I, Michael E. Lees, hereby submit this original work as part of the requirements for the degree of Master of Science in Geology.

It is entitled:
Corrosion of brass meters in drinking water: the influence of alloy composition and water chemistry on metal release and corrosion scale

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Corrosion of brass meters in drinking water: the influence of alloy composition and water chemistry on metal release and corrosion scale

A thesis submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

Master of Science

in the Department of Geology
of the College of Arts and Sciences
by

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B.S. University of Cincinnati, 2011

Submitted June 2017

Committee Chair: Warren Huff, Ph.D.
ABSTRACT

Brass plumbing components including meters, fittings and valves are used extensively in drinking water distribution systems. Until recently, most in-line brass components contained toxic lead, many of which are still presently in use. Corrosion of brass components leads to the release of metals to drinking water. The primary factors of brass corrosion in drinking water are temperature, alloy composition and water chemistry. In this thesis, a combination of mathematic modeling, analytical techniques and geochemical modeling were used to better understand what causes corrosion in brass components.

A comprehensive model for the release of copper, lead and zinc from brass water meters has been developed. This model provides a framework to evaluate how meter parameters, such as alloy composition and age, influence metal leaching from brass components. When considering brass composition, zinc concentration within the alloy is shown to be the primary factor in copper and zinc release. Brasses with greater than 8 – 9% zinc exhibit more rapid corrosion when compared to brasses with less than 8% zinc. Age was found to have more influence over lead release than alloy composition, with newer meters releasing significantly higher concentrations of lead versus older meters.

In addition to the oxidation of metallic surfaces, corrosion scale formation and dissolution also have a significant impact upon metal concentrations within drinking water. Optical microscopy, X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), were
used to characterize the morphology and mineralogy of corrosion scale in two sets of residential water meters. The meters, which were in service for up to 40 years, came from two locations with contrasting water chemistries; Seattle, with relatively low alkalinity, hardness and total dissolved solids (TDS), and Cincinnati, which has moderate alkalinity, hardness and TDS. Results showed the copper minerals cuprite and malachite, to be most abundant within the corrosion scale from both sources. Lead minerals were much more prevalent within the Cincinnati meters, as were carbonates (both Cu & Pb). In general, the Cincinnati meters contained more substantial and consistent scale coverage whereas coverage on the Seattle meters was patchier and more localized.

Real world use of drinking water systems cycle between flow and periods of stagnation, where water sits quiescently within the system. During stagnation, changes in water chemistry can include metal concentration, solution pH, and oxidation reduction (redox) potential. PHREEQC was utilized to calculate the saturation index (SI) of metallic species with changing water chemistry. The SI values were used to evaluate whether a given mineral will dissolve or precipitate from water during stagnation. These values were compared to the mineralogy identified in the meters to better understand the mechanism of scale development. Changes in redox potential had the most significant effect upon SI values. Minerals present within the scale were found to form under distinctly different conditions suggesting that dissolution and precipitation rates must also be considered.
AKNOWLEDGEMENTS

Foremost, I would like to express my gratitude to my advisor Dr. Barry Maynard for his continued guidance, support and encouragement throughout my graduate studies. I would also like to thank my committee members Dr. Warren Huff and Dr. Andy Czaja for their valuable advice and expertise.

I thank Phillip Hart for his help with the development of mathematical models and Dr. Melodie Fickenscher for assisting with SEM work. To Bill Matulewicz and Dr. Peter Vogt, thank you for funding my graduate studies and encouraging my continued professional development.

Lastly, I would like to thank my parents David and Patricia Lees, and my wife, Autumn, for their continued support and patience.
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Chapter 1: Corrosion of brass water meters connected to copper in drinking water: a model of metal release

Michael Lees, Phillip Hart, J. Barry Maynard

Abstract

Corrosion of service lines and plumbing components and the subsequent release of metallic species to drinking water has been studied extensively due to the wide impact on public health. Copper, lead and zinc are of particular concern due to their extensive use in water distribution systems and potential toxicity. Previous studies have modeled corrosion of these metals from their pure sources while others have considered the impact of alloy composition on the corrosion of new brass plumbing fixtures. We propose a comprehensive model for the release of copper, lead and zinc from brass water meters of varying age tied to copper pipe in residential water distribution systems. The model is based on reaction rates as well as diffusive transport and provides a framework to evaluate how meter composition, age and scale extent impact metal release. The results confirm prior evidence that alloy composition is the primary factor influencing the extent of copper and zinc leaching but also places greater consideration on scale development versus prior studies. The model also provides an overview of dezincification rates over extended time periods in traditional brasses. Lead release is shown to be inversely related to meter age with age having greater influence than alloy composition.
Introduction

Brass alloys have been used in a wide range of applications for centuries owing to the wide availability of their constituent metals and durability. One of the most significant modern day uses of brass is its application in water distribution systems. Brass alloys are comprised of two metals – copper and zinc – mixed in various proportions to permit a wide range of properties. Brasses used for in-line plumbing devices are of the alpha type crystal structure, having less than 38% zinc in solid solution with copper. Additional metals are added to brasses to obtain specific properties such as hardness, strength, conductivity, and corrosion resistance. Lead, a soft and ductile metal, was until 2011 commonly added to plumbing brass at a range of 2 – 8% to aid in machinability. The lead is not present as part of the homogenous alloy but rather as distinct, randomly distributed islands. Because of the toxicity of lead, even in minimal amounts, brass used in water systems must now be “zero lead.” Some brass manufacturers have introduced brasses that contain selenium or bismuth in place of lead. Figure 1-1 shows the structure of brass containing lead through an SEM image in backscatter mode. The brightness within the image is directly proportional to the atomic number of the element with the white spots indicating lead (atomic number 82) and the light grey background indicating the copper/zinc alloy. The overall composition of brass used in plumbing is 60 – 80% copper, 4 – 32% zinc, 2 – 8% lead (or bismuth and selenium) and a balance of iron and antimony or tin and cadmium (Lytle and Schock, 1996).
Oxidation of brass initiates dissolution of metals into the water leaving behind voids in the near-surface region of the metal. Figure 1-2 shows a number of voids within a brass plumbing fixture resulting from leaching of metals. This creates a porous zone which reaches as much as 100 micrometers into the metal in some areas. This porous zone allows water access below the surface of the meter, thereby increasing the area of the metal-water interface. Once these metals have dissolved into the water, they can be carried through the distribution system with the flow of water (i.e. by advection) or by diffusive processes. Alternatively, if the metal ions complex with compounds such as carbonates, oxides or hydroxides to form salts that are supersaturated within the water, they will precipitate out on the surface of the meters as mineral scale.

There have been several mathematical models proposed to define the oxidation and general corrosion of copper pipe in drinking water (Taxen 2012, Vargas 2010, Merkel 2004) as well as lead leaching from lead pipes (Cardew 2006, Van Der Leer 2002, Kuch 1983)). While these do a good job of defining the release of metals from their respectively pure sources, no prior work has been conducted which models the release of all of the major elements in plumbing brasses. In this study, we provide a comprehensive model on the corrosion of brass water meters connected to copper pipe in drinking water. The model reflects the release of copper, lead and zinc downstream through the distribution system.

Exposure to metals found within plumbing fixtures can lead to both acute and chronic health effects. Short term exposure to copper is known to cause gastrointestinal distress and upon long term exposure can lead to liver and kidney damage. Lead can
lead to high blood pressure and kidney problems in adults and has much more severe
effects on children and infants such as delays in mental and physical development (US
EPA 2009). Because of these public health concerns, the United States Environmental
Protection Agency (EPA) has established action levels of 0.015 mg/L for Pb and 1.3
mg/L for Cu in the 90th percentile of water samples (US EPA 1991). This rule states
that if more than 10% of samples taken at the customers tap are greater than these
values, treatment is required. While zinc is undesirable in drinking water due to its
metallic taste, it has not been shown to cause significant health problems at typical
levels. The EPA has set the Secondary Maximum Zinc Contaminant level at 5 mg/L
(US EPA 2009).

There have been several studies carried out to determine the primary factor in
predicting metal release from brass plumbing components. Many of these studies point
to the brass composition or, in particular, the zinc to copper ratio as a significant factor.
Manufacturers of fittings and in-line devices such as valves and meters have often been
the target of litigation which alleges ‘yellow brass’ – containing around 67% copper and
33% zinc – is particularly prone to significant corrosion and subsequent lead release.
Zinc compounds are known to be relatively soluble under drinking water conditions
(Zhou 2017). Dezincification, or the selective leaching of zinc, has long been thought to
be the primary factor in premature failure of brass plumbing fixtures (Joseph 1967,
Horton 1970, Heidersbach 1972). Zinc leaching from the metal leads to a porous
copper skeleton (Marshakov 2005, Langenegger 1965) with high permeability and
allows diffusion of the dissolved metals through both the copper and any overlying scale
that may be present. SEM images of plumbing fixtures not only show the distribution of
lead and voids within the brass but also show differences within the copper-zinc solid solution. Figure 1-3 shows an image of a brass water meter taken in backscatter mode. It is notable that there are different shades of gray which indicate varying ratios of zinc to copper. On the light grey area, machining grooves on the brass can be seen, which indicate minimal alteration. The normal brass has a zinc to copper ratio of 0.209, whereas the darker grey area has a ratio of 0.069. These darker areas indicate the preferential leaching of zinc leaving behind a copper enriched zone which can extend to depths of more than 100 microns from the surface.

