

CHAPTER II

LONG TERM EFFECTS OF TEMPERATURE, CHLORINE, AND ORGANIC MATTER ON COPPER CORROSION BY-PRODUCT RELEASE IN SOFT DRINKING WATERS

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ABSTRACT--Soft, low alkalinity drinking waters tend to cause relatively high copper corrosion by-product release in plumbing systems. Long term tests (6 to 8 months) in such waters revealed that lower pHs and higher temperatures increased copper release to water, with greater soluble release at lower temperature and lower pH. The addition of organic matter also typically worsened copper by-product release by 25-100% when compared to waters without organic matter. Gum xanthan (0.25% by weight) and sodium alginate (2% by weight) produced a microbially unstable water which decreased the pH and D.O. of the water in the pipes, with concomitant adverse effects on water quality. In contrast, free chlorine (0.7 mg/L) caused a 0.10 mg/L increase in copper release at pH 9.5 but no adverse effect was observed at pH 7.0.

INTRODUCTION

Copper metal is a commonly used plumbing material and is generally corrosion resistant. However, certain water qualities tend to sustain relatively high levels of copper corrosion by-product release of copper, thereby causing compliance problems with drinking water and wastewater regulations. Soft, low alkalinity waters are particularly susceptible to problems of copper corrosion by-product release (Edwards, 1999; Dodrill et al., 1995), and are the focus of this investigation. This work attempts to 1) evaluate previous research findings about copper corrosion in soft water, 2) examine unifying factors thought to exacerbate copper corrosion and 3) carry out long term tests to determine their impact on copper corrosion by-product release.

In past investigations, three types of data have been used to characterize copper corrosion including weight loss, electrochemical measures, and by-product release. For weight loss, a copper pipe is weighed before and after an aging period (after any developed scale has been scraped away) and the loss of metal mass per unit time is calculated. Electrochemical techniques are used under flow conditions to measure the corrosion rate in terms of the corrosion current with units of $\mu\text{A}/\text{cm}^2$. Both of these measures are a sum of the copper released to the water and the copper deposited on the pipe wall as scale. Therefore, higher weight loss and corrosion rates do not necessarily indicate higher by-product release. Because the EPA's Lead and Copper Rule is exclusively concerned with the concentration of metal actually released from the pipe, by-product release was used to characterize corrosion throughout this work.

Temperature Effects

Among the factors thought to control corrosion in these waters are temperature, chlorine, natural organic matter (NOM) and bacterial extracellular polymeric substances (EPS).

Previous research suggests that high temperatures exacerbate aspects of copper corrosion (Obrecht et al., 1960; Obrecht et al., 1961; Rehring et al., 1996; Mor et al., 1979; Stone et al., 1987). Obrecht et al. (1960), using continuous flow corrosion rate and weight loss tests lasting up to 3 years in duration, concluded that soft waters at pH 7.0 and medium alkalinity contribute to erosion-corrosion of copper when the temperature of the water is above 45°C and maximum corrosion was observed near 77°C . They theorized that this temperature effect could be due to increases in ionization, diffusion rates and electrical conductivities which may speed the corrosion process. However, they also anticipated that decreases in dissolved gas content at high temperatures could counteract this effect by encouraging scale formation. It was noted that when the water hardness was increased to 110 ppm as CaCO_3 , maximum corrosion was observed at 60°C instead of 77°C . A black copper oxide scale was found to form at about 60°C instead of the basic copper carbonate film which forms at lower temperatures.

Kristiansen (1977) also found that copper corrosion during continuous flow conditions is exacerbated at high temperatures in low alkalinity waters between pH 5.6 and 6.1. His three month test illustrated that water containing organic matter further aggravates corrosion rate with

increasing temperature. He reasoned that the organic matter might prevent the formation of the black, protective copper oxide film that often forms in high temperature waters.

In contrast, high temperatures have been noted to decrease copper corrosion by-product release when harmful microorganisms are thought to be present (Arens et al., 1995). Over a two week test, Arens et al. used pipes producing high levels of copper corrosion (pipes contained soft, low alkalinity high pH water) to show that elevated temperatures (64°C) can reduce copper corrosion under stagnant conditions, possibly by killing microorganisms. They also noted that copper corrosion in their system was at a maximum at 30°C, which coincided with the maximum number of microorganisms detected. This is consistent with results of others who have demonstrated maximum bacterial activity between 25°C and 45°C (Angell et al., 1991, Walker et al., 1990).

These conflicting results achieved for different water qualities suggest that further study is needed. In particular, what are the effects of temperature on copper corrosion by-product release during stagnation in soft waters not containing bacteria? Moreover, data is lacking on the role of temperature on copper speciation.

Effects due to Chlorine Residual

Chlorine has been observed to both increase and decrease the corrosion of copper in drinking water pipes (Table 2-1) (Atlas et al., 1982; Stone et al., 1987; Reiber, 1989; Edwards et al., 1993; Hong et al., 1998). Copper leaching due to chlorine addition has been shown to increase at pH < 7.0 (Atlas et al., 1981, Hong et al., 1998). This effect has been explained by the observation that the hypochlorite ion, which is the dominant chlorine species at higher pH, is not as strong an oxidizing agent as hypochlorous acid. Some researchers have further concluded that chlorine is dominant over oxygen as an oxidizing agent on copper surfaces (Atlas et al., 1981, Reiber, 1989). However, Edwards et al. (1993) showed that a chlorine residual of 2 mg/L Cl₂ decreased the copper corrosion rate in a water at pH 9.3, leading to the conclusion that a chlorine residual might prevent soft-water pitting.

Table 2-1: Previous research on the effect of chlorine on copper corrosion

Author, Date	Duration of Cl₂ Exposure	Water Type	Cl₂ Conc. (mg/L)	Result of Test
Atlas et al., 1981	24 hrs	pH 5.0 and 8.0; Amherst, MA tap water	0, 1, 2, 5, 7.5 and 10	Higher free chlorine concentrations caused more copper dissolution especially at lower pH.
Stone et al., 1987	< 3 hr in pipe aged months	Seattle Tap water, pH 7.0, 12.8°C	0 to 3.2	Increased copper corrosion rate with increased chlorine residual.
Reiber, 1989	10 minutes in pipe aged months	Tap water, pH 7.0	0 to 1.0	Corrosion current is increased with increasing chlorine residual. When present, chlorine becomes the dominant oxidant.
Edwards et al., 1993	24 hours	pH 9.3, alk 18 mg/L	2	Accelerated testing showed that chlorine residual decreased the corrosion rate of copper at pH 9.3.
Hong et al., 1998	8 hrs	pH 5.7–8.8, alk 0-3 mM total CO ₃ ²⁻ , 22-25°C	0, 1.2, 3.6, 6 mg/L as Cl ₂	Copper leaching increased with the level of chlorine at pH 6.8. Copper leaching was found to be highest at low pH.

To date, only two studies on chlorine effects have used by-product release as an indicator of copper corrosion. In addition, 24 hours is the longest test duration to date. This short exposure time may be representative of much longer exposure times observed in practice, but given the importance of chlorine in water treatment, it is essential to confirm this result for more realistic time periods.

NOM Effects

A thorough literature review on the effects of NOM on copper corrosion through the year 1993 is provided by Rehring et al. (1996) and Edwards et al. (1996). A summary of that review, along with recent additions to the literature will be provided here. In terms of copper corrosion by-product release, NOM has generally been noted to have detrimental effects. Kristiansen (1977 and 1982) found that both copper corrosion rate and by-product release increased with temperature in waters containing humic substances over a three month testing period. He also

found that corrosion is particularly severe when copper is subjected to very high (over 35 mg/L TOC) concentrations of NOM. During a 1 year test duration, Rehring et al. (1996) demonstrated that NOM caused an increase in copper by-product release, which was mostly soluble copper, at pH 6.0, 7.5 and 9.0. Similarly, Korshin et al. (1996) found that, in a moderately alkaline water with a pH of 7.3 and a seven week testing period, low concentrations of NOM increased copper by-product release.

