetics (rates), rather than changes in equilibrium conditions. That is, the rate of copper oxidation and transport into a solution may be accelerated by the oxidants, and thus misinterpreted as representing a greater equilibrium solubility.

1.2. Impact of pH on copper release

In oxic and disinfected drinking waters, Cu²⁺ mineralogy and chemistry largely control copper release into the water. A great deal of work has been conducted on the effect of water chemistry on the corrosion of copper and solubility of copper minerals. Cu(II) solubility in tap water is most significantly affected by pH. Excessive copper release in low pH water is sometimes attributed to corrosion by dissolved CO₂, or "carbonic acid," though the mechanism for elevated copper concentrations is due to an increase in soluble Cu(II) complexes and ions. Increase in the pH of water generally decreases the release of soluble copper. The adjustment of pH is a common and well understood treatment approach to reduce Cu(II) levels at the tap (Ferguson et al., 1996; Schocket al., 1995a; Schock et al., 1995b). While it is recognized that sufficient dissolved inorganic concentration (DIC) is important, high levels of DIC may increase Cu(II) solubility (Schock et al., 1995a). Recent work has concluded that, under certain conditions, the adverse effects of bicarbonate outweigh its overall usefulness in preventing cuprosolvency. For example, DIC complexes in new plumbing have been found to dominate copper speciation above a pH of 6.5, resulting in increased Cu(II) solubility. Concentrations of Cu(II) by-products in drinking water increase linearly with bicarbonate concentration at a constant pH. The same is true when the pH of the water is high, and either cupric hydroxide or cupric oxide controls the Cu(II) solubility.

At lower pH values, adding orthophosphate decreases Cu(II) solubility. However, at high pH and over long periods of time, orthophosphate could stabilize higher levels of copper than would naturally occur (Schock and Sandvig, 2009; Schock et al., 1995a). These possible effects should be considered when attempting to reduce the release of copper corrosion by-products from consumer

plumbing. Conversely, Werner et al., 1994 reported that higher copper levels are produced by the presence of orthophosphate when the overall pH is 7.2 and the DIC levels are high (where the formation of malachite would be more likely). Although the proper dosage of orthophosphate necessary to reduce copper levels is hard to quantify, orthophosphate is predicted to have the greatest impact toward further reducing copper levels in new plumbing in the pH range of approximately 6.5–7 (Schock et al., 1995a).

1.3. Impact of orthophosphate on copper release

Orthophosphate tends to slow the oxidation rate of copper metal and Cu₂O, and inhibit its transformation into cupric oxide and malachite through the formation of a thin surface film. Orthophosphate might play a role in copper corrosion by causing an alteration of the nature or growth rate of passivating films, or the kinetics of oxidation/reduction reactions at the copper pipe surface. For example, visual and X-Ray diffractions of copper pipe surfaces exposed to water with DIC of 5 mg C/L at pH 7, 8 and 9 in ongoing EPA studies indicate substantial differences in appearance and mineralogy with and without the presence of 3 mg PO₄/L orthophosphate. Pipe specimens from the systems having the orthophosphate were almost free of crystalline Cu(II) solids. Those experimental systems, as well as identical ones for 10 mg C/L, also indicate a drastic reduction in the rate of free chlorine residual depletion in the presence of 3 mg PO_4/L orthophosphate, especially below pH 8. This implies that orthophosphate also plays a critical role somewhere in the oxidation process of copper metal to cupric ion. A German study has reported 3 mg PO₄/L orthophosphate at pH 7.2 and DIC of about 75 mg C/L allows higher copper levels upon stagnation in aged (426-512 days) pipe than without orthophosphate (AWWARF, 1994; Drogowska et al., 1992), which also indicates that orthophosphate may interfere with the normal corrosion scale oxidation and aging processes. Under some chemical conditions, orthophosphate could preserve higher copper levels that might otherwise be reduced when a stable malachite film formed.