Previous work on brass corrosion in drinking water has provided information on the effects of brass composition. For example, Kohler (1996) found duplex brasses, or those with higher zinc content, tend to be more susceptible to dezincification when compared to alpha brasses. Brandl (2009) found that increasing lead content in duplex brasses caused significantly less dezincification through corrosion studies in tap water. Alternatively, Zhou (2017) found dezincification to be much more rapid in low-lead brass compared to lead free brasses which contained zinc and phosphorous. Maas (2002) conducted short term studies which compared new “no-lead” type brass components (0.07% Pb) to traditional alloys (5 – 7% Pb) and found that after 19 days, the leaded brasses were releasing 14 times more lead as the no-lead parts. Lytle and Shock (2000) studied the effect of stagnation time in experiments that ran 160 days and presented graphs that indicate yellow brass (C85400) releases 3.5 times as much zinc as red brass (C84500) and 2.0 times as much copper. On the other hand, lead leached more slowly from the yellow brass, half the amount as from the red brass in 24 and in 72-hour stagnation times. Zhang and Edwards (2011) further explored this reversal
using a set of five duplex brass fittings ranging from 35.4 to 36.6 % Zn and a set of two alpha brass fittings with 8.2 and 10.4 % Zn, all exposed to tap water for 112 days. The duplex brasses leached more than eight times the Zn as the alpha brass, but only one-fourth the Pb. Maynard et al. (2008) and Sandvig et al. (2008) reported on a 370-day leaching study of a set of faucets that ranged from 0.5 to 0.9 in Zn/Cu ratio. After an initial period of about 120 days with erratic Pb releases, the faucets settled into a pattern of higher Pb leaching from brass with lower Zn/Cu ratios (2.5 ug/l for a Zn/Cu ratio of 0.5 to 0.65 compared to 0.5 ug/l for a Zn/Cu of 0.7 to 0.9). No data on Cu or Zn leaching were collected. All three of these studies used new brass. They collectively confirm that, when new, higher Zn brasses had faster Zn releases, but slower Pb releases. In the present study, we examine the effects of Zn/Cu ratios and other parameters on metal leaching from brass water meters of a range of ages, from new to 40 years in service.

**Development of a mathematical model of brass corrosion**

Merkel (2004) has suggested that general copper corrosion is based on three sub-processes of oxidation, scale formation and dissolution. These three sub-processes account for the entirety of the metal transfer within a given system. During stagnation periods, the corrosion process is initially driven primarily by oxidation which leads to rapid metal dissolution. As time progresses, the oxygen is depleted within the system, dissolution reactions slow, and subsequent diffusion processes dominate. We have used Merkel’s copper corrosion model as a starting point for generating a model for corrosion of brass water meters attached to copper tubing. We modified the model to
include Crank’s (1975) first law of diffusion to account for the diffusive transfer of metals through the system.

**The Merkel Equation**

T.H. Merkel’s mathematical model for copper corrosion (Merkel et al. 2004) was derived from pipe rig experiments and literature studies and is based on three sub-processes: oxidation, scale formation and dissolution. Merkel proposed that the concentration of copper within a system is rate limited by reaction kinetics rather than diffusion processes based on an estimation of radial diffusion rates.

Merkel suggested that the primary step in the corrosion mechanism is the oxidation of metallic copper to the cuprous or cupric ion. He showed through the pipe rig experiment that copper oxidation is directly coupled to oxygen depletion with both following first order kinetic rate laws dictated by the chemical reactions. Interestingly, Merkel found through his experiments that at temperatures below 25°C (temperatures ranging from 12°C – 25°C were tested) all dissolved copper was present as the bivalent cupric ion. Therefore, in the mathematical model below, the concentration of the monovalent cuprous ion can be neglected.

Following oxidation of the metallic copper a fraction of the resulting copper will be present within the water as dissolved ions. In his model, Merkel represents this fraction by the symbol $\alpha$. The remaining portion of copper will transfer directly to the solid phase through rapid precipitation or more gradual crystallization leading to the next sub process of scale formation. Merkel found through stagnation experiments that total
dissolved copper rose rapidly to a maximum level then gradually fell to a steady concentration. Merkel states that the steady or equilibrium concentration of total copper is similar to the solubility of the carbonate malachite, the dominant copper mineral at these conditions.

The last sub process of general copper corrosion is the dissolution of existing scales. This sub process occurs as the result of under saturated water with respect to copper minerals and follows first order reaction kinetics. Through experimentation, Merkel found that when considering copper, dissolution is most significant when water is flowing through the system rather than during periods of stagnation.

It is important to remember that all three of these sub processes occur simultaneously and all contribute to total dissolved copper within the system. The rates of each sub process will vary depending on whether water is flowing through the system or whether the system is stagnant and thus different sub processes may be dominant throughout.

The simplified mathematical model for total copper concentration proposed by Merkel is shown by Equation 1.

\[
[Cu^{II}]_t = [Cu^{II}_{eq}] \cdot (1 - \exp[-k_st]) + [Cu^{II}]_0 \cdot \exp[-k_st] + \\
\alpha \cdot [O_2]_0 \cdot \frac{k_{ox}}{k_{ox} - k_s} \cdot (\exp[-k_st] - \exp[-k_{ox}t])
\]

Eq. 1

Where,

\([Cu^{II}]_t = \) total dissolved cupric species at time t (mol/L)

\([Cu^{II}_{eq}] = \) concentration of dissolved cupric species at equilibrium (mol/L)

\([Cu^{II}]_0 = \) initial concentration of cupric species (mol/L)
\[
[O_2]_0 = \text{initial concentration of dissolved oxygen (mol/L)}
\]

\[k_s = \text{time constant of the scale processes (formation or dissolution) (s}^{-1})\]

\[k_{ox} = \text{time constant of copper oxidation (s}^{-1})\]

\[\alpha = \text{molar yield of metal oxidation with respect to dissolved cupric species}\]

**Development of a corrosion model for brass attached to copper**

We have developed a model for brass corrosion based on data from American Water Works Association Research Foundation (AwwaRF) project 3018 which measured the release of copper, zinc, and lead from brass residential water meters over the course of a year. The test rig consisted of six water meters from the Seattle area connected in line with copper pipe. The meters ranged in age from unused up to 40 years in service and also varied in size, shape and metallic composition (Table 1-1). Potable water from Seattle’s Cedar Rapids supply system was used for the experiment. Water was analyzed following stagnation to determine the concentration of metals leached from the plumbing fixtures. In order to reproduce real-world residential use conditions, stagnation times varied from zero to 20 hours. This data was used to develop a mathematical model for brass corrosion coupled to copper piping in drinking water distribution systems. The proposed equations model the release of each metal – copper, lead and zinc – exclusively, in order to determine which properties play a role in the corrosion process.
Copper release from brass water meters connected to copper pipe

The copper release model is based primarily on the Merkel equation for general copper corrosion with several modifications. Since the data obtained was from a system that contained both pure copper pipe and copper as part of the brass water meter, the Merkel equation appears twice. In order to differentiate what fraction of copper was derived from each metal source, ratios of the volume of water contained within the pipe and the meter were normalized and factored into each Merkel equation, respectively. Finally, the initial cupric concentration within the test water was assumed to be zero for simplification and the molar values multiplied by molecular weight to report values in milligrams per liter rather than molar concentrations.

Merkel's notion that diffusive transport is not a significant factor in metal concentration is, strictly, applicable to newer copper components only. In our case, the older meters have considerable scale development, requiring transport through the scale to also be considered. We propose that areas of the meter covered in scale are rate limited by
diffusion rather than reaction kinetics. This has been proposed in previous studies (Feng 1997). Corrosion scales that develop on pipe and meter surfaces create diffusive barriers that impede the transfer of ions resulting in decreased corrosion rates (Awaal 1996). Diffusion coefficients of various dissolved cations can be reduced by nearly an order of magnitude due to the tortuosity of solid components when compared to the same ions at infinite dilution (Li 1974). To account for this, we have added Crank’s (1975) equation for diffusion for the fraction of surface area covered in scale.