Two practical studies found adverse effects of NOM on copper by-product release. Hongve et al. (1995) observed that bog water, high in NOM and color, caused significantly higher copper by-product release than did tap water with the same pH (pH 7 and 8). Meanwhile, Holmstrum et al. (1997) found a strong correlation between COD (a measure of organic matter) in treated drinking water and copper content of sludge from the corresponding wastewater treatment plants.

In contrast, benefits attributed to NOM have generally been associated with reduced pitting frequency or reduced corrosion rates. Campbell (1954) observed that surface waters were less likely to cause pitting than groundwaters. He noted that the presence of NOM alters the nature of the scale that forms, making it more uniform and dense and, therefore, more protective. More recently, an accelerated corrosion test run by Edwards et al. (1993) revealed that, in a water with a pH of 9.3, long-term exposure to NOM had a beneficial effect on soft water pitting. Korshin et al. (1996) found beneficial effects of NOM on corrosion rate in a moderately alkaline water at pH 7.3. Short term beneficial effects of NOM on by-product release in a water at pH 6.0 were demonstrated by Rehring et al. (1996) however, after 1 year of aging, both by-product release and copper corrosion rates were adversely affected.

Even with the recent wealth of knowledge acquired on the effects of NOM on copper corrosion, the literature is still lacking in many areas. Most laboratory studies to date have used NOM in a soluble form. To the best of our knowledge, particulate NOM has not been examined as a possible contributor to copper corrosion. The literature is also lacking in tests on the long term effect of NOM in water types similar to those that cause blue water (low alkalinity, low hardness, high pH waters).

Effects Due to Extracellular Polymeric Substances (EPS)

Extracellular polymeric substances are organic materials (i.e. polysaccharides, glycolipids and oligopeptides) produced by bacteria. To the best of our knowledge, there is no conclusive research demonstrating the effects of EPS constituents (such as alginate and gum xanthan) on copper corrosion under conditions typical of water distribution pipes. However, there have been studies showing that EPS can cause the deterioration of a copper film (Geesey et al., 1986; Geesey et al., 1987; Jolley et al., 1989) and that EPS readily binds copper (Mittelman et al., 1985; Jang et al., 1990) in pure water (Table 2-2).

Table 2-2: Effects of extracellular polymeric substances on copper metal

Author, Date	Length of Experiment	Water Type	Polymer Tested	Effect of Polymer
Mittelman et al., 1984	36 hrs	Distilled water, pH 5.0-7.0, 4°C,	Natural EPS, Xanthan, humic acids	Exopolymers bind copper.
Geesey et al., 1986	1 hr	Distilled water, pH 6.8	Isolated natural exopolymer	Isolated exopolymer could enhance the corrosion of a copper film.
Geesey et al., 1987	1 hr	Distilled water, pH 6.5	Gum arabic (25%), alginic acid (2%), crude exopolymer (1%)	Destruction of the copper surface by each polysaccharide was observed.
Jolley et al. 1989	24 hrs	Nanopure water, pH 7.0	Alginic acid (2%)	In 24 hours of exposure using FTIS, 41% of a copper film was removed by alginic acid and incorporated into solution.
Jang et al., 1990	8 hrs	Distilled water, pH 5.1-5.8, low alk	Calcium alginate (3.2%)	Using sodium alginate to absorb dissolved copper was determined to be feasible.

Related studies have isolated EPS from corrosive biofilms, such as those found in “blue water” conditions. Angell et al. (1991) cultured bacteria from blue water pipes revealing that the EPS produced by these bacteria varies with temperature and is enhanced in a mixed culture. Wallace et al. (1994) found that several bacterial strains isolated from corrosive biofilms contained

alginate biosynthetic genes. In addition, several practical blue water studies have revealed solid corrosion byproducts mixed with a gelatinous blue-green biofilm (Reiber et al., 1995; Fischer et al., 1995). Webster et al. (1996) tried to replicate the effect of the bacteria from a gelatinous blue water biofilm with limited success.

Considering the numerous studies that seem to implicate EPS in the corrosion of copper metal, a long term bench scale study examining copper corrosion by-product release in the presence of EPS is sorely needed.

Restatement of Research Objective

This review has established that a long term study is needed to examine factors implicated in high copper by-product release in soft water. Though some information is available on the effects of temperature, chlorine residual, NOM and EPS, the vast majority of experimental results are from short term tests of less than one day. An experimental time of between 6 to 12 months is recommended to draw conclusions relevant to drinking water corrosion relevant to copper (AWWARF, 1996). The goal of this work was to determine the long term (8 to 12 months) effects of temperature, chlorine and organic matter on copper by-product release.

MATERIALS AND METHODS

Solution Preparation

The base solution water was a soft, low alkalinity water similar to that described by Arens et al. (1995) in which “blue water” was noted to occur (Table 2-3).

Table 2-3: Final ion concentrations in the base solution*

Ion	Concentration (mg/L)
Magnesium	3
Chloride	9
Calcium	5
Nitrate	16
Sulfate	16
Sodium	17
Silica	20
Alkalinity (as CaCO ₃)	5

* added as reagent grade MgCl₂, Ca(NO₃)₂*4H₂O, Na₂SO₄, Na₂SiO₃, and Na₂CO₃

Experimental solutions were adjusted to pH 7.0 and 9.5 +/- 0.2 pH units immediately prior to copper pipe exposure using NaOH and HNO₃ solutions. Fresh base solutions were prepared and replaced at least once every other week. Chlorine and organic material were added to the base solution (Table 2-4) as noted in specific experiments.

Table 2-4: Concentrations of chlorine and organic matter added to the base solution

Material Added	Concentration
Chlorine (mg/L as Cl ₂)	0.7 and 1.5
Soluble NOM (mg/L as TOC)	2
Particulate NOM (mg/L as TOC)	100
Sodium Alginate	2 % by weight
Gum xanthan	0.25 % by weight

Chlorine was dosed using a diluted solution of 2% by weight NaOCl which was maintained in a constant temperature room at 4° C in a bottle wrapped in aluminum foil. At the target pH value of 7.0, the pKa for chlorine of 7.5 indicates that 86% will be in the form of HOCl and the remaining 14% is present as OCl⁻. At pH 9.5, virtually 100% of the chlorine is present as OCl⁻.

The soluble NOM solution was isolated from Lake Pleasant, WA and prepared as discussed elsewhere (Edwards, 1992). Particulate NOM was prepared from peat purchased at a local garden supply store. Approximately 30 grams of peat was rinsed in 1L of deionized water, then

filtered through a 0.45 μm filter. The particulate fraction was then scraped off of the filter and re-suspended in deionized water. This rinsing and filtering process was repeated three times after which a final sample of particulate NOM was achieved. Concentrated NOM solutions were then measured for total organic carbon using a Dorhrmann DC-80 Total Organic Carbon Analyzer with a DC-80 Sludge/Sediment Sampler according to Standard Method #5310 (American Public Health Association, 1998).

The alginate and gum xanthan concentrations were selected to be the same as was tested by Geesey et al. (1987). The resultant solutions were very viscous and not representative of bulk drinking waters found in practice, but the high concentrations used by Geesey et al. were expected to highlight key effects.

Copper Pipe Preparation

Copper pipes were 12" long, $\frac{3}{4}$ " diameter Type L tubes with a volume of approximately 100 ml. Number two rubber stoppers were used to plug the ends of each pipe after careful rinsing before use. The copper pipes were used as purchased from a local hardware store without additional treatment.

During exposure, the pipes were laid side by side in a horizontal position. Water in the pipes was changed Monday, Wednesday and Friday of each week resulting in a regular 3, 2 and 2 day weekly stagnation schedule. The pH of each water was adjusted to pH 7.0 or 9.5 \pm 0.2 pH units before changing the water in the pipes. Whenever a change was made in exposure, water samples were analyzed after each stagnation time for the first two weeks. Thereafter, samples were collected once every one or two weeks after the 3 day stagnation time. Unless stated otherwise, pipes were tested in duplicate.