1.4. Impact of copper on disinfectant demand

Copper has been indirectly associated with drinking water disinfection demand through the catalysis of the oxidation of natural organic material (NOM) and the formation of resulting regulated drinking water disinfection by-products (DBPs). For example, copper catalysis of free chlorine and monochloramine degredation, and trihalomethane (THM) formation has been reported (Blatchley et al., 2003; Fu et al., 2009; Li et al., 2007). Chlorine degradation and haloacetic acids (HAAs) formation in the presence of copper corrosion by-products including Cu(II), cuprite (Cu₂O), tenorite (CuO) and malachite [Cu₂(OH)₂CO₃] have been reported (Zhang and Andrews, 2012). Chlorine decay and HAA formation were enhanced in the presence of copper. Copper catalysis was impacted by pH and copper concentration. Enhanced chlorine decay was attributed to increased reactivity of dissolved and surface associated Cu(II)-NOM complexes. Liu et al. (2013) showed that the oxidation of bromide by chlorine to bromate, a drinking water DBP, in water was accelerated by CuO by enhancing the decay of hypobromous acid, an intermediate in the oxidation process. Phosphate inhibited bromate formation while sulfate and bicarbonate only slightly inhibited bromate formation. Chlorine dioxide decay associated with oxidation of CuO₂ by a one-electron mechanism following first order decay kinetics has been reported (Zhang et al., 2008). Liu et al. (2013) showed that Cu₂O enhanced the decay of chlorine-dioxide (ClO₂) through the oxidation of Cu(I) to Cu(II). They also reported that CuO catalyzed ClO₂ disproportionation and NOM enhanced the reaction. Chlorine-dioxide loss resulted in chorite/chlorate formation (undesirable inorganic byproducts). Nguyen et al. (2011) reported on the rapid consumption of free chlorine through the direct reaction with Cu(II)-hydroxide [Cu(OH)₂] leading to enhanced aging of CuO. The authors suggested that the reaction involved the formation of a Cu(III) intermediate with silica, orthophosphate and pH affecting the reaction rate.

A number of potential pathways exist that can account for the consumption of oxidants, including free chlorine, at the surface of a copper pipe. These include the oxidation of copper metal, oxidation of Cu(I) minerals or ions, and reactions with Cu(II) minerals such as Cu(OH)₂ and CuO. The reaction rates are likely to be different for each case and will be impacted by water quality parameters including pH, orthophosphate and TOC differently. This adds complexity to interpreting chlorine consumption trends with time and in different waters.

2. Materials and methods

A recirculating copper pipe test loop system was designed and constructed to study the impact of water chemistry on copper corrosion and solubility, and oxidant consumption. Three parallel test loops each consisting of a 10 L polyacrylic covered water reservoir plumbed to two parallel copper pipe test sections in a recirculation configuration were used (Fig. 1). Water sampling ports were located just after the reservoir outlet and at the end of each copper section. Water reservoirs were covered to minimize water interaction with the atmosphere. The cover had three ports for a pH probe and chemical feed lines. Each loop recirculated a total of 12 L (reservoir plus recirculation plumbing) of water using orbital magnetic drive pumps (March Model AC-3CP-MD) at a rate of 8 L/ min. Tygon[®] tubing connected the reservoirs to two, 2 ft long, ½ in diameter type M sections and one- 1 ft long copper pipe longitudinally cut section enclosed in clear Tygon[®] tubing to visually observe surface changes. Approximately 2 ft of the tubing was submerged in a refrigerated water bath (Neslab RTE-221) to counter the rise of temperature associated with pump heating and to maintain the temperature at 19 °C \pm 1 °C.

Schott Blueline 11 (Schott Geräte, Germany) pH probes were used to measure the pH of the reservoir water and were connected to an 8-port pH sensor interface (SensoLab, Jensen Systems). The inline pH probes were calibrated daily with a two point calibration curve in buffer standards at pH 7 and 10. If the calibration slope was



Fig. 1. Copper recirculating loop experimental set up.

less than 95%, a portable pH electrode and meter were used to measure and adjust pH manually until the in-line pH electrode performance issue was resolved or replaced. A HACH pH/dissolved oxygen (DO) (Loveland, CO) meter was used for external and manual pH measurements and it was calibrated daily as needed. Multi-T 2.2^{TM} software (Jensen Systems) was used to monitor and maintain the pH of reservoir waters to ± 0.15 units. Two automatic titrators (Schott Titronic Universal Model), one for acid injection and one for base injection, connected to the Jensen Systems controller were used to maintain the pH with 0.6 N hydrochloric acid and sodium hydroxide.

Test water was initially created by adding appropriate amounts of analytical grade sodium bicarbonate (NaHCO₃), sodium chloride (NaCl), sodium sulfate (Na₂SO₄), and sodium phosphate (Na₂PO₄·12H₂O) (Fisher Scientific, Fairlawn, NJ) to 11 L double deionized (DDI) water to target concentrations of 10 mg C/L, 100 mg Cl⁻/L, 100 mg SO₄/L, and 3 mg PO₄/L when designated. Double deionized (DDI) water was prepared by passing building demineralized water through a Milli-Q Plus cartridge deionized water system (Millipore Corp., Bedford, MA), having a resistivity g18.2M Ω cm. Free chlorine was added as sodium hypochlorite (4-6% NaOCl, purified grade) (Fisher Scientific, Fairlawn, NJ) solution to an initial target concentration of 2 mg Cl₂/L. The pH was adjusted and maintained at the test target value by the computer controlled titration system as previously described. Test water quality parameters were within drinking water ranges and regulatory limits.