Accounting for these modifications, we arrive at the mathematical model for copper release seen in equation 2 below. Note: Concentration is measured in mg/L rather than molarity.

\[
Cu_t = \frac{V_p}{V_p + V_m} * 63.55 * \left( \frac{Cu_{eq} * (1 - \exp[-k_s t]) + \alpha * [O_2]_0 * \frac{k_{ox}}{k_{ox} - k_s} * (\exp[-k_s t] - \exp[-k_{ox} t])}{(1 - S_m) * \left( \alpha * [O_2]_0 * \frac{k_{ox}}{k_{ox} - k_s} * (\exp[-k_s t] - \exp[-k_{ox} t]) + S_m * Cu_{eq} * \left( 1 - \exp\left(-t * \frac{D}{x} * \frac{S_m*A}{V_m}\right) \right) } \right) \\
\text{Eq. 2}
\]

Where,

- \( V_p \) = volume of the pipe (cm\(^3\))
- \( V_m \) = volume of the meter (cm\(^3\))
- \( A \) = internal surface area of the meter (cm\(^2\))
- \( S_m \) = ratio of surface area covered by scale
- \( %Cu_m \) = percent copper within meter alloy
- \( D \) = diffusion coefficient (cm\(^2\)/hr.)
- \( x \) = scale thickness (cm)
Meter composition, geometry and water chemistry were determined to obtain measured values for the parameters in the equation. The composition of brass alloy in each meter was determined by inductively coupled plasma mass spectrometry (ICP-MS). The percentage of copper was utilized within the equation to account for available copper within each meter. After the pipe rig study, scale thickness was measured using microscopy with the extent of scale coverage being estimated visually both with and without the use of a microscope. Oxygen depletion and scale process time constants were estimated by giving the model an acceptable visual fit, then Microsoft Excel Solver was utilized to obtain the statistically optimum values for the unmeasured constants in the equation.

Figure 1-4 below shows both the modelled and measured values for dissolved copper for each of the meters. The model and data numbers in the figure correspond to the meter numbers. It is apparent that copper release in all meters is initially rapid and levels off over time to a steady state or equilibrium concentration. The rapid rise in copper concentration can be attributed to abundant oxygen available within the water. Oxygen consumption within the system is congruent to retardation in copper release. While copper-oxygen reaction kinetics remain unchanged, the concentration of available oxygen is diminished following first order rates. Once all the oxygen (or more accurately all oxidizing agents) within the system has been consumed, some copper is still released through diffusive transport.

Having an optimized equation for copper release for each meter, we then tested for the relative effect of each parameter on the rate of corrosion. Figures 1-5 and 1-6 show the
relationship between meter age and scale development, as measured by scale thickness and areal extent. As would be expected, both parameters are strongly correlated to meter age, lending confidence to the validity of the model. Most parameters, however, do not show strong relationships to properties of the meters (age, composition, source). An exception is the copper oxidation time constant, $k_{\text{ox}}$, which correlates to the amount of zinc contained within the brass alloy of the meters (Figure 1-7). This correlation suggests that the zinc content of water meters plays a significant role in the rate of corrosion with higher zinc concentrations leading to more rapid copper oxidation. Brass water meters containing zinc above 8-9% will exhibit accelerated corrosion when compared to meters with less than 8% zinc (Figure 1-7). Meter age and the time constant of scale processes for copper, $k_s$, showed only a comparatively weak correlation (Figure 1-8). The relationship may be diminished by the variability of scale composition which includes metallic species other than copper minerals.

**Lead release from brass water meters**

Equation 2 was also applied to lead release from each of the meters within the test rig. Since the pipe used in the test rig was pure copper, all of the lead was derived from the meter and thus the pipe term in the equation was omitted. While total lead leached from the meters was two orders of magnitude lower than copper, the curves followed a similar shape.

Lead release is initially rapid over shorter stagnation times with abundant oxygen available within the system (Figure 1-9). As oxygen levels deplete, lead release is relatively stable with only minor contributions from diffusive transport through the scale.
and water contained within the meter. For all meters, except for meter 1, this occurs around 10 hours of stagnation. The distinct shape of the curve in meter 1 is not fully understood but may be explained by the physical exposure of one of the lead islands to the water over the 20-hour stagnation period resulting in a spike of lead oxidation.

Meter 6, an unused meter up until testing, shows the highest lead leaching values in those tested (Figure 1-9). This supports the idea that corrosion scales formed over time act as a physical barrier and prevent corrosive ions such as oxygen and chlorides from reaching the metallic surface. Meter 5 is also an unused meter and shows the lowest dissolved lead levels following extended stagnation, however this is to be expected as this meter is the no-lead brass type. Meter 4, the oldest meter in the rig, shows a curve similar to that of the no-lead brass meter with total dissolved lead being significantly lower than the younger traditional brass type meters.

Figure 1-10 shows a plot of lead release after 6-hour stagnation periods versus meter age. Meter 5 has been omitted from this data set since it is of the no-lead brass type. This figure shows an inverse relationship with the youngest meter releasing more than 6 times the amount of lead as the oldest meter. This provides evidence that meter age and scale formation play a significant role in lead contamination in drinking water and that diffusion must be considered when investigating release rates.

Looking at the effect of meter composition on lead release rates did not uncover any substantial relationships. We did not find a correlation between zinc content and metal release as previous studies have done. This is likely the result of our data set containing meters of considerable age variation, where previous studies have looked
explicitly at new plumbing fixtures. The lack of correlation provides additional support for scale development and coverage being a principal factor controlling corrosion mechanisms.

Zinc release from brass water meters

Modeling zinc release with the new equation (Eq. 2) was attempted with limited success. Fundamentally, zinc is more reactive and more soluble than copper and lead in potable water systems and thus there is reason to believe it behaves differently. The relative solubility of zinc is supported by the fact that there is minimal zinc present within the scale mineralogy where copper and lead compounds can be found in abundance. Since zinc solubility is so high in residential water distribution systems, both scale processes of dissolution and precipitation (or crystallization) can be neglected. We propose a novel model for zinc corrosion that is transport dominant rather than controlled by reaction kinetics.

In order to understand the model, we must first step back and consider cycles of flow and stagnation. When the faucet is open and water is flowing through the distribution system, there is an abundance of oxygen present throughout the water body and in contact with the meter. When the faucet is turned off we begin a period of stagnation where the water stops flowing. At this time, there is oxygen available throughout the zinc depleted layer and in contact with metallic zinc which will rapidly oxidize the zinc to the divalent species. The dissolved zinc concentration within the water is rate limited by zinc diffusion through the zinc depleted layer. Zinc leaching rates follow this mechanism until enough oxygen has been depleted from the system that it is no longer
available within the zinc depleted layer in order to react with the metal. This leads to a
gradient of oxygen concentration in the water being high in the center of the meter and
negligible at the water-meter interface. At this time, which we have called t-critical,
oxygen must diffuse from the water body through the zinc depleted layer prior to
reaching and reacting with metallic zinc. After t-critical, zinc leaching is significantly
retarded due to its rate limiting mechanism of both oxygen diffusion into the zinc
depleted layer and zinc diffusion out of the layer.

Equation 3 below represents zinc corrosion prior to time t-critical. This equation uses
the term \( \text{Zn}_{eq} \), or zinc at equilibrium, which was determined by modelling zincite
saturation indices using PHREEQC model from the US Geological Survey with the
MINTEQ database. Equation 4 represents zinc release prior to time t-critical and uses
the term \( \text{Zn}_{ss} \), or zinc at steady state, which is different from zinc at equilibrium. A
different term was required due to the high solubility of zinc compounds leading to the
model significantly over-estimating the zinc concentration at longer stagnation periods.
Zinc at steady state was estimated using an extrapolation from the overall curve trend.
In both equations, the diffusion coefficients are modified by the tortuosity constant \( \tau \)
which was estimated from Li and Gregory (1974). It is important to note that the x term
below represents the thickness of the zinc depleted layer rather than the thickness of
scale as it did in the above equations.
\[ Zn_t = \frac{\tau * D_{Zn} * Zn_{eq}}{V_m / A * x * k_{ox}} * (1 - e^{-k_{ox} * t}) \]  

Eq. 3

\[ Zn_t = \frac{\tau * D_{Ox} * Zn_{ss}}{V_m / A * x * k_{ox}} * (1 - e^{-k_{ox} * t}) \]  

Eq. 4

Figure 1-11 shows the modeled and measured values for zinc release versus stagnation time in the Seattle test rig. It is evident that time t-critical for all meters occurs between one and two hours of stagnation as indicated by the sharp change in curve shape from rather linear to more logarithmic. The modeled and measured values for all meters follow the same general trend with the exception of meter 1 which shows the lowest slope until time t-critical and then the highest slope of all meters tested after time t-critical.

Having an optimized model for zinc corrosion allows us to consider meter parameters that contribute to release rates. As one would expect, we see a strong relationship between meter age and the thickness of the zinc-depleted zone. The correlation is linear positive suggesting that dezincification is a consistent process that treats both young and old meters indifferently. However, the time-averaged zinc-depleted zone thickness, which effectively provides a rate, has a different relationship with meter age. Dezincification is considerably more rapid in younger meters with rates slowing down exponentially over time (Figure 1-12). The zinc depleted zone was not actually measured but rather determined by visual best fit of the measured values. This gives merit to the validity of the model since age is not a term used in the equation and dezincification rates have been previously shown to decrease over time (Zhou 2017).
There is also a relationship between the zinc oxidation time constant and the amount of zinc within each meter (Figure 1-13). This correlation might seem obvious since we are dealing with zinc oxidation in a zinc containing alloy. When looking at oxidation time constants for copper, however, they did not correlate with the copper content within the alloy, but rather with zinc content. Once again, as we approach greater than 9% zinc content, zinc release during extended periods of stagnation is significantly accelerated.