Constant temperature rooms were used to maintain the temperature of the pipes at 4°C, 20°C and 24°C \pm 0.1°C. For tests at 60°C, pipes were placed in a heated insulated metal box mounted on top of a hot plate. On 3 occasions during the 12 months of testing, a power outage disrupted the

constant temperature of the 60°C heating device. Temperatures in this device were usually 60 +/- 3°C.

Copper Corrosion By-Product Release Measurements

Water samples from the copper pipes were measured for total copper, soluble copper and pH. In this work, soluble copper is operationally defined by filtration through a 0.45 um pore size syringe filter. After acidification to pH 2.5-4.0, copper in samples was determined using a Hach DR/2010 Spectrophotometer (Loveland, CO). In the initial phase of work, results of the Hach analysis were carefully cross-checked with those for an inductively coupled plasma emission spectrophotometer (ICP-ES) (SpectroFlame Modula, Model # FTMOA85D, Spectro Analytical Instruments, Fitchburg, MA) according to Standard Method 3120 (American Public Health Association, 1998). Results between the two tests were consistent in that, of 50 samples tested for total and soluble copper on both the Hach spectrophotometer and the ICP-ES, the measurements for all but 4 of the samples were within 15% of each other.

Alginate and gum xanthan samples were too viscous to measure using an ICP-ES. Using several quality control/quality assurance (QA/QC) tests, the Hach spectrophotometer was found to accurately measure total and soluble copper in these samples. The QA/QC included “spike and recovery” tests for alginate, gum xanthan, soluble NOM and particulate NOM, in which the samples were measured without copper, with only a Hach copper “powder pillow”, and with the powder pillow plus 2 mg/L Cu²⁺. Somewhat surprisingly, the organic matter solutions did not interfere with the Hach test as long as the absorbance of the organic matter solution itself was accounted for. Thus, the Hach test provided accurate measures of soluble copper in these solutions when it was not possible to do so using Standard Methods.

Oxygen Depletion Tests

Dissolved oxygen (D.O.) depletion tests were set up according to Standard Method # 5210 (American Public Health Association, 1998) except that no inorganic nutrients were added and dissolved oxygen was measured at various points in time, rather than at 5 days. Organic matter

solutions were made up just as they were before putting samples into the pipes, so any measured decrease in D.O. was attributable exclusively to reactions between the sample and dissolved oxygen since no copper metal was present. The samples were held at a constant temperature of 20°C and they were not aerated before the tests began.

Other Measurements

Sample pH was measured using a Beckman 11 pH meter. Dissolved oxygen (D.O.) was measured using a Hanna Instruments HI 9141 D.O. probe.

RESULTS AND DISCUSSION

This section is organized into three main sub-sections. First, the results of long term tests on the effects of temperature, pH and chlorine dose on copper corrosion by-product release are discussed. Thereafter, long term effects of organic matter on copper by-product release are examined. The final section describes the indirect effects of organic matter on dissolved oxygen and pH, and the resulting impacts on copper corrosion by-product release.

Role of Temperature, pH, and Chlorine Dose on Copper Corrosion in Soft Waters

The effect of temperature, pH and chlorine dose on copper by-product release in soft waters was examined for a period of six months. Pipes were tested at four different temperatures (4, 20, 24 and 60°C), two different pH values (7.0 and 9.5) and in the presence or absence of chlorine, making 32 pipes total after accounting for duplication. Though samples were collected throughout the experiment, for brevity the last 6 sampling were averaged and statistically analyzed for this analysis. Results earlier in the pipe life were qualitatively consistent unless stated otherwise in the text.

Copper by-product release was typically 5 times higher in pipes at pH 7.0 than at pH 9.5 (Figure 2-1). Holding the water temperature at 60°C also seemed to aggravate copper release when compared to identical pipes held at 4°C, 20°C, and 24°C, although this trend was not always

significant at 95% confidence. Pipes at the three lower temperatures were not significantly different from one another.

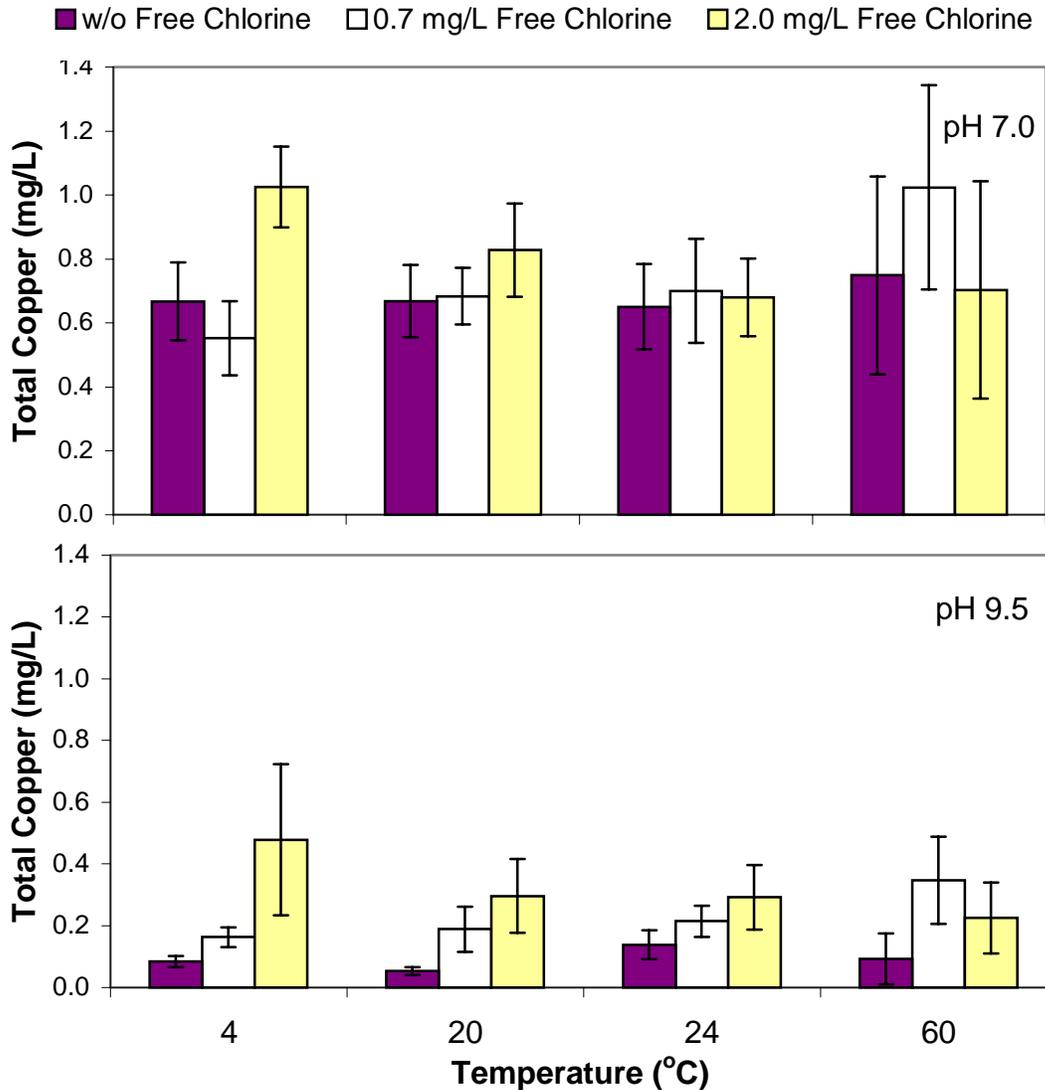


Figure 2-1: Influence of chlorine dose and temperature on copper by-product release. Total copper values are long term averages during the period the pipes were exposed to the respective Cl₂ concentrations. The error bars indicate 95% confidence on 12 data points for the control and 0.7 mg/L Cl₂ and on 6 data points for 1.5 mg/L Cl₂.