Test water was drained and replaced three times a week (Monday, Wednesday and Friday). A small volume of water was left closed in the pipe sections to avoid contact with the air. After the test water was prepared, initial water samples were collected and analyzed for metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES) according to EPA method 200.7 (USEPA, 1994). Water samples for metal analyses were preserved with ultrapure nitric acid (0.15% v/v) (J.T. Baker Chemical Company, Phillipsburg, NJ) upon collection. Initial water samples were also collected for chloride, phosphate, and either total alkalinity or total inorganic carbon analysis. Chloride analyses were performed using APHA method 4500-Cl D (APHA, 1992). Orthophosphate analyses were performed using colorimetric spectroscopy according to EPA method 365.1 (USEPA, 1993). Total alkalinity analyses were performed using APHA method 2320 b.4.6 (APHA, 1992) and total inorganic carbon analyses were performed using American Society for Testing and Materials (ASTM) method D-513-92 (ASTM, 1994). Lastly, temperature, free chlorine and pH were measured and recorded. Free chlorine was measured using the DPD method (adapted from APHA method 4500-Cl G) with a HACH DR/2700 spectrophotometer (Loveland, CO). The detection limit for free chlorine was defined as 0.05 mg Cl₂/L based on variability in blank (DI water) controls.

Test water was sampled from the reservoirs after recirculating for 24 and 48 h on Tuesdays and Fridays, and 72 h on Mondays, and was submitted for the same water chemistry analysis as the initial water. After the 48 and 72 h samples were taken, the recirculating water was drained from the tanks and replaced with new initial water. A small volume of water was left in the copper loop section by closing valves at both ends of the loops to avoid exposure to air. Free chlorine levels were measured after recirculating for 6, 18 and 66 h, and then readjusted back to 2 mg Cl₂/L immediately after each sampling. Chlorine demand associated with bulk water reactions and losses to materials in the pipe loop test apparatus other than copper (e.g., tubing, valves, etc.) was determined and found to be very small relative to losses in the presence of copper pipe sections. Recirculation, sampling and water quality adjustment times were chosen in part out of convenience. Sampling and water quality adjustment were very labor intensive and the times selected were manageable. The recirculating time was also estimated to be long enough to achieve copper solubility equilibrium.

Data was managed in a Microsoft Excel spreadsheet and plotted using SigmaPlot®11 (Systat Software Inc., San Jose, CA) statistical software. Statistical analysis was used to determine whether copper release and chlorine consumption trends were different. Data normality was determined by the Shapiro–Wilk Test. In nearly all cases, data sets failed the normality test (at 95% confidence). When the data set was normal, the Kruskal–Wallis One Way Analysis of Variance (ANOVA) on Ranks was used to compare data trends. The Student-Newman-Keuls method and the Dunn's method were used to make multiple comparisons between data sets when not normal. The Student-Newman-Keuls test was used when group sizes were are equal and Dunn's test is used when group sizes were not equal. All statistical comparison tests were made at 95% confidence (P = 0.05). All statistical calculations were made using SigmaPlotTM (version 13 0.0) (SPSS Inc., Chicago, IL).

After approximately six months, the test system was drained and shut down. The copper pipes were removed and solids analysis on the internal pipe surfaces was performed. Corrosion by-product samples were taken by cutting sections with a band saw to desired sizes that fit into the instruments, or by directly scraping the copper pipes. Pipe sections were prepared for scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. For SEM, a JEOL-6490LV with an Oxford X-Act EDS system was used for imaging and elemental analysis. Images and EDS spectra were captured using an accelerating voltage of 15-30 kV. Spectra were collected for 50 live seconds using a process time of 5 percent, and a 30 to 50 percent dead-time. PANalytical Xpert Pro theta-two theta diffractometer using a Cu K α radiation at 45 kV and 40 mA was used for XRD analysis. Scans were typically over the range of 5–90 °C. Pattern analysis was performed using the Jade + software v.7 or later (MDI, Inc., Livermore, CA, USA), which generally followed the ASTM D934-80 procedure. Reference patterns were from 2002 PDF-2 released from the International Center for Diffraction Data (ICDD, Newtown Square, PA, USA). Digital images were taken of the 1 ft half sections of copper pipe after the pipes were removed from the Tygon plastic tube with a Nikon 8400 digital camera. Digital images were also taken of the pipes with a Keyence VHX-600 digital microscope.

3. Results

3.1. General water chemistry

Table 1 summarizes the measured water quality of "initial" (newly prepared or adjusted water) and "final" (after recirculated before adjustment or change-out) during the test runs. In nearly all test runs, final pH values were within 0.1 pH of the target value and standard deviations were less than 0.07 pH units. The pH of runs used to evaluate the impact of orthophosphate on chlorine demand and, when a test run was repeated, the pH values were nearly identical. Copper corrosion and solubility are largely impacted by pH so having tight control of the pH, as was the case in this work, is critical in accurately drawing conclusions from the data. Final water temperatures were also very similar and average measurements over the entire test runs ranged between 19.1 and 19.9 °C. Average initial free chlorine and DIC levels were also very tightly controlled and very near to the target values in all test runs. Average free chlorine and DIC concentrations ranged between 2.06 and 2.13 mg Cl₂/L, and 10.0 and 10.8 mg C/L, respectively. Initial chloride concentration averaged between 106 and 122 mg/L, and average final chloride levels ranged between 117 and 159 mg/L. Increases in chloride concentrations were attributed to hydrochloric acid

Table	1
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General water chemistry measurements over the project runs (target free chlorine concentration 2 mg/L, dissolved inorganic carbon 10 mg C/L, chloride 100 mg/L, sulfate 100 mg/L and phosphate 3 mg PO₄/L when applicable) (average \pm deviation standard).