Looking at the standard electrode potentials for copper, lead and zinc gives us some understanding of why zinc is the primary factor driving corrosion when considering alloy composition. Table 1-1 shows the standard electrode potentials for the reduction half reaction of each metal. Reversing the reactions indicates that oxidizing zinc from its metallic form to the divalent species requires the least amount of energy of the three. This tells us that when conditions are constant, zinc oxidation is the most favorable among the metals listed. Copper will favorably accept electrons and is thus an oxidizing agent whereas lead and zinc are reducing agents. In fact, the cupric ion can oxidize other metals such as zinc further catalyzing corrosion within the distribution system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^o$ Volt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Zn}^{2+} + 2e^- \leftrightarrow \text{Zn(s)}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} + 2e^- \leftrightarrow \text{Pb(s)}$</td>
<td>-0.13</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu(s)}$</td>
<td>+0.34</td>
</tr>
</tbody>
</table>

Table 1-2: Standard Electrode Potentials at 25°C. Source: Snoeyink and Jenkins, Water Chemistry 1980.
Conclusion

The present study provides mathematical models for the release of copper, lead and zinc in residential brass water meters attached to copper. The model incorporates kinetic rates of chemical reactions, scale processes of formation and dissolution and the diffusive transfer of metal species. The model provides a framework to help understand how meter parameters such as alloy composition and age affect the release of metals to drinking water. The results outlined in the present study strongly support prior evidence that when considering alloy composition, the main contributor to brass corrosion within in-line plumbing fixtures in residential water distribution systems is the zinc content. The oxidation time constants for copper and zinc were directly correlated with the zinc content of the meters. Brass alloys containing greater than 8 – 9% zinc are subject to accelerated corrosion rates when compared to alloys containing less than 8% zinc.

The model also supports previous work that shows dezincification is rapid in newer plumbing fixtures with rates slowing down exponentially with time. Dezincification leads to a porous copper skeleton, allowing oxygen and additional oxidizing agents access to metals below the meter surface. Once oxidized, metal cations are free to diffuse through overlying scale and into the water column. Zinc oxidation kinetics are so rapid that zinc leaching rates are transport limited with diffusion of oxygen and Zn\textsuperscript{2+} as rate limiting processes. The solubility of zinc in potable water systems leads to negligible re-precipitation as corrosion scale and ensures that zinc will flow with water as it leaves the system.
Copper and lead on the other hand undergo a more complex corrosion process which includes scale formation and dissolution. The leaching rates of these metals are rate limited by reaction kinetics in areas not covered by scale, or diffusion processes in areas containing scale coverage. The present study shows that lead release rates are not related to meter composition in tradition brasses; instead rates are inversely related to meter age with newer meters leaching significantly higher levels of lead. Therefore, scale coverage must be considered when determining treatment options as well-developed scale may play a greater role in reducing lead contamination than does alloy composition in traditional brasses.

Reference


Figure 1-1: SEM image of polished brass using backscattered electron detector. White spots indicate lead ‘islands’ within Cu/Zn alloy. Source: Maynard 2008
Figure 1-2: SEM backscatter image of the interior edge of a brass plumbing device. Dark spots indicate voids leading to a porous zone near the surface. Source: Maynard 2008

Figure 1-3: SEM backscatter image showing zinc depleted areas in brass. Note machining marks on light grey area showing little alteration.
Figure 1-4: Modeled total copper (lines) values and measured (points) values vs. stagnation time. Seattle test rig.

Figure 1-5: Plot of scale thickness vs. water meter age shows positive linear relationship.
Figure 1-6: Plot of scale coverage vs. water meter age. Scale coverage is a normalized ratio of surface area.

Figure 1-7: Plot of copper oxidation time constant vs. brass alloy zinc content.
Figure 1-8: Plot of scale processes time constant vs. meter age.

Figure 1-9: Modeled total lead (lines) values and measured (points) values vs. stagnation time. Seattle test rig.
Figure 1-10: Plot of lead release after 6-hour stagnation periods versus meter age.

Figure 1-11: Modeled total zinc (lines) values and measured (points) values vs. stagnation time.

Seattle test rig.
Figure 1-12: Plot of time averaged zinc depleted zone thickness vs. meter age

Figure 1-13: Plot of zinc oxidation time constant vs. meter zinc content
Dissolution of pre-established corrosion scale can be a significant source of metal leaching in drinking water distribution systems. The primary sources of lead within drinking water are older lead service lines and in-line brass plumbing fixtures. Previous laboratory studies have shown that specific water quality variables can influence the formation or dissolution of corrosion products. The present study uses optical microscopy, X-ray diffraction, Raman spectroscopy, and scanning electron microscopy with energy dispersive X-ray spectroscopy to characterize corrosion scale mineralogy and morphology from brass water meters. Two sets of residential meters which were exposed to contrasting water chemistries were investigated to determine how water quality influences scale development over many years of service.

Introduction

Corrosion of metals in drinking water has been of significant concern recently but is by no means a novel issue. One of the primary factors influencing the rate and extent of metal corrosion is water chemistry. While this subject has been studied for decades, the number of variables and their seemingly random interaction leaves us with only limited understanding. In order to better comprehend what factors lead to enhanced corrosion and metal release in residential water distribution systems, the scale mineralogy and morphology must be considered. While oxidation reactions of metallic
surfaces will leach metals into the water, dissolution of existing scale can also be a significant contribution source (Kim 2010, Xie 2011, Noel 2014, Mohammadzadeh 2015).

Since many household plumbing fixtures are made of copper or alloys thereof, much of the corrosion scale within residential drinking water systems is comprised of copper compounds. Some of the common minerals include cuprite ($\text{Cu}_2\text{O}$), tenorite ($\text{CuO}$), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) and cupric hydroxide ($\text{Cu(OH)}_2$) (Lagos 2001, Schock 1995, Edwards 1996). Mineral formation is dependent on the concentration and speciation of compounds present within the water, solution pH and the oxidation reduction (redox) potential, with small variations having significant impacts upon corrosion products (Huang 2016, Broo 1997). Shim (2004) found through long term corrosion experiments, that cuprite was the most dominant copper oxide present after 100 days in moderately hard water. Merkel (2002) found the copper oxide, cuprite, and the copper carbonate, malachite, to be the primary scale minerals on copper surfaces. Merkel also suggests that dissolved copper within the water is dictated by malachite equilibrium concentrations in long term stagnation periods. Numerous studies show that copper concentration within drinking water will reach a maximum concentration based on equilibrium with the meta-stable cupric hydroxide and then decrease as more stable minerals precipitate (Broo 1997, Merkel 2002).

Lead compounds present within scale must also be considered since lead distribution lines remain upstream from residential properties and many brass plumbing fixtures commonly contain lead. The most common lead minerals found in drinking water systems are the oxides plattnerite ($\text{PbO}_2$) and litharge ($\text{PbO}$), and the carbonates
cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)₂) (Maynard 2008). Additional lead phosphate compounds are less common but possible, especially in municipalities that use a phosphate corrosion control program. Again, the type of lead mineral formed will be greatly dependent upon the pH-pe relationship (Lytle 2005, Xie 2010). Lytle (2005) showed that plattnerite (Pb⁴⁺) will form in drinking water if free chlorine levels remain above 1 mg/L but that reversion to cerussite (Pb²⁺) occurs as chlorine levels drop. Xie (2010) shows that plattnerite dissolution rates will decrease with the addition of disinfectants with higher redox potentials giving lower rates. Previous studies have also demonstrated that lead carbonate dissolution is greatly impacted by alkalinity, with lower alkalinity solutions being more aggressive to the lead carbonates (Mohammadzadeh 2015).

Zinc is generally soluble in drinking water conditions and thus is not typically found in significance in the corrosion scale. Zhou (2017) found very little solid zinc corrosion products on the surface of new brasses through dissolution studies in synthetic tap water.