Adding 0.7 mg/L free chlorine did not significantly increase by-product release at a given temperature at pH 7.0. However, this chlorine dose did significantly increase copper release at pH 9.5 at every temperature tested. It should be noted, however, that the chlorine only increased total copper by-product release at pH 9.5 from approximately 0.1 mg/L to 0.2 mg/L. Given that

the EPA's action level for copper is 1.3 mg/L, these levels are still very low. The greater effect of chlorine at pH 9.5 could be due to the speciation of free chlorine with pH. For example, at pH 9.5 free chlorine is present as 100% hypochlorite ion (OCl^-) while at pH 7.0, 14% is in the form of OCl^- and 86% is present as hypochlorous acid (HOCl). It is possible that, in soft waters, OCl^- may be more reactive with copper than HOCl , but other factors are also likely to be involved.

The percentage of soluble copper released from the pipes was dependent on both temperature and pH (Figure 2-2). Although the pipes held at 60°C released the most total copper, they also had the least soluble copper, consistent with trends in solubility models (Edwards et al., 1993). This trend was also apparent at other temperatures although it is of low significance. Chlorine did not have a significant effect on soluble copper release.

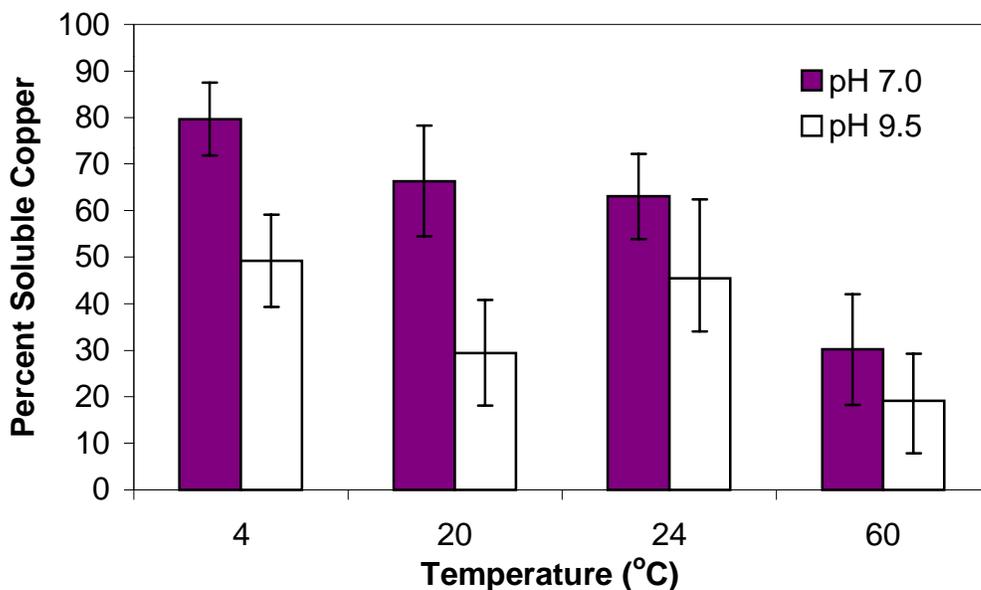


Figure 2-2: Percent soluble copper at different temperatures and pH values for pipes without chlorine. Percent soluble copper values are averaged over months 2 to 6 for duplicate samples. The error bars indicate 95% confidence on 12 data points at each condition.

To examine the effects of varying chlorine dose, pipes previously exposed to free chlorine at 0.7 mg/L as Cl_2 were dosed with 2.0 mg/L as Cl_2 for four sequential sampling events. With the exception of the pipes at 4°C, the higher Cl_2 dose did not significantly increase copper by-product release over the release caused by 0.7 mg/L Cl_2 at both pH values (Figure 2-1).

However, there seemed to be a trend of increased copper by-product release with increased chlorine concentration.

Examining this trend in more detail at 20°C, copper by-product release increased with chlorine dose at both pH values (Figure 2-3). Although there were only three Cl₂ doses tested, the increase in copper by-product release with chlorine dose was nearly linear. Regression analysis indicated that the slopes for pH 9.5 (p value = .002) and for pH 7.0 (p value = .073) were significantly greater than zero, proving that the higher chlorine doses led to higher copper release at 20°C. The slope for pH 9.5 was slightly higher than for pH 7.0, consistent with the earlier conclusion that chlorine had a greater effect on the corrosion of pipes containing water at pH 9.5. However, it is re-emphasized that chlorine has a relatively small adverse effect on copper corrosion by-product release in soft waters when compared to the drinking water action level for copper of 1.3 mg/L.

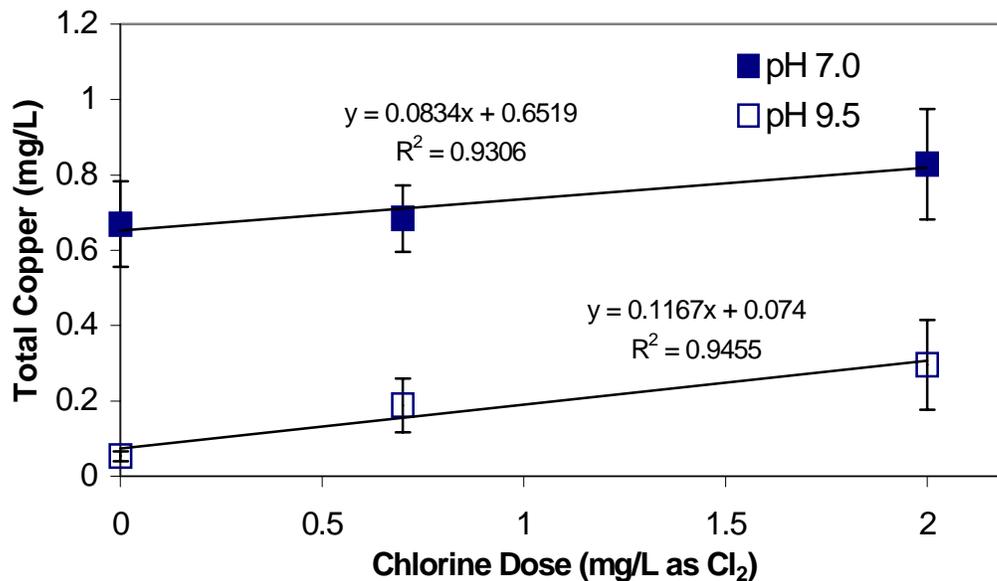


Figure 2-3: The effect of chlorine dose on copper by-product release at 20°C. Total copper values are long term averages during the period the pipes were exposed to the respective Cl₂ concentrations. The error bars indicate 95% confidence on 12 data points for the control and 0.7 mg/L Cl₂ and on 6 data points for 1.5 mg/L Cl₂.

The Effect of Organic Matter on Copper By-Product Release in Soft Waters at Varying Temperature and pH

Copper pipes were exposed to organic material including soluble NOM, particulate NOM, alginate and gum xanthan for a period of 8 months. Each of these were tested at two temperatures (20 and 60°C) and two pH values (7.0 and 9.5). These pipes were run concurrently with those described in the preceding section.

The effects of aging (i.e. the length of time that the pipes were exposed to the different waters) in pipes containing organic material were important (Figure 2-4). For example, in most of the pipes containing particulate NOM, copper by-product release started low, increased erratically and eventually leveled off at a relatively high value. In contrast, in some pipes containing gum xanthan the copper by-product release started out relatively high and decreased. Most of the control pipes (containing solution water with no organic material) stayed relatively constant throughout the testing period with the exception of a slightly higher level of release in the first month of exposure, presumably as a protective scale layer was being deposited on the pipe. In sum, copper release can either increase, decrease, or remain relatively constant over months of aging. Unless stated otherwise, the more meaningful long term result is summarized here, but the data highlights the dangers of extrapolating experimental results obtained after less than one week of exposure to actual conditions.