Target pH pH		Temperature, °C	Free chlorine, mg Cl ₂ /L	Dissolved inorganic carbon, mg C/L	Chloride mg Cl ⁻ /l	, 	Sodium,	mg Na/L	Sulfate, m	ng SO ₄ /L	Phosphate, 1	mg PO ₄ /L	
	Initial	Final	Final	Initial	Initial	Initial	Final	Initial	Final	Initial	Final	Initial	Final
7.2	7.05 ± 0.06	7.13 ± 0.03	19.9 ± 1.08	2.11 ± 0.18	$10.0^{a} \pm 0.67$	121 ± 9	159 ± 16	138 ± 5	154 ± 12	103 ± 4	102 ± 4	<0.015	<0.015
7.2	7.08 ± 0.07	7.14 ± 0.06	19.1 ± 1.09	2.13 ± 0.15	$10.2^{a} \pm 0.42$	122 ± 6	146 ± 12	141 ± 6	147 ± 6	104 ± 5	104 ± 4	2.99 ± 0.27	3.00 ± 0.19
8.2	8.01 ± 0.18	8.06 ± 0.04	19.4 ± 1.03	2.13 ± 0.17	$10.7^{a} \pm 0.52$	112 ± 6	135 ± 16	141 ± 8	152 ± 12	105 ± 13	105 ± 6	< 0.015	< 0.015
8.2	8.06 ± 0.07	8.09 ± 0.05	19.8 ± 0.75	2.06 ± 0.08	10.6 ^a ± 3.39	106 ± 6	117 ± 17	134 ± 7	139 ± 7	105 ± 12	101 ± 13	< 0.015	<0.015
8.5	8.69 ± 0.05	8.60 ± 0.07	19.1 ± 1.38	2.10 ± 0.17	10.8 ± 0.24	111 ± 1	127 ± 4	139 ± 4	152 ± 6	105 ± 3	104 ± 3	< 0.015	<0.015
9.2	9.18 ± 0.05	9.16 ± 0.05	19.6 ± 1.11	2.11 ± 0.18	10.7 ± 0.24	108 ± 1	122 ± 7	138 ± 3	150 ± 5	103 ± 3	102 ± 3	< 0.015	<0.015
9.2	9.17 ± 0.04	9.17 ± 0.05	19.2 ± 1.32	2.10 ± 0.23	10.8 ± 0.26	108 ± 2	120 ± 5	140 ± 4	151 ± 5	103 ± 3	102 ± 13	2.40 ± 0.33	2.44 ± 0.35

^a Dissolved inorganic concentration was calculated from measured total alkalinity and pH.

addition to maintain the desired pH values. Increase in chloride concentration was greatest during the pH 7.2 runs where the natural drift to higher pH related to CO_2 exchange with the atmosphere was greatest. Sulfate concentrations were similar amongst test

runs, unchanged between initial and final test waters, and close to the target concentration. Average sulfate levels of initial and final waters were 101 and 105 mg SO₄/L, respectively.



Fig. 2. Copper release measured over elapsed time during test runs performed at pH (a) 7.2, (b) 8.2, (c) 8.5, and (d) 9.2 at 24, 48, and 72 h sampling periods.



Fig. 3. Effect of pH on copper release over elapsed time at 24 h.

3.2. Copper release

The impact of elapsed time, recirculation time (24, 48 and 72 h) and pH on copper levels was evaluated (Fig. 2). At pH 7.2, copper concentrations varied greatly particularly over the first 100 days of the test run (Fig. 2a). During this time period, copper concentrations ranged from 0.15 to 2 mg/L. Recirculation time did not have an impact on copper levels with the exception of the 24 and 72 h sample sets which were statistically different (P = 0.011) and wide variability was observed at all times. The degree of variability decreased with time and copper concentrations merged toward a narrower range of between approximately 1 and 1.5 mg/L from 100 days until the end of the run. There was a slight upward trend in

copper concentrations with elapsed time based on linear regression. At pH 8.2, copper levels were greatest (0.7 mg/L) at the beginning of the test run and gradually decreased with elapsed time over up to 110 days (Fig. 2b). Copper concentrations stabilized between 0.07 and 0.1 mg/L for the remainder of the test run. Recirculation time had no impact on copper concentrations at pH 8.2 indicating that copper solubility equilibrium was achieved before 24 h. The copper release trend at pH 8.5 was nearly parallel to that at pH 8.2 (Fig. 2c). Copper concentrations started the test run at the highest value of 0.3 mg/L after which copper concentration gradually decreased over the next 110 days of the test run. Copper levels stabilized around 0.03 mg/L by the end of the run and recirculation time had no impact on copper levels. Lastly, at pH 9.2, copper levels started out at the highest value of 0.2 mg/L in one of the initial sampling events of the test run and rapidly dropped within 14 days to a very low level (Fig. 2d). Copper levels remained around 0.02 mg/L over the entire study with the exception of several random copper spikes and recirculation time had no impact on copper concentration.