The present study outlines existing knowledge of how water chemistry influences corrosion scale mineralogy and investigates whether results from laboratory experiments are applicable to real world water distribution systems. This study considers corrosion scales formed in measurably different water chemistries to determine the extent of scale variation as a result of water quality. This is accomplished through the characterization of mineralogy and morphology of residential drinking water meters using complementary analytical techniques some of which have not been used extensively in brass corrosion applications.
Materials and Methods

Two sets of water meters from differing geographical locations were analyzed to determine any differences in scale composition due to exposure to different water chemistries. One set of meters was obtained from Seattle, Washington, which gets its drinking water supply from two sources: the Cedar River and the South Fork Tolt River watersheds. Both of these rivers originate in the mountains of the Cascade Range east of Seattle. Table 2-1 shows the average water quality of Seattle drinking water (SPU 2010a, 2010b) as it leaves each of the treatment sites. The water is generally low in total dissolved solids, alkalinity and hardness as well as chloride and sulfate, two anions which are known to be corrosive to copper (Lytle 2008). Seattle uses chlorine as disinfectant in its drinking water. Fenkel (1999) found corrosion scale on brass plumbing fixtures from Seattle, WA to be comprised primarily of malachite and hydrocerussite.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cedar</th>
<th>Tolt</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.2</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.4</td>
<td>0.07</td>
<td>NTU</td>
</tr>
<tr>
<td>TDS</td>
<td>40.8</td>
<td>38.8</td>
<td>mg/L</td>
</tr>
<tr>
<td>TOC</td>
<td>0.9</td>
<td>1.3</td>
<td>mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>20.2</td>
<td>19.2</td>
<td>mg/L (as CaCO3)</td>
</tr>
<tr>
<td>Hardness</td>
<td>26.9</td>
<td>27.4</td>
<td>mg/L (as CaCO3)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.84</td>
<td>0.84</td>
<td>ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>3.6</td>
<td>2.8</td>
<td>mg/L</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.95</td>
<td>1</td>
<td>mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.02</td>
<td>0.13</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1.4</td>
<td>1.9</td>
<td>mg/L</td>
</tr>
<tr>
<td>Phosphate</td>
<td>1.6</td>
<td>2.2</td>
<td>ug/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>1.9</td>
<td>1.32</td>
<td>mg/L</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.26</td>
<td>0.14</td>
<td>mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.94</td>
<td>0.37</td>
<td>mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>9.2</td>
<td>10.4</td>
<td>mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>66</td>
<td>41</td>
<td>ug/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>3.4</td>
<td>0.7</td>
<td>ug/L</td>
</tr>
</tbody>
</table>

The second set of meters was obtained from Cincinnati, Ohio, which also gets its drinking water supply from two sources. The Miller Plant is located on the Ohio River and is the primary supply of drinking water to the city. A second source for Cincinnati drinking water is from the Bolton Wellfield which is located on the Great Miami Aquifer. Table 2-2 below shows the average water quality of Cincinnati drinking water (GCWW 2010) for each of the treatment plants. Drinking water in Cincinnati contains much higher levels of total dissolved solids, alkalinity and hardness when compared with Seattle’s water supply. Levels of chloride and sulfate are at least an order of magnitude higher. Cincinnati treatment facilities also use chlorine for disinfection in drinking water.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Miller</th>
<th>Bolton</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.6</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.07</td>
<td>0.05</td>
<td>NTU</td>
</tr>
<tr>
<td>TDS</td>
<td>238</td>
<td>267</td>
<td>mg/L</td>
</tr>
<tr>
<td>TOC</td>
<td>0.88</td>
<td>0.74</td>
<td>mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>79</td>
<td>75</td>
<td>mg/L (as CaCO3)</td>
</tr>
<tr>
<td>Hardness</td>
<td>138</td>
<td>151</td>
<td>mg/L (as CaCO3)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.26</td>
<td>1.15</td>
<td>mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>38</td>
<td>68</td>
<td>mg/L</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.97</td>
<td>1.08</td>
<td>mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.82</td>
<td>0.98</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>76</td>
<td>55</td>
<td>mg/L</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.23</td>
<td>0.15</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>28</td>
<td>31</td>
<td>mg/L</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.8</td>
<td>1.8</td>
<td>mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>9</td>
<td>20</td>
<td>mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>41</td>
<td>27</td>
<td>mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt;10</td>
<td>&lt;20</td>
<td>ug/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;10</td>
<td>&lt;1</td>
<td>ug/L</td>
</tr>
</tbody>
</table>

Table 2-2: Water quality results for Cincinnati drinking water. Source: Greater Cincinnati Water Works 2010 Annual Report

The present study used the following methods to characterize corrosion products. Each water meter was cut using a reciprocating saw equipped with fine-tooth metal cutting blades. A new blade was used for each meter to avoid contamination among samples. The pieces were cut so they could be mounted or inserted into each instrument accordingly.

**Optical Microscopy**

Corrosion scale was inspected primarily using an Olympus BX60 microscope with reflected light. This microscope was equipped with 4x, 10x, 20x, and 40x dry objectives. Images were captured using an Olympus SC50 camera connected to a PC. Some regions of the samples were difficult to photograph in focus due to the
inconsistent relief of scale surface. For those regions, the Process Management function in the cellSens software package (Olympus, Inc., Shinjuku, Japan) was used to make Z-stack compositions, which combines images taken at multiple focal planes. Additional images were captured using an Olympus SZ61 stereo microscope equipped with an Olympus DP73 camera.

**X-Ray Diffraction**

The corrosion scale for each meter was analyzed for mineralogy using a Rigaku XRD Ultima IV X–Ray Diffraction System. Pieces of the meter were mounted on various slides using molding putty in order to prepare a flat surface for analysis. Samples were scanned from 0 – 70 degrees 2-theta with a step size of 0.02 degrees and analysis time of 2 seconds per step. Analysis cycle time lasted just under 2 hours per sample. Data was then transferred to a PC and was analyzed using Jade software and the RRUFF.info spectral database. Spectra were converted into Adobe Illustrator .ai file type for publishing. The X-Ray diffraction patterns are all dominated by metallic brass since the scale was not removed from the meter. The reader should focus on the smaller mineral peaks which are labeled. The d-spacing values for peaks are listed in parenthesis in figure captions.

**Scanning Electron Microscopy with Energy-dispersive X-ray spectroscopy**

To obtain hi-resolution images as well as elemental data, a Philips XL-30 FEG Environmental Scanning Electron Microscope (SEM) was utilized. Images were captured using 30kV excitation voltage. This instrument was equipped with energy-dispersive X-ray (EDX) spectroscopy to determine the elemental composition of
corrosion scale. Data was obtained using the SEM in both secondary electron and backscatter electron detectors.

**Raman Spectroscopy**

Raman spectra were obtained with two different systems. Some spectra were collected using a Horiba T64000 Raman spectrometer (Horiba, Inc., Edison, NJ) equipped with a 5 volt Innova 90C FreD Ar+ laser (Coherent, Inc., CA). Point spectra were acquired using a 50x long working distance objective (NA=0.50) with a laser wavelength of 458 nm. The majority of Raman data were obtained using a Renishaw InVia Raman Microscope located in the University of Cincinnati Chemical Sensors and Biosensors facility. The best results were obtained by collecting point spectra using a 633-nm helium-neon laser and a 50x dry objective. Data was obtained over a range of ~100 to ~2000 cm⁻¹.

**Results**

**Seattle Meters**

The first set of meters is from Seattle and is the same set of meters used in the pipe rig study for metal release modelling in Chapter 1. These meters range in age from unused (prior to testing) to 40 years in service.

**Meter 1**

Meter 1 from manufacturer A was in service for 26 years. This meter has a brass composition of 83.6% copper, 4.5% zinc, and 5.0% lead with a balance of iron, antimony and iron. The zinc to copper ratio is 0.054. The majority of the inside of the
meter is covered in a thin white film (Figure 2-1) which appears to sit on top of the corrosion scale. Below the white film there are areas of green-grey and yellow scale minerals.

SEM images (Figure 2-2) show the thin white film to be the siliceous frustules of diatoms (Maynard 2008). The frustules average 10 - 15 microns in length and 3 microns wide. Raman spectra (Figure 2-3) confirm the presence of diatomaceous silica with characteristic peaks at 493 cm\(^{-1}\) and 607cm\(^{-1}\) (Yuan 2004) but also show the presence of residual organic material.
The scale beneath the diatoms contains the copper oxide cuprite as well as the copper carbonate malachite, as measured in a diatom-free region. This was confirmed in both Figure 2-3: Raman spectra of diatoms on meter 1. Broad peaks at 1300 cm\(^{-1}\) to 1600 cm\(^{-1}\) are indicative of residual organic material. Data obtained using 458 nm laser.

Figure 2-2: SEM image of diatoms on meter 1. Source: Maynard 2008
XRD (Figure 2-4) and Raman spectroscopy (Figure 2-5). EDX analysis also shows minor amounts of iron oxide.

![Microscopic image of green and brown corrosion scale](image1)

**Figure 2-4:** Microscopic image of green and brown corrosion scale (left) on meter 1. X-ray diffraction pattern (right) indicates this to be a mix of cuprite (2.47, 3.02) and malachite (2.86).

![Raman spectra](image2)

**Figure 2-5:** Raman spectra of green and brown scale on meter 1 confirms cuprite and malachite mineralogy. Data obtained using 633 nm laser.
**Meter 2**

Meter 2 from manufacturer B was in service for 19 years. This meter has a brass composition of 80.1% copper, 7.9% zinc, and 6.8% lead with a balance of iron and antimony. The zinc to copper ratio is 0.099. The inside of this meter is mostly covered in a green-brown scale as seen in Figure 2-6. XRD (Figure 2-7) and Raman (Figure 2-8) analysis show this scale to be cuprite. Similar to meter 1, this meter contains a white film that sits overtop of the corrosion scale. The white film is not as extensive as in meter 1. SEM imaging again confirms this film to be diatom frustules. EDX analysis also shows minimal lead oxide.