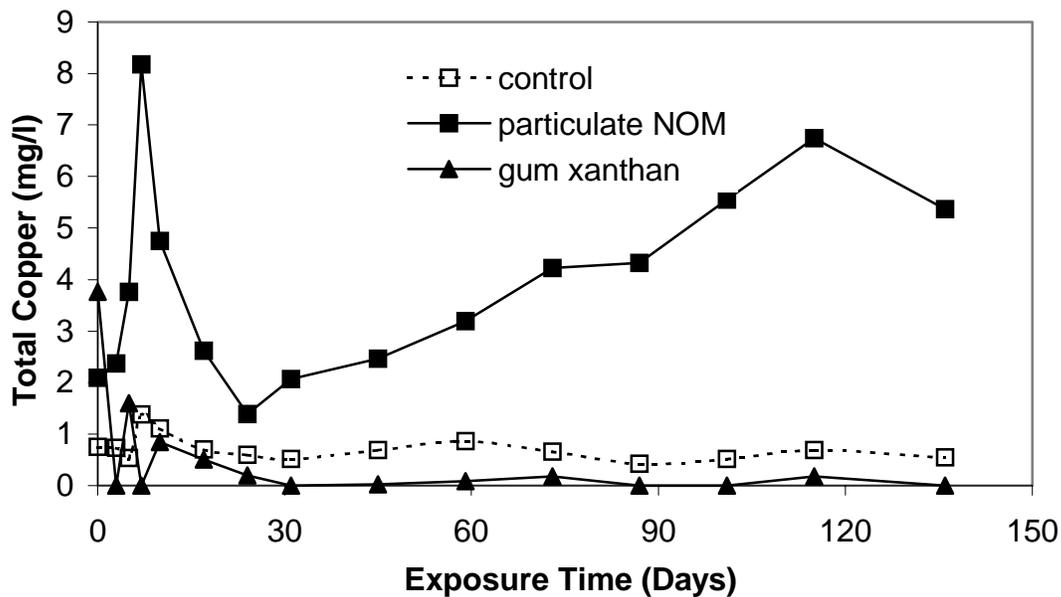


Figure 2-4: Illustrative effects of pipe aging on copper by-product release (20°C, pH 7.0).

Average copper release over the last two months of pipe exposure proved that the effects of organic material on copper release in soft waters is highly variable (Figure 2-5). However, some generalizations can be made. The only organic material found to reduce copper release compared to the control was gum xanthan at pH 7.0 and 20°C. With some exceptions, copper release was higher at 60°C than at 20°C and pipes at pH 7.0 released more copper than pipes at pH 9.5. It should be noted, however, that both gum xanthan and alginate reduced the pH of the pipe solution during the three day stagnation period so that solutions starting out at pH 9.5 ended up at pH 6.5 after three days. This effect is discussed in greater detail later.

Along with total copper release, soluble copper release varied among the different types of organic matter (Figure 2-6). The results at 60°C and 20°C were qualitatively similar, so only the results for 20°C are shown. In the presence of alginate and gum xanthan copper release was almost 100% soluble. Pipes containing particulate NOM exhibited the opposite effect in that most of the copper release was in the particulate form. The percentage of soluble copper was increased in the presence of soluble NOM at pH 7.0 relative to the control, but was unchanged at

pH 9.5. The highest soluble copper concentrations were observed in the presence of soluble NOM.

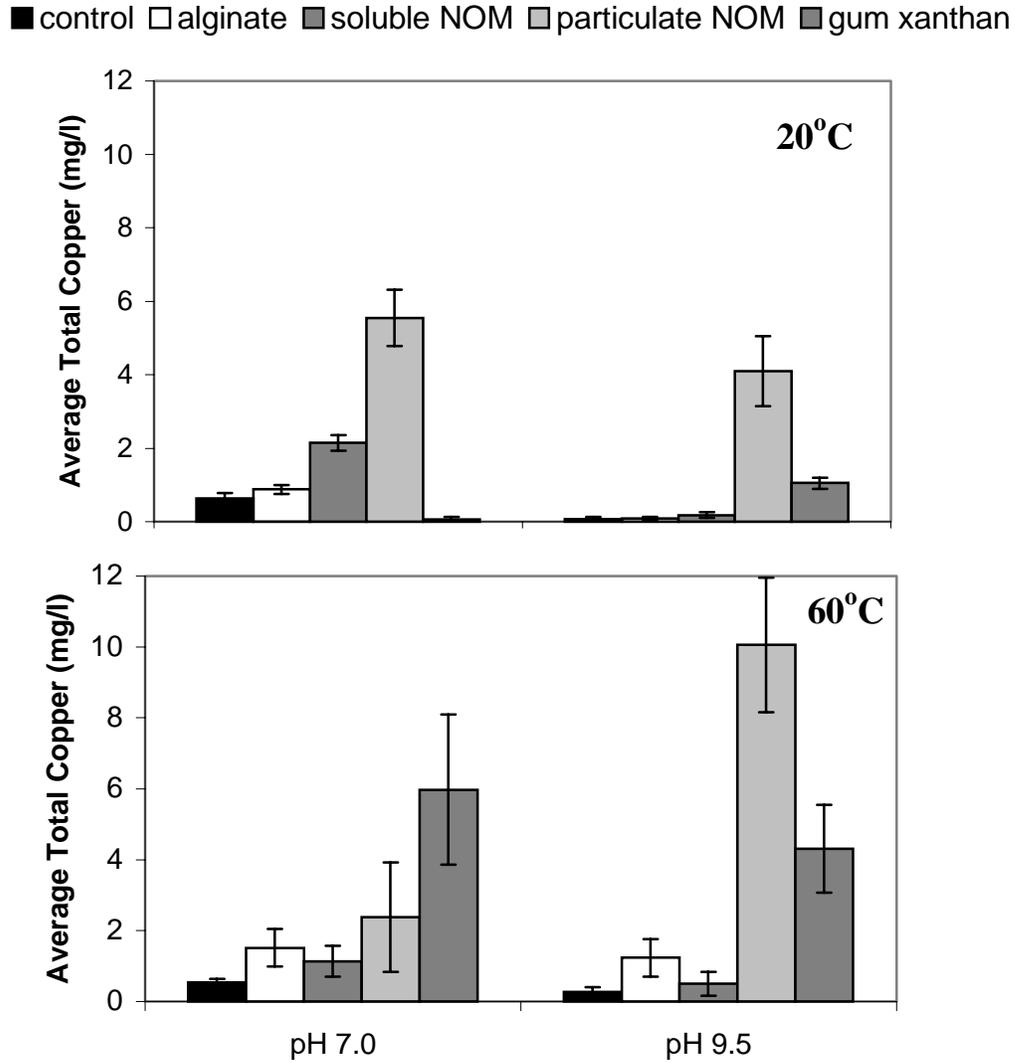


Figure 2-5: Long term effects of organic matter on total copper by-product release at 20°C and 60°C. Total copper values are averaged over a two month period at the end of the 8 month test duration. The error bars indicate 95% confidence on the 4 data points at each condition.