The impact of pH on copper concentration and elapsed time was more closely examined (Fig. 3 for 24 h samples). Copper concentrations decreased with elapsed time at all pH values with the exception of pH 7.2. The decrease in copper concentration with time or "aging" effect has been described by others (Schock et al., 1995a) as a reflection of transitions in copper mineralogy of solids on the copper pipe surface with time to achieve a thermodynamically favorable state and minimum solubility. The aging rate increased with increasing pH. At pH 7.2, the aging rate was very slow and 200 days did not appear to be long enough to see the aging effect. Secondly, copper levels decreased with increasing pH in a very predictable and well understood way according to Cu(II) solubility basic relationships.

The impact of orthophosphate on copper concentrations at pH 7.2 was dramatic (Figs. 2a and 4a). In the presence of 3 mg PO₄/L, copper concentration was approximately 0.5 mg/L at the beginning of the test run (Fig. 4a) which was very low relative to the test run where no chlorine was present (Fig. 2a). A gradual drop in copper concentration or aging period over the first 60 days of the test run was observed. Copper concentrations after 60 days did not change and remained low averaging 0.23 \pm 0.02 (standard deviation) mg/L



Fig. 4. Copper release, measured over elapsed time during test runs performed at pH (a) 7.2 with 3 mg PO₄/L, (b) 9.2 with 3 mg PO₄/L at 24, 48, and 72 h sampling periods.



Fig. 5. Free chlorine measured over elapsed time during test runs performed at pH (a) 7.2, (b) 8.2, (c) 8.5, and (d) 9.2 at initial, and 6, 18, and 66 h sampling periods.

over the last 50 days of the run. There was very little variability in copper levels over the entire test run and recirculation time did not have an impact on copper concentrations based on statistical comparisons. Orthophosphate reduced copper levels by over 1 mg/ L and variability at pH 7.2 (P \leq 0.001). Copper levels at pH 7.2 in the absence of orthophosphate averaged 1.38 ± 0.08 mg/L over the last 50 days of the run in comparison. At pH 9.2, the copper concentrations started low and did not change over the entire test run (i.e., no aging period was observed) (Fig. 4b). Copper concentrations ranged between 0.05 and 0.06 mg/L, and elapsed time and recirculation time had no impact on copper levels. Unlike pH 7.2, orthophosphate actually increased copper concentrations at pH 9.2 (Figs. 2d and 4b) ($P \le 0.001$). Over the last 50 days of the runs, copper in the presence of orthophosphate at pH 9.2 averaged 0.06 ± 0.03 mg/L as compared to 0.04 ± 0.03 mg/L in the absence of orthophosphate. The impact of orthophosphate on copper solubility and corrosion are also described by others (Schock et al., 1995a).

Orthophosphate provides a rapid reduction in copper concentration by essentially avoiding high copper levels attributable to cupric hydroxide solubility at the early stages of ageing. However, as aging progresses in the absence of orthophosphate, copper levels could eventually be lower than if orthophosphate was present such as the case at pH 9.2 (Fig. 4b).

3.3. Chlorine consumption

The impacts of elapsed time, recirculation time (6, 18 and 66 h) and pH on free chlorine levels were evaluated (Fig. 5). At pH 7.2, chlorine concentrations at all recirculation times were very low, presumably because of a rapid reaction rate with the fresh copper surfaces (Fig. 5a). After approximately 70 days, the 6 h water samples began to contain a measurable chlorine concentration and by 150 days, the 18 h samples contained a chlorine residual. In the case of both recirculation times, chlorine concentrations gradually

3.0

6hi

3.0

2 5 25 Free chlorine concentration, mg/I Free chlorine concentration, mg/ 1.0 1.0 0.5 0.5 0.0 0.0 50 100 150 200 50 150 200 100 Elapsed time, days Elapsed time, days

Fig. 6. Free chlorine measured over elapsed time during test runs performed at pH (a) 7.2 with 3 mg PO₄/L, (b) 9.2 with 3 mg PO₄/L at initial, and 6, 18, and 66 h sampling periods.

