

# 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

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

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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

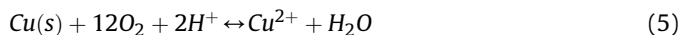
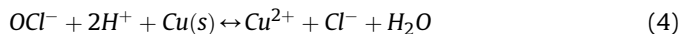
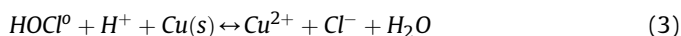
In drinking water distribution systems, there are several pathways that result in the loss of oxidants, including oxygen (O<sub>2</sub>), and disinfectants such as free chlorine (Cl<sub>2</sub>), monochloramine (NH<sub>2</sub>Cl) and chlorine-dioxide (ClO<sub>2</sub>). At the surface of premise plumbing 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 (Cu<sup>0</sup>) 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:



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<sup>+</sup> to Cu<sup>2+</sup> is essentially the rate-limiting factor, with Cu<sup>+</sup> 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):



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<sup>0</sup>, OCl<sup>-</sup> and Cl<sub>2</sub>) 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 Cu<sub>2</sub>O(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, Cu<sup>2+</sup> 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 CO<sub>2</sub> 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 et al., 1995a; Schocket 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 cupro-solvency. 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

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