■ control □ alginate ■ soluble NOM □ particulate NOM ■ gum xanthan

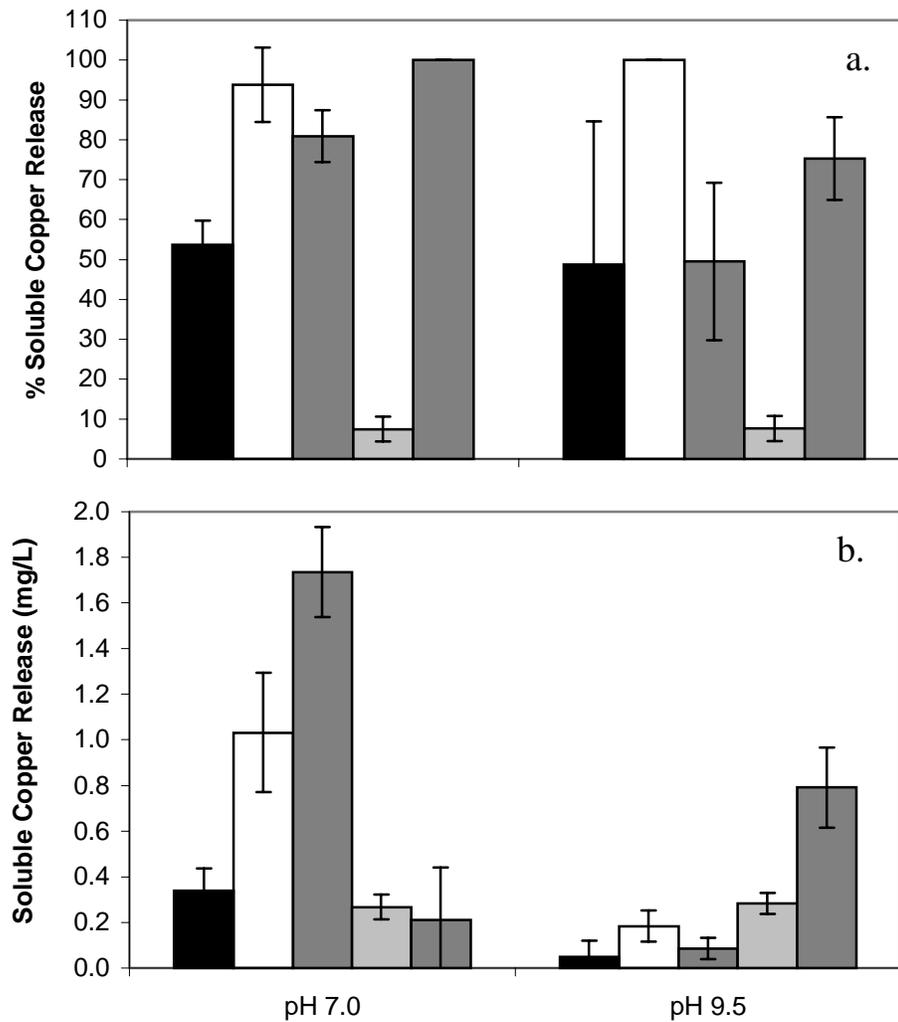


Figure 2-6: Percent soluble copper (a.) and soluble copper concentration released (b.) at 20°C. Percent soluble copper and soluble copper concentrations are averaged over a two month time period at the end of the 8 month test duration. The error bars indicate 95% confidence on the 4 data points at each condition.

Some of the pipes containing organic matter solutions were cut open at the end of the test in order to examine the scale morphology. In the case of the pipe containing particulate NOM, differences could be observed between the top and bottom halves of the pipe (Figure 2-7). The scale on the bottom half contained a significant amount of particulate matter that had presumably settled out of solution, while the scale on the top half consisted of multi-colored (red, yellow and blue) shiny material seemingly coated with black particles. The pipe containing soluble NOM contained a scale layer similar in appearance to the scale of the control pipe. In both cases, the inside of the pipe was a shiny orange color at pH 9.5 and appeared more dull, with obvious scale material at pH 7.0. The scale layers of pipes containing alginate were loosely adherent and started to flake off when the pipes were dried (Figure 2-8). In contrast, a pipe containing gum xanthan had a uniform black scale layer that did not flake off when dried.



Figure 2-7: The top and bottom sections of pipes exposed to particulate NOM. The bottom section contained a dense layer of particulate matter that had settled from solution, while the top layer was multi-colored and coated with black particles.

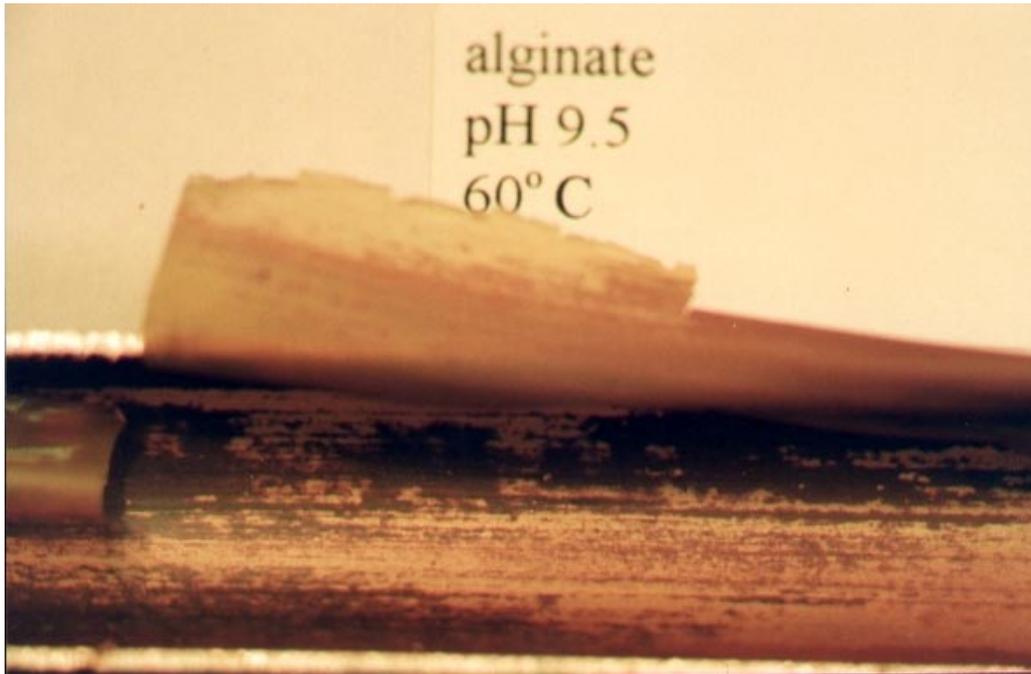


Figure 2-8: The scale layer of pipes containing alginate. When dried, the scale layer easily flaked off.

Dissolved Oxygen and pH Effects on Copper By-Product Release in Pipes Exposed to Organic Matter

A series of intensive sampling events in which stagnation time was systematically varied was run for the pipes containing organic material. At the end of each stagnation time, water from the pipes was analyzed for total copper, soluble copper, dissolved oxygen and pH. For each of the conditions, two common trends were observed between total copper released and D.O. consumed (Figure 2-9). When oxygen was present in the pipes throughout the stagnation period, the amount of copper released seemed to be a function of the amount of D.O. consumed. However, when there was minimal oxygen present in the water at the start of the test, as in the case of alginate and gum xanthan, there was nearly zero copper release since there was no oxygen to be consumed.

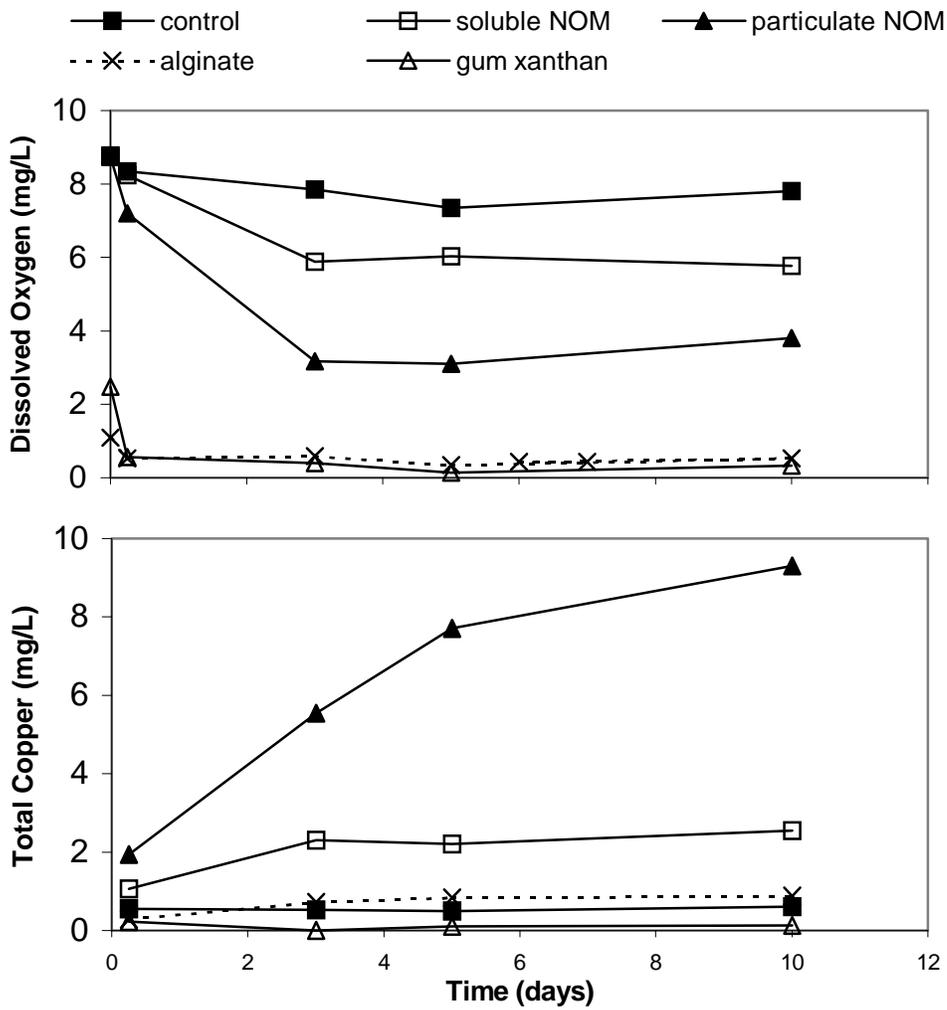
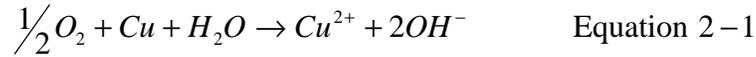