increased with elapsed time over the remainder of the study period. By the end of the run (206 days), 6 and 18 h chlorine residuals were approximately 1.2 and 0.5 mg Cl₂/L, respectively. Free chlorine was not detected in 66 h samples at any time during the test run. At pH 8.2, chlorine residuals of approximately 0.5 mg Cl₂/L were measured after 6 and 18 h of recirculation at the beginning of the test run. Chlorine concentrations actually rapidly increased to 1.6 mg Cl₂/L after only 15 days into the test run (Fig. 5b). Interestingly free chlorine residuals at the end of both recirculation times after 20 days dropped to nearly non-detectable levels by 100 and 50 elapsed days for 6 and 18 h samples, respectively. The chlorine concentrations remained at near the detection limit for the remainder of the study. The 66 h samples never had detectable levels of free chlorine over the entire study. Chlorine reaction profiles at pH 8.5 began at a relatively small demand for the 6 and 18 h recirculation times (Fig. 5c). The 6 h samples started the run at approximately 1.5 mg Cl_2/L and dropped to 0.2 mg Cl_2/L by 50 days. After 50 days, remaining chlorine residual increased gradually back up to 1.6 mg Cl_2/L by the end of the run at 174 days. The chlorine residual trend of the 18 h samples was parallel to the 6 h trend but chlorine residuals were lower. Chlorine residual started at 1 mg/L at the start-up then rapidly dropped to non-detectable over the first 20 days. After 110 days, chlorine residual was detected in the 18 h samples. Chlorine levels gradually increased in the 18 h samples over the remainder of the study up to 0.6 mg Cl₂/L by the termination of the run. The 66 h samples never had a detectable level of free chlorine over the entire study. Free chlorine residuals at pH 9.2 followed yet another unique trend (Fig. 5d). Chlorine residuals in the 6 and 18 h samples started very low at or near detection in the beginning of the run. Over the next 50–60 days, the chlorine levels sharply increased to approximately 1.5 and 1 mg/L for the 6 and 18 h samples, respectively. The chlorine residuals in the samples remained relatively consistent after 50 days to the end of the run at 174 days. The 66 h samples did not have detectable free chlorine levels for the first 120 days of the study. However, after 120 days chlorine residuals between 0.1 and 0.2 mg Cl₂/L were measured. This run was the only one to consistently detect measurable chlorine concentrations in the 66 h water sample.

The impact of orthophosphate on chlorine residuals after 6, 18 and 66 h of recirculation was striking (Figs. 5 and 6). At pH 7.2,

orthophosphate had almost an immediate impact of free chlorine residuals (Figs. 5a and 6a). From the start-up, chlorine residuals in the 6 and 18 h samples were high. Although there was some scatter in the data, chlorine residuals did not change over the course of the study. The chlorine residuals in 18 h samples were slightly lower than the 6 h samples. The averages (±standard deviation) (number of samples) of the initial, 6 and 18 h samples over the entire run were 2.13 \pm 0.15 (269), 1.62 \pm 0.27 (128) and 1.38 \pm 0.34 (109) mg Cl₂/L, respectively. In addition, chlorine residual was present in most of the 66 h samples, and most of the remaining residuals were greater than 0.5 mg/L. The chlorine residuals averaged 0.50 ± 0.30 (28) mg Cl₂/L over the entire run. At pH 9.2 with orthophosphate, the residual chlorine trends looked identical to the pH 7.2 trends (Figs. 5dc and 6b). There was not a trend in residual with time and chlorine residuals were high with 6 h samples being slightly higher than 18 h samples. The averages of the initial, 6 and 18 h samples over the entire run were 2.12 \pm 0.13 (240), 1.61 \pm 0.23 (118) and 1.25 ± 0.28 (98) mg Cl₂/L, respectively. Chlorine residuals were also present in the 66 h samples but not as high as at pH 7.2. Chlorine residuals in the 66 h samples never increased above 0.5 mg Cl₂/L. The chlorine residuals averaged 0.36 ± 0.41 (22) mg Cl₂/L over the entire run.

h

3.4. Cumulative copper and chlorine changes

Copper release and chlorine consumption trends were examined and compared alternatively by cumulatively summing the amount of copper release (mg Cu/L) and chlorine consumed (mg Cl₂/L) over the entire course of the respective runs (Fig. 7a and b). Some limitations in the analysis should be acknowledged. Copper levels typically reached equilibrium sometime before 24 h yet the recirculating time continued for 48 h during the week and 72 h over the weekend. The results might be different if the test water was changed out earlier (just before equilibrium is reached). Secondly, chlorine residuals were, in many cases, completely gone at the end of recirculation times and could have been gone for hours before the sample was collected. Nonetheless the comparisons and discussion are still important and relevant.

The total amount of copper released to the water at pH 7.2 after 206 days was 89.8 mg Cu/L (Fig. 7a) (or a total of 898 mg Cu).



Fig. 7. The impact of pH and orthophosphate on the cumulative concentration of (a) copper released and (b) chlorine consumed over the course of entire test runs.