![Figure 2-6: Photograph and micrograph showing scale coverage on Meter 2 from Seattle.](image-url)
Figure 2-7: Meter 2 X-ray diffraction shows the presence of cuprite (2.47, 1.51) and possible silica (3.06).

Figure 2-8: Raman shifts confirm cuprite to be the primary scale mineral on meter 2. Data obtained using 458 nm laser.
**Meter 3**

Meter 3, also from manufacturer B, was in service for 4 years. The meter has a brass alloy composition of 80.9% copper, 8.8% zinc, and 7.0% lead with a balance of iron and antimony. The zinc to copper ratio is 0.108. Scale coverage for this meter is not as homogenous as the previous two meters and is mostly brown with patchy areas of green and white. The patchy scale coverage tends to follow the grooves of the meter. Figure 2-9 shows the patchy distribution of scale as well as close up images of various minerals. The X-ray diffraction pattern (Figure 2-10) shows the majority of scale to be cuprite and also designates the green mineral to be malachite. SEM indicates an abundances of copper oxide and carbonate with some lead oxide. The white scale (Figure 2-11) was determined to be the lead carbonate cerussite by the characteristic Raman CO$_3^{2-}$ stretching vibration at 1053 cm$^{-1}$ (Brooker 1983, Martens 2004). This shift has also been reported at 1054 cm$^{-1}$ in the literature (Couture 1947).
Figure 2-9: Photograph (top left) and micrographs of meter 3. Note the patchy nature of the scale. Micrographs show distribution of green malachite (bottom left) and cuprite.
Figure 2-10: Meter 3 X-Ray diffraction pattern shows presence of abundant cuprite (2.47, 1.51, 3.02) and some malachite (2.86).

Figure 2-11: Micrograph of white lead carbonate cerussite on meter 3.
Meter 4

Meter 4 from manufacturer C is the oldest meter in the set being in service for 40 years. The alloy composition is 79.4% copper, 9.6% zinc, and 6.5% lead with a balance of iron. The zinc to copper ratio is 0.121 – the highest of the Seattle set. The inside of this meter is almost entirely covered by extensive areas of dark brown and tan colored scale with blotches of white and green. The X-ray diffraction pattern (Figure 2-15) indicates that copper is present as both oxides, cuprite and tenorite. Visual and microscopic inspection (Figure 2-13, bottom right) also show a green mineral, likely the carbonate malachite. In some areas, there are small round islands of the cupric sulfate, brochantite. Figure 2-13 shows these bright blue minerals are exclusively in areas dominated by the dark brown cuprite with intermixed tenorite. Figure 2-14 shows SEM
image and EDX analysis of complex mineral aggregate containing copper, lead, and iron oxides. The X-Ray diffraction pattern (Figure 2-15) and Raman spectra (Figure 2-16) also indicate quartz present within the scale.

Figure 2-13: Photograph (top left) and micrographs of meter 4. The blue mineral brochantite appears in areas dominated by cuprite with some tenorite intermixed.
Figure 2-14: Meter 4 SEM image (left) and EDX analysis (right) of copper, lead, and iron oxides. EDX shows 13% Cu, 11.5% Fe, 9% Pb, 16% Si, & 25% O by weight. Source: Maynard 2008

Figure 2-15: XRD pattern for meter 4. Peaks indicate an abundance of tenorite (1.87, 2.32, 2.22) with additional quartz (3.35) and some cuprite (1.51, 2.47).
Meter 5

Meter 5 from manufacturer D was a new meter prior to testing which was never used in service. This is the only meter in the set comprised of the newer no-lead brass. The alloy composition was analyzed to contain 90.0% copper, 5.7% zinc, and 1.7% bismuth with a balance of selenium. Although this is of the no-lead brass type, it did analyze to contain 0.03% lead. The zinc to copper ratio is 0.063. Visually, this meter does not appear to have undergone significant corrosion. Figure 2-17 shows the tan-bronze color across all wetted surfaces. There is no substantial scale present beyond a thin layer of the copper oxide, cuprite as determined by X-ray diffraction (Figure 2-18) and Raman spectroscopy (Figure 2-19).
Figure 2-17: Photograph (left) and micrograph (right) shows little corrosion on meter 5.

Figure 2-18: X-ray diffraction pattern of meter 5 only shows the presence of cuprite (2.47, 1.51).
Meter 6

Meter 6 from manufacturer B was also a new, unused meter prior to testing. This meter is of the traditional brass type with a composition of 79.0% copper, 8.2% zinc, and 6.7% lead with a balance of iron and bismuth. Unlike meter 5, this meter appears to have undergone moderate corrosion with extensive areas of white patchy scale. Figure 2-20 shows a micrograph of the white scale as well as an SEM image with the characteristic plate-like mineral structure of hydrocerussite (Liu 2009, Korshin 2000). The X-Ray diffraction pattern (Figure 2-21) also shows the presence of copper minerals cuprite and malachite, as well as the iron oxide hematite. Raman analysis uncovered prominent peaks at 1371 & 1401 cm⁻¹ (Figure 2-22) which were not able to be identified through the literature.

Figure 2-19: Raman spectra indicate brass with minimal cuprite coverage. Small shoulder at 215 cm⁻¹ and broad peak around 600 cm⁻¹ indicate more than simply brass present on meter 5. Data obtained using 633 nm laser.
Figure 2-20: Photograph (top), micrograph (left) and SEM image of meter 6 showing patchy white scale comprised of the lead carbonate hydrocerussite. Plate-like minerals in SEM image are characteristic of hydrocerussite.
Figure 2-21: XRD pattern for meter 6 indicates presence of cuprite (2.47, 1.51), malachite (2.86), hematite (2.63, 3.37).

Figure 2-22: Unidentified Raman shifts of grey material on meter 6. Peaks at 1371 & 1401 cm⁻¹. Data obtained using 633 nm laser.
**Cincinnati Meters**

The Cincinnati meters were all removed from service at the same time and, while we do not know absolute ages, were in use for similar time frames. These meters were analyzed by ICP to determine the alloy composition. Unfortunately, the results for the major elements within the alloy were above the detection limit of the instrument. A request to each of the meter manufacturers regarding alloy content of the major elements went unanswered. While alloy composition would have added to the dataset, it was not necessary for this study since the goal was to determine how water quality effects scale formation and mineralogy. All of these meters are of the traditional brass type containing at least 5% lead in addition to copper and zinc.

**Meter 7**

Meter 7 was from manufacturer E. Besides copper, zinc and lead, the alloy composition is balanced with iron and nickel. The wetted surfaces of the meter are entirely covered in brown and green scale as seen in Figure 2-23. The scale is mostly uniform across the entire surface of the meter with patchy areas of white scale. Raman analysis (Figure 2-24) designates cuprite to be dominant with XRD patterns (Figure 2-25) also showing the presence of malachite and quartz with minimal tenorite. Figure 2-26 shows an SEM image with EDX analysis confirming the background to be dominated by cuprite and malachite with minimal iron oxides and the white spots indicating lead oxide.
Figure 2-23: Photograph (left) and micrograph (right) of meter 7 from Cincinnati. Note the consistent coverage which contains brown-grey cuprite and green malachite.

Figure 2-24: Raman pattern for meter 7 indicates cuprite as the primary mineral scale. Data obtained using 633 nm laser.
Figure 2-25: XRD pattern for meter 7 shows cuprite (2.47), malachite (2.86), quartz (3.35) and minor tenorite (2.32).
Figure 2-26: SEM image (top) and EDX analysis of scale on meter 7. Grey background is a mix of copper oxides and carbonates with white spots of lead oxide.
**Meter 8**

Meter 8 was from the same manufacturer as the no-leaded meter 5 in the Seattle set. In contrast to the Seattle meter, this alloy is of the traditional brass type with analysis showing at least 5% lead. The balance of minor elements is phosphorous, antimony and iron. This meter has dark brown to black scale with small islands of red and green minerals randomly distributed. Figure 2-27 shows the entire wetted surface corroded with scale and the immense variety of color representing diverse mineralogy. Bulk mineralogy is primarily cuprite, malachite and tenorite with some hematite as indicated by X-Ray diffraction (Figure 2-28). EDX analysis also designates the presence of lead oxide, likely plattnerite (Figure 2-29) and lead carbonate. SEM imaging (Figure 2-30) also shows substantial variation in scale morphology tied to differences in mineral assemblages. Figure 2-31 shows significant fluorescence interfered with the Raman signal, which was a common issue encountered with the Cincinnati meters. The broad bands near 1350 and 1600 cm\(^{-1}\) are typical for aromatic carbon stretching vibrations and suggest an organic carbon component that is potentially producing the fluorescence background.
Figure 2-27: Photograph (top) and micrographs of scale on meter 8. Green areas are the copper carbonate malachite intermixed with cuprite, tenorite, hematite and some cerussite.

Figure 2-28: XRD pattern shows bulk mineralogy to be primarily cuprite (2.47), tenorite (2.32) malachite (2.86), and hematite (2.69)
Figure 2-29: SEM image and EDX analysis shows a mix of copper and lead oxides in meter 8.
Figure 2-30: Additional SEM image and EDX results for meter 8 show the bright spots to be the lead oxide plattnerite intermixed with copper and lead carbonates. Note the varying texture of scale.
Meter 9

Meter 9, from manufacturer F, has a minor element balance of nickel, phosphorous, and iron. As with the other meters from Cincinnati, the inner surface is completely covered in scale (Figure 2-32). The scale is primarily dark brown to black with areas of tan and green. EDX designates a mix of copper and lead oxides with some copper carbonate. In addition, there are patches covered in white scale and Raman spectra indicate it is the lead carbonate cerussite (Figure 2-33). The X-ray diffraction pattern (Figure 2-34) indicates the scale to contain abundant cuprite with some hematite.

Figure 2-31: Laser induced fluorescence as seen by Raman analysis of meter 8. Data obtained using 633 nm laser.
Figure 2-32: Photographs (top) of meter 9 show complete coverage of wetted surface in dark brown and tan scale. SEM (bottom) indicates a mix of copper and lead oxides and copper carbonate.
Figure 2-33: Micrograph (top) showing white patchy scale of lead carbonate cerussite as determined by Raman shift at 1053 cm$^{-1}$. Data obtained using 633 nm laser.
**Meter 10**

Meter 10, from manufacturer G, was also of the traditional brass type with a minor element balance of nickel, iron and antimony. As with the other meters from Cincinnati, Figure 2-35 shows this meter was entirely covered in tan to dark brown scale with small areas of green. The X-ray diffraction pattern (Figure 2-36) shows that the majority of the scale contains cuprite and hematite with some tenorite and malachite. In some very localized areas of the scale there are small geode-like structures of red prismatic crystals within pockets of a blue-green mineral (Figure 2-37). Raman spectra of the red prismatic crystals indicate they are cuprite (Figure 2-38) and the blue-green mineral is the copper sulfate brochantite (Figure 2-39). Figure 2-40 shows an SEM image that
illustrates botryoidal malachite along with small crystals of copper oxide – likely cuprite.

SEM also shows the presence of lead oxides and carbonates (Figures 2-40, 2-41).

Figure 2-35: Photographs of meter 10 show complete coverage of dark brown scale with patchy areas of green.

Figure 2-36: XRD pattern of meter 10 shows cuprite (2.47) and hematite (2.69) with some tenorite (2.32) and minimal malachite (2.86).
Figure 2-37: Micrographs of meter 10 show red prismatic cuprite crystals surrounded by blue-green enclosures of brochantite.

Figure 2-38: Raman spectra confirms the red prismatic minerals to be the copper oxide cuprite. Data obtained using 633 nm laser.
Figure 2-39: Micrograph (top) and Raman activity of the blue-green mineral brochantite. Data obtained using 633 nm laser.
Figure 2-40: SEM image (top) and EDX analysis of meter 10. Area 1 is the copper carbonate malachite and area 2 copper oxide.
Discussion

Morphology

Overall, the Cincinnati meters contained scale which was thicker, denser and more extensive than the meters from Seattle. All of the internal wetted surfaces of the Cincinnati meters were entirely covered in substantial scale with no exposure of metallic brass. The scale on the Cincinnati meters was also more homogenous with a consistent appearance across all surfaces whereas the Seattle meters showed a much patchier scale with spatial variations in mineralogy (see Figures 2-23, 2-27 & 2-32 and Figures 2-9 & 2-13, respectively).

A few of the Seattle meters showed scale variability which followed the geometry of the meter curves or grooves (see Figures 2-9 & 2-20). This is evidence of a physical factor in scale development affecting morphology by erosion of scale by the flow wheel. In
some cases, mineralogy also appears to follow meter geometry indicating localized areas of variable water chemistry likely due to differences in flow velocity. Nawrocki (2009) discusses this idea of steady water in corroded iron distribution pipes which may also manifest in brass meters.

Diatom frustules were present in meter 1 and 2 from Seattle. Coverage on meter 1 was extensive with a thin film that only showed a few patches of mineral scale whereas meter 2 had minimal coverage. These two meters are of similar age but there were no diatoms present in the older Seattle meter 4 which suggests a difference in source water. It is unknown whether these diatoms were living within the distribution system or rather just their skeletons were transported in. The frustules appeared to be a superficial feature on the corrosion scale but their presence after pipe rig testing shows they are not removed by water flow. It is uncertain how their presence affects scale development.

**Mineralogy**

Cuprite is present in all meters as an amorphous dark brown scale that covers the majority of all wetted surfaces. While the Seattle water is relatively soft, the Cincinnati water is moderately hard and high in alkalinity lending support to Shim’s 2004 findings as cuprite being the dominant mineral. Cuprite also manifests in localized areas of prismatic minerals, most notably in Cincinnati meter 10 (see Figure 2-37). Whether cuprite is present as an amorphous mass or rather a crystalline mineral is likely due to rapid precipitation or more gradual crystallization, respectively.
Tenorite was present in all of the Cincinnati meters but in minor amounts relative to cuprite. The Seattle set only had tenorite identified in meter 4 – the oldest in the set. The presence of both cuprite and tenorite in many of the meters is notable since they contain copper at different oxidation states – the bivalent cupric and monovalent cuprous ion, respectively. In solutions with higher redox potentials, tenorite is more likely to form and in solutions with lower redox potentials, cuprite is expected. Since each mineral forms under different conditions, having both present in the same environment suggests continual shifts in water chemistry. This is best explained by cycles of flow and extended stagnation. Water quality reports (SPU 2010a, 2010b; GCWW 2010) show that both water sources have residual chlorine when they leave the treatment facility – 1.2 mg/L for Cincinnati and 0.8 mg/L for Seattle. When water is moving through the system, redox potentials will be sufficiently high to favor the formation of tenorite. During extended periods of stagnation through reduction-oxidation reactions, the redox potential will drop and cuprite will be dominant. The higher chlorine levels in Cincinnati water allow tenorite formation to be more likely when compared to Seattle.

The copper carbonate malachite was found in most meters including all from Cincinnati. This evidence supports Merkel’s 2002 findings of cuprite and malachite being the dominant copper minerals in drinking water. In fact, the only meters in which malachite was not identified were the unused no-lead meter 5 as well as meter 2 – both from Seattle. Malachite was mostly present as part of the amorphous mineral aggregation rather than crystal form. Meter 10 showed small amounts of this copper carbonate in its
botryoidal structure (Figure 2-40). In no instance was malachite found in its “sea urchin”
type crystal structure as noted by Merkel (2002).

Brochantite was present in two of the meters tested – one from each region – both of
which had significantly developed scale with near complete coverage as well as the
widest variety of mineralogy. This copper sulfate mineral was always found in small
highly localized areas associated with cuprite. The small localized ‘islands’ of
brochantite provide evidence for sulfates role in pitting corrosion of copper as discussed

Iron oxide was found in minor amounts in most scales from both sets of meters. X-Ray
diffraction patterns indicate that most is present as the ferric hematite rather than the
oxy-hydroxide goethite. There is likely some goethite also present.

The Cincinnati meters contain an abundance of lead minerals compared to the Seattle
set. Both lead oxides and carbonates were found as corrosion products in all of the
Cincinnati meters – the carbonate as cerussite and the oxide likely as plattnerite. Both
of these minerals were incorporated in the amorphous scale covering the entire inner
surface. Lead oxide was also found in most of the Seattle meters but was relatively low
in abundance compared to the Cincinnati meters. Lead carbonate minerals were only
found in two of the Seattle meters. In contrast to Fenkel’s (1999) findings,
hydrocerussite was only positively identified in the unused Seattle meter 6.

The significant variation in scale development when considering the two unused Seattle
meters shows the importance of alloy composition in new plumbing fixtures. The no-
lead brass only had cuprite present and retained its brass-like color, whereas the
traditional brass type had cuprite and malachite coverages with large patchy areas of the lead carbonate hydrocerussite. This provides evidence that in relatively brief time periods, brasses of the traditional composition can undergo rapid corrosion, leaching and re-precipitation of metallic species.

**Conclusion**

A classic approach to determine the relative corrosivity of water which is still used today is the Langelier Saturation Index (LSI) (Langelier 1936). The LSI calculation is a comparison of measured water parameters to the theoretical pH of the same water in equilibrium with calcium carbonate. In general, a negative LSI indicates that the water is undersaturated with respect to calcium carbonate and will be corrosive to, or will dissolve carbonate scale. A positive LSI indicates that the water is likely to be scale forming.

Using the measured water parameters from the Cincinnati Miller plant listed in Table 2-2 above, the calculated LSI is +0.43 suggesting that the water is slightly saturated with respect to carbonate and that there is mild probability of scale formation. When we input the measured parameters from the Seattle Cedar river supply listed in Table 2-1, the calculated LSI is -1.2. This suggests that the Seattle water, being much lower in alkalinity, hardness and total solids, is likely to be more aggressive to carbonate species.

While we do not know the explicit ages of each of the Cincinnati meters, they were all removed at the same time and were in service for similar time periods. The would compare most directly to the older meters from the Seattle set. The analysis of
corrosion scale from the two sets of water meters exposed to significantly different water chemistry throughout service shows the following conclusions:

- Higher levels of alkalinity, hardness and dissolved solids in the Cincinnati meters produced more significant and consistent scale development.
- Cuprite and malachite were the most dominant scale minerals overall, lending support to previous laboratory studies (Merkel 2002, Shim 2004).
- Lead minerals were much more prevalent in the corrosion scale of the Cincinnati meters, likely a result of higher alkalinity and redox potentials.
- The copper(II) and lead(II) oxides, tenorite and plattnerite, respectively, were more widespread in the Cincinnati meters due to higher chlorine residuals and accordingly redox potentials.
- Carbonate minerals, including copper and lead species, were found in abundance in the higher alkalinity Cincinnati water compared to the Seattle water.
- The presence of zinc in the corrosion scale was negligible for all meters analyzed, supporting Zhou’s (2017) laboratory experiments.

The present study shows that scale mineralogy and morphology is highly dependent upon water chemistry with higher alkalinity water showing more substantial scale. Higher prevalence of lead minerals in the Cincinnati scale suggests that lead release in this water ultimately manifests as solid corrosion products rather than soluble compounds. However, if water quality changes, these corrosion products could dissolve and increase lead concentration as water travels through the system. Changes in treatment programs, especially those which vary pH, alkalinity, and redox potentials,
can significantly alter pre-established scale and have the potential to contribute toxic species throughout the water supply.

Reference


Chapter 3: Effect of changing water chemistry in brass corrosion products and metal release

Michael Lees

Abstract

Periods of stagnation in drinking water systems can lead to changes in water chemistry, including metal concentration, solution pH, and oxidation reduction potential. Slight changes in these conditions can significantly affect scale formation or dissolution and subsequent leaching or sequestration of metals. The present study uses PHREEQC, geochemical modelling software from the United States Geological Survey, to evaluate how changes in water chemistry during periods of stagnation can affect equilibrium with established corrosion scale. Equilibrium calculations are compared to mineralogy identified within the corrosion scale of brass water meters to determine when particular minerals are likely to form in real world use conditions.

Introduction

Corrosion of brass plumbing fixtures in residential drinking water systems leads to the dissolution of metals which will either be deposited as scale or remain in the water as it leaves the tap. Brass components used in plumbing systems are primarily an alloy of copper and zinc at varying ratios, but also contain lead as well as other metals. Lead is used in plumbing fixtures to aide in machinability and to reduce the corrosion of additional metals in the alloy (OECD 1994).
Previous studies have shown that in addition to alloy composition, water quality may be the principal factor which impacts the rate and extent of corrosion in drinking water (Sarver 2010, Brandl 2009, Lytle 2000). Periods of extended stagnation are known to significantly alter water quality in drinking water systems including an increase in metal concentration, changes in solution pH, and the reduction of dissolved oxygen and disinfectant concentrations (Ng 2016, Cartier 2012, Sarver 2011, Merkel 2004, Lagos 2001). Even slight changes in water quality can lead to considerable variations in equilibrium concentrations of concerned species.

Metal concentration within aqueous solutions impacts the types of minerals formed through association with other ions and their equilibrium solubility. It is generally accepted that higher metal concentrations lead to more probable scale formation as water reaches saturation. Broo (1997) conducted laboratory stagnation experiments using copper coupons and found that copper concentration is initially driven by reaction kinetics and then reaches a maximum through equilibrium with the metastable cupric hydroxide. Finally, copper levels decrease due to precipitation of corrosion products. Merkel (2004) found long term copper concentrations to be dictated by equilibrium with malachite.

The solubility of corrosion scale products in drinking water and their rate of formation and dissolution is highly dependent upon solution pH. Noel (2014) showed through laboratory experimentation that the dissolution rate of hydrocerussite was inversely related to solution pH in the absence of dissolved inorganic carbon (DIC). In the
presence of DIC, dissolution rates were much lower and similar across all pH values tested. Xie (2010) carried out similar studies with the lead oxide plattnerite that showed dissolution rates to be inversely related to pH in water containing sufficient DIC. Shock (1995) showed the solubility of cupric oxide, tenorite and the carbonate, malachite decreases with increasing pH. Periods of stagnation can also lead to changes in solution pH. Cantor (2003) found through long term copper pipe rig experiments using municipal water that pH varied ± 0.2 units over 24 hour periods of stagnation. The variation included both an increase and decrease from initial values.

The redox potential plays a significant role in the leaching of metallic compounds in drinking water. Edwards (2004) found that lead release from brass was much more substantial in drinking water which contained chloramine, versus the stronger oxidizer chlorine. This is supported by the stability of passivating lead oxide films in higher redox potentials (i.e. chlorine), which are unstable at lower potentials (Schock 2004). Liu (2009) showed that chlorine can oxidize lead(II) carbonates to form the lead(IV) oxide plattnerite and during this transformation, soluble lead release from cerussite is increased whereas lead release in hydrocerrusite is decreased. The redox potential is controlled by both disinfectant type and dissolved oxygen and can vary during periods of stagnation. Merkel (2004) showed that oxygen depletion follows first order kinetics and approaches zero after 20 hours of stagnation. Additional studies have shown that chlorine consumption in water distribution systems also follows first order models (Kim 2015, Zheng 2013, Vasconcelos 1997).
Eh-pH diagrams can serve as useful tools in determining equilibrium in aqueous solutions (Huang 2016, Pourbaix 1966). Figure 3-1 shows how slight variations in redox potential and pH can lead to the formation of different corrosion products.

![Eh-pH diagram](image)

**Figure 3-1:** Redox potential vs. pH for lead carbonates and plattnerite in Cincinnati Miller water. Adapted from Maynard 2008. Redox potential estimated from Copeland 2014.

Previous studies have shown how individual variables impact corrosion within drinking water for specific metals, while others have shown the effect of stagnation on water quality. There is still only a limited understanding of how these changes are manifested in brass corrosion scale development over many years and which parameters have the greatest impact. The present study uses geochemical modeling along with scale mineralogy identified in Chapter 2, to better understand how changes in metal concentration, solution pH, and redox potential within a distribution system influence corrosion scale and metal release in well-established brass water meter scales. The study focuses on changes in water chemistry during times of extended stagnation in two
substantially different water sources that may affect the formation or dissolution of corrosion scale and associated metal species.

**Materials and Methods**

*Corrosion Scale Mineralogy*

In Chapter 2 of this thesis, various analytical techniques were used to determine what mineral species were present in two sets of water meters ranging in age from new to 40 years of service and from water sources of significantly different aqueous chemistry. The copper minerals found in most abundance were the oxides cuprite (Cu$_2$O) and tenorite (CuO), the carbonate malachite (Cu$_2$CO$_3$(OH)$_2$), and a minor amount of brochantite (Cu$_4$SO$_4$(OH)$_6$). The lead oxide plattnerite (PbO$_2$) as well as the lead carbonates cerussite (PbCO$_3$) and hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$) were found throughout both sets, but not in all meters. The iron oxide hematite (Fe$_2$O$_3$) and oxy-hydroxide goethite (FeOOH) were also found throughout the scale of most of the meters, though in minimal quantities. Table 3-1 shows a summary of the scale mineralogy for each meter that was analyzed.
Water quality has a significant impact upon the corrosion of metals and the types of minerals which will precipitate or crystallize on the surface of plumbing fixtures. Chapter 2 demonstrated that there were significant differences in mineralogy between corrosion scale on the two sets of meters. The difference in scale was the result of two distinct water qualities – the high alkalinity Cincinnati water, and the low alkalinity Seattle water. Table 3-2 below shows the water quality results for the two localities based on 2010 analysis which will be used for geochemical modeling (SPU 2010a, SPU 2010b, GCWW 2010).
Geochemical Modeling

PHREEQC software from the United States Geological Survey is a tool commonly used for a variety of aqueous geochemical calculations (Parkhurst 1999). In the present study, it is used in conjunction with the MinteqV4 database, to determine the solubility of common compounds found in drinking water or more specifically the saturation index of the water in relation to given species. The saturation index uses measured concentrations of species within a solution and relates them to equilibrium...
concentrations. A positive saturation index shows that the water is supersaturated and likely to precipitate a mineral whereas a negative saturation index means the water is undersaturated and is likely to dissolve that species. A saturation index of 0 indicates the water is saturated and in equilibrium with a given species.

Using the analysis in Table 3-2 for each respective water source and estimating the redox potential from chlorine concentrations and their corresponding half reaction electrode potentials as determined by Copeland (2014), it can theoretically be determined what minerals should be present in the scale for each of the meter sets. The 90th percentile values for copper and lead have been used as reported in both the Seattle and Cincinnati annual reports (SPU 2010, GCWW 2010). These are added in the analysis so that copper and lead species will be included in the saturation index calculations. Since the water contained within residential distribution meters is from cold water lines, the temperature of