Figure 2-9: Typical trends for dissolved oxygen consumption and copper release. When dissolved oxygen starts out and remains at zero, such as the case with gum xanthan and alginate, there is no copper release. When dissolved oxygen is present then the more dissolved oxygen consumption, the more copper released.

Under aerobic conditions, without chlorine or other oxidants present, copper will spontaneously react with oxygen to form cupric ion according to the following balanced redox reaction:



According to this reaction, 4.0 mg/L cupric ion will be produced for every 1.0 mg/L D.O. consumed. For comparison, the relationship between cupric ion produced and D.O. consumed was examined for the pipes which contained oxygen throughout the stagnation period including those containing control water, soluble NOM and particulate NOM (Figure 2-10). Newer, unconditioned pipes were found to release more copper per unit of D.O. consumed than older, conditioned pipes. Specifically, new pipes were found to release 1.2 mg/L cupric ion for every 1.0 mg/L D.O. consumed while older pipes were found to release 0.5 mg/L cupric ion per mg/L D.O. consumed. One possible explanation for this result is that, in older pipes, more copper is going into building a scale layer. Nevertheless, regardless of pipe age, the general tendency is for greater copper release with high D.O. consumption.

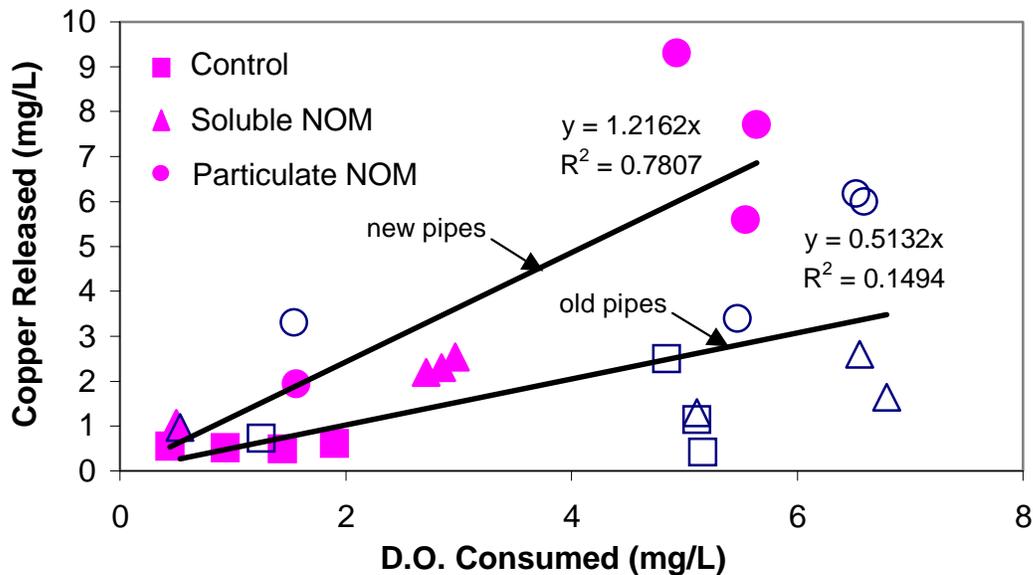


Figure 2-10: Copper released versus dissolved oxygen consumed at pH 7.0 and 20°C. Filled shapes are newer pipes while open shapes are older pipes. Alginate and gum xanthan are not considered since oxygen was consumed in the pipes independent of corrosion reactions.

The fact that there was essentially zero oxygen in the pipes with gum xanthan and alginate at short stagnation times was curious. According to equation 2-1, this would indicate very little capability to corrode copper and sustain high by-product release. To examine the cause for the depletion of D.O., a series of dissolved oxygen depletion tests were conducted.

Using solutions identical to those added to the pipes, the first series of tests illustrated that the dissolved oxygen in the gum xanthan and alginate samples was completely consumed within three days even without the pipe present. In contrast, solutions containing soluble NOM and particulate NOM did not consume any measurable oxygen. This result was consistent with the earlier observation that oxygen consumed in pipes with soluble, particulate or no NOM was mostly due to corrosion reactions and it also raised the prospect that aerobic bacteria were active in the solutions containing gum xanthan and alginate.

To further examine this possibility, another series of D.O. depletion tests was run on 1) control (no organic matter), 2% alginate, and 0.25% gum xanthan solutions prepared as they were placed in the pipes, 2) the same samples filtered through a 0.45 μm pore size filter, and 3) the same samples incubated for 2 days, after which time 2% sodium azide was dosed. All percentage based concentrations are expressed as a weight/volume. The sodium azide inhibits microbial activity (Megnell et al., 1970), but preliminary tests proved that it did not deplete oxygen itself.

Over a three day period, dissolved oxygen was not significantly depleted in filtered samples. However, in unfiltered samples oxygen was depleted to undetectable levels, whereas sodium azide immediately stopped dissolved oxygen depletion after it was added (Figure 2-11). This result proves that bacteria were causing the observed decrease in dissolved oxygen, and that addition of the EPS constituents to water produced samples that were microbiologically unstable. The resulting microbial activity had a strong positive influence on copper corrosion by-product release since there was little, if any, oxygen remaining to fuel corrosion reactions.