Increase in cumulative copper release was rapid and nearly linear over the entire run. The normalized average copper release rate (linear slope) over the entire run was 4.4 mg Cu/day. Orthophosphate greatly decreased total copper release at pH 7.2. Total copper release at the end of the 206 day run was 20.9 mg Cu/L (209 mg Cu), or 78% lower. Copper release rate in the presence of orthophosphate went through two regions, one from 0 to 50 days where the slope was approximately 0.15 mg Cu/L per day, and from 50 days to the end of the runs where the release rate decreased to 0.08 mg Cu/L per day (Fig. 7a). On average, the normalized copper release rate was 1.0 mg Cu/day. Total copper release at pH 9.2 totaled to 2.34 mg Cu/L (23.4 mg Cu) which was 97% lower than at pH 7.2 (compared

after 174 days). The rate of copper release was linear and also very low at an average rate of 0.14 mg Cu/day which was 97% lower than at pH 7.2. As noted earlier, orthophosphate actually increased copper concentration in the water which translated to the total amount of copper released by 4.7 mg Cu/L (47 mg Cu) over the entire run which was nearly twice the amount without orthophosphate. Copper was released slowly at a rate of 0.27 mg Cu/day but was released at a greater rate (nearly double) than when orthophosphate was absent. Average copper release rates at pH 8.2 and 8.5 were 1.1 and 0.20 mg Cu/day, respectively (not shown). An increase in pH from 7.2 to 8.2 (1 pH unit) decreased copper release by 75% over the course of the study. Increasing the pH from 8.2 to 8.5 (only 0.3 pH units) had comparably a larger relative reduction in copper release rate of 82%. Increasing pH from 8.5 to 9.2 dropped average copper release rate by 30%.

Cumulative chlorine consumption rate at pH 7.2 was the greatest of all conditions (Fig. 7b) and a total loss of 499 mg Cl₂/L (4990 mg Cl₂) over the entire run (206 days). Chlorine loss was linear at a rate of approximately 2.8 mg Cl₂/L per day over the first 50 days. There was a slight decrease in rate of loss over the next 20 days which corresponded to the time period where the variability in copper concentrations decreased. Between 70 and 150 days, the chlorine consumption rate resumed to the same rate as at the beginning of the run. The rate appeared to gradually decrease over the time period leading up to the end of the run. Total chlorine depletion rate on average was 24.2 mg Cl₂/day which was 44% times higher than at pH 9.2 (compared at 173 days). The chlorine consumption rate at pH 9.2 was nearly identical to the pH 7.2 case over the first 30 days of the run. The chlorine release rate went through two linear regions. Between 0 and 30 days, chlorine was consumed linearly at a rate of 2.6 mg Cl₂/L per day. There was a transition period between 30 and 50 days. The rate slowed to 1.3 mg Cl_2/L per day after 50 days. Overall, a total loss of 278 mg $Cl_2/$ L (2780 mg Cl₂) over the entire run (174 days) at pH 9.2 was measured which was about 45% less than at pH 7.2 over the same time period (Fig. 7b). On average, 16.0 mg Cl_2/day was consumed or 33% less than at pH 7.2. Orthophosphate dramatically reduced the chlorine consumption rate at both pH values tested by 61% and 33% at pH 7.2 and 9.2, respectively. Interestingly, the chlorine consumption rates were independent of pH and both trends were nearly identical. They increased linearly at a rate of 0.94 mg Cl₂/L per day and 1.1 mg Cl₂/L per day at pH 7.2 and 9. Averaged over the entire study period, a total value of 9.59 and 10.6 mg Cl₂/day, at pH 7.2 and 9.2, respectively, were measured.

3.5. Copper pipe surface analysis

Pipe sections were removed after each test run and the surfaces were examined visually and by X-ray diffraction (XRD). It should be noted that XRD analysis was limited to identifying only crystalline solids and was not quantitative. The impact of pH on the surface is apparent from visual inspection (Table 2). In the absence of orthophosphate, the surface of the copper was coated with a relatively uniform layer of light blue material at pH 7.2. At pH 8.2, the pipe was covered by a relatively uniform black layer that was covered by long streaks of light blue material. Pipes were covered by a black solid at pH 8.5 and 9.2. The density, thickness and uniformity of the black material appeared to increase with increasing pH from 8.2 to 9.2. X-ray diffraction identified the Cu(II) solids posnjakite [($Cu_4(SO_4)$ (OH)₆·H₂O], brochantite [$Cu_4SO_4(OH)_6$], tenorite [CuO], and malachite [Cu₂CO₃(OH)₂], and the Cu(I) solid cuprite (Cu₂O) on the pipe sections (Table 2). There did not appear to be any obvious trends in the presence of solids with pH or orthophosphate. Orthophosphate has a dramatic impact on pipe surface appearance at pH 7.2 and 9.2. There was no visible sign of

Table 2
Mineralogy determined by X-ray diffraction for pH 7.20, 8.20, 8.50, and 9.20 with and without 3 mg PO ₄ /L for pH 7.20 and 9.20.

рН	PO ₄	Minerals formed	Pipe cross-section
7.20	No	Posnjakite	Part of the second seco
7.20	Yes	Cuprite	
8.20	No	Cuprite, Posnjakite, Tenorite	
8.50	No	Malachite, Tenorite	
9.20	No	Brochantite, Posnjakite	
9.20	Yes	Cuprite, Posnjakite	

any corrosion deposits on the pipe at pH 7.2. At pH 9.2, only some streaks of a light blue material were visible (Table 2). Orthophosphate limited the number of crystalline to Cu₂O (a Cu[II] mineral phase) and Cu₄(SO₄) (OH)₆·H₂O (only Cu[II] phase). No black material characteristic of CuO was visually observed on the pipes exposed to orthophosphate.

4. Discussion and conclusions

The results of this work have several important and practical implications. First, the relationships between pH, orthophosphate and time (age of copper pipe surface) on copper levels were illustrated and consistent with past research. The rate at which copper decreased or aged to achieve thermodynamic stability decreased with increasing pH. Copper concentrations decreased with increasing pH and, correspondingly, the total amount of copper released over all of the test runs decreased. This work also illustrated the recognized but less understood impact of orthophosphate on copper. At pH 7.2 where copper aged very slowly, orthophosphate rapidly decreased copper levels (and total copper release) to a narrow concentration range over the entire test run. Orthophosphate, however, increased copper levels (and total copper release) at pH 9.2 compared to when not present and where copper aged rapidly. These observations were consistent with the work of Schock et al. (1995a) that suggested orthophosphate provides a rapid benefit to slowly aging copper systems by quickly reducing copper levels. But when copper aging is rapid, the final product is more insoluble than the copper-phosphate complex resulting in an increase in copper concentration. Orthophosphate has been used to reduce copper to meet LCR copper action levels in building settings with success (Grace et al., 2012). The authors have been approached by building managers regarding strategies to reduce copper wastewater discharge levels to meet imposed facility limits while in compliance with the LCR. This work showed that pH adjustment and orthophosphate (at pH 7.2) are effective strategies to reduce total copper release from copper plumbing pipes.

Chlorine consumption trends over time were different for each pH condition tested, and the total amount of chlorine consumed over the test runs increased with increasing pH. Orthophosphate eliminated chlorine consumption trends with elapsed time (e.g., chlorine demand was consistent across all test runs). Orthophosphate also greatly reduced the total amount of chlorine consumed over the test runs. Interestingly, the total amount of chlorine consumed and the consumption rate were not pH dependent when orthophosphate was present. Despite no chlorine relationship with pH, total copper release in the presence of orthophosphate was impacted by pH. Total copper release at pH 7.2 was nearly five times greater than at pH 9.2 when orthophosphate was present. The comparison also showed that chlorine consumption was not predictive of copper release. This point was further demonstrated at pH 9.2 when orthophosphate was present as less chlorine was consumed yet more copper was released.

Chlorine reactions with copper were attributed to chlorine loss. Chlorine demand associated with bulk water reactions and losses to materials in the pipe loop test apparatus other than copper (i.e., tubing, valves, etc.) was very small. Chlorine demand could also result from reactions with organic carbon and biofilm. The deionized source water used in this work contained negligible levels of organic carbon and total nitrogen (necessary for biofilm growth), therefore the chlorine demand was primarily attributed to reactions with copper sources. Reactions between chlorine and the copper pipe wall are likely very complicated and can be attributed to multiple sources. For example, chlorine species can react with base copper metal, Cu(I) in the form of CuO_2 or aqueous ions, and Cu(II) mineral phases. Water quality parameters such as pH impact chlorine chemistry, corrosion rate, copper chemistry and mineralogy, to further complicate the system. Orthophosphate greatly reduced the loss of chlorine to the pipe walls independent of pH, indicating that orthophosphate altered the surface. More research is necessary to understand chlorine reaction mechanisms, and the importance and relative contribution of each.

The findings of this work have important practical implications. Common corrosion control practices of pH adjustment and orthophosphate addition can not only be used to reduce copper levels but also improve the ability to maintain chlorine residuals in buildings with copper plumbing. Grace et al. (2012) observed the benefits of an increase in free chlorine residual in a building premise plumbing system that treated the water with orthophosphate for corrosion control. Maintaining disinfectant residual in buildings such as hospitals is essential in controlling biofilm-associated pathogens such as *Legionella* and the associated risks. Although phosphorus is an essential biological nutrient, the benefit of orthophosphate in maintaining chlorine demand in premise plumbing may outweigh other considerations.

This work considered the impact of a small number of important water quality parameters on copper levels and chlorine demand. Future work should consider how other water quality variables such as temperature, silicate, DIC, and organic carbon impact chlorine demand.

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