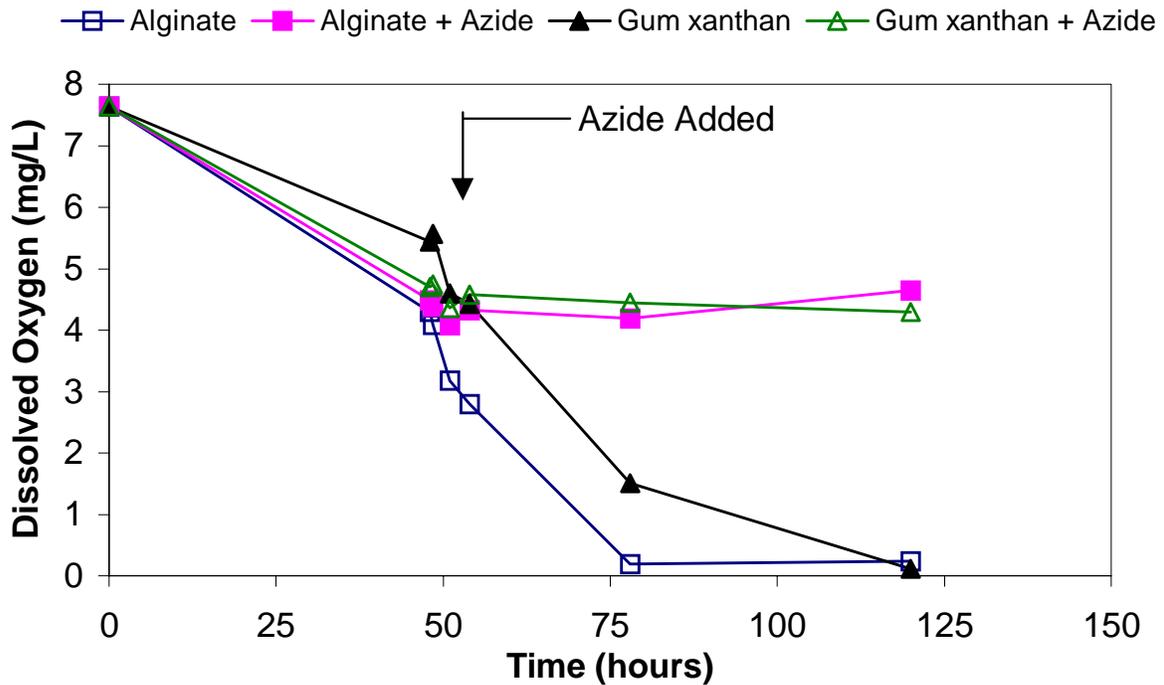


Figure 2-11: Oxygen depletion with time at 20°C. When 0.2% sodium azide was added to solutions of alginate and gum xanthan dissolved oxygen stopped decreasing indicating bacterial activity in the alginate and gum xanthan solutions.

In addition to dissolved oxygen effects, significant pH effects were also observed in pipes containing alginate and gum xanthan. During the three day pipe stagnation period, gum xanthan consistently lowered the solution pH within both the pH 9.5 and pH 7.0 pipes to around 6.3 after three days. Alginate lowered the pH in the pH 9.5 pipes to about pH 7.0 while the pH 7.0 pipes remained relatively constant in pH throughout the stagnation period.

To test whether this decline in pH was a direct effect of the gum xanthan and alginate, or if it was caused by interactions of the organic matter with the copper pipe, a batch test was set up to measure pH change with time for isolated alginate and gum xanthan solutions (Figure 2-12). Gum xanthan and alginate solutions were freshly made up just as they were before putting samples into the pipes and placed in covered beakers. Both gum xanthan and alginate were found to exert the same pH effect as when they were inside the pipe. Over 24 hours, gum xanthan lowered the pH from 9.5 to 6.5 and from 7.0 to 6.3 in both 20°C and 60°C environments.

Similarly, in 24 hours, alginate lowered the pH from 9.5 to 7.5 and from 7.0 to 6.8 at 20°C. At 60°C, alginate seemed to exert a lesser effect on the pH in that, after 24 hours, the pH 9.5 solution only dropped to 8.1 and the pH 7.0 solution actually was raised to 7.5. Nevertheless, it would seem that both alginate and gum xanthan instigate a buffering effect in that gum xanthan keeps the pH around 6.3 and alginate buffers the pH to around 7.0.

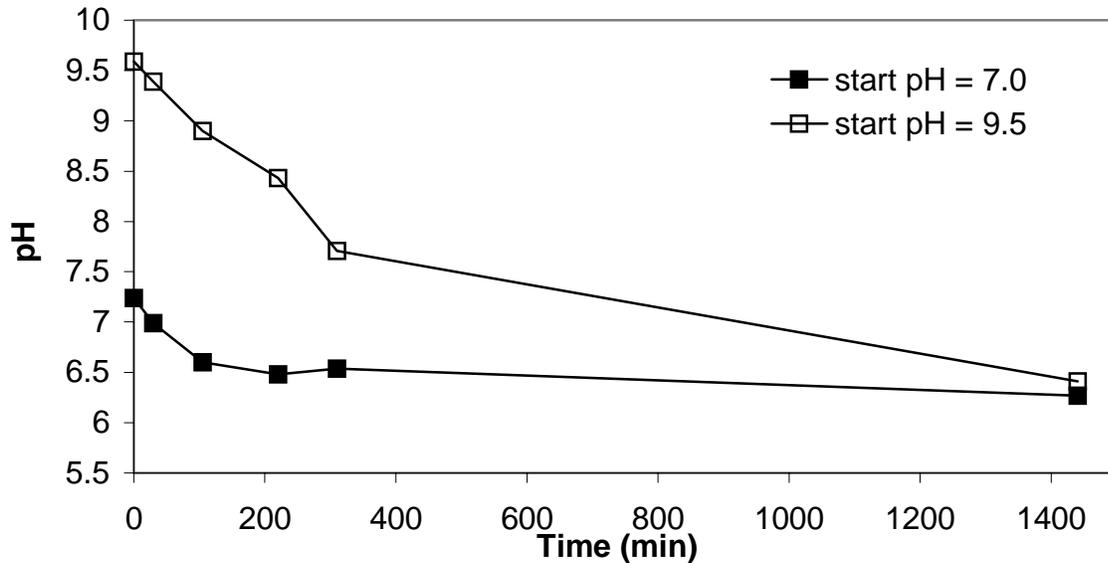


Figure 2-12: Change in pH with time for gum xanthan at 20°C.

Particulate NOM and soluble NOM also slightly decreased the pH of the pipe solutions over time. For example, over a three day stagnation period, waters with particulate NOM were decrease in pH from 7.0 to approximately 6.5 and from 9.5 to about 8.0, while waters with soluble NOM decreased in pH from 7.0 to about 6.7 and from 9.5 to approximately 8.5. Two possible explanations for this effect are that corrosion reactions within pipes containing NOM are causing a decrease in pH or that organic matter, in general, has acidic properties and causes a decrease in solution pH on its own. This topic was not explored further as for the gum xanthan and alginate.

CONCLUSIONS

The following conclusions about copper corrosion by-product release in soft, low alkalinity waters can be drawn from this investigation.

- Consistent with expectations, in the absence of organic matter, copper by-product release was higher at pH 7.0 than at pH 9.5. Pipes at pH 9.5 were found to release a higher percentage of particulate copper than pipes at pH 7.0.
- When compared to 4°C, 20°C and 24°C, a temperature of 60°C instigated higher copper release. Pipes at 60°C were found to release a higher percentage of particulate copper than pipes at lower temperatures.
- Over a six month test duration, a chlorine dose of 0.7 mg/L Cl₂ significantly increased copper by-product release at pH 9.5 for all temperatures tested, but did not significantly increase release at pH 7.0. However, the increased release at pH 9.5 was only 0.1 mg/L total copper and would not be a concern in terms of meeting the EPA's MCL for copper of 1.3 mg/L. Chlorine dose was not found to have a significant effect on the percentage of soluble copper released.
- The relative effects of organic matter varied with pipe age, thereby demonstrating the importance of long-term tests when determining impacts of organic matter on copper corrosion.
- According to long-term averages (after 8 months of exposure) copper by-product release due to organic matter is highly variable. However, with a few exceptions, copper release was higher at 60°C than at 20°C and at pH 7.0 than at pH 9.5.
- In the presence of alginate, gum xanthan and soluble NOM, copper release was almost 100% soluble. The opposite was true for pipes exposed to particulate NOM in which copper release was almost 100% particulate.

- When oxygen was present, copper by-product release increased as a function of dissolved oxygen consumed. When dissolved oxygen was mostly consumed before samples were added to the pipes, copper by-product release was greatly reduced.
- The presence of alginate and gum xanthan lowered pH 7.0 solutions to around pH 6.5 and pH 9.5 solutions to approximately pH 7.0 in a three day stagnation period. These results highlight possible indirect effects of EPS constituents on copper corrosion not previously considered.
- In all cases except one, the presence of organic matter increased copper corrosion by-product release. In one case (gum xanthan, pH 7.0, 20°C) copper by-product release decreased, but this was attributed to undesirable microbial activity. Therefore, in all situations, organic matter had an undesirable effect on drinking water quality as manifested by either higher copper or decreased microbial stability.
- When faced with a copper-by-product release problem, utilities should consider removal of organic matter as a possible remediation strategy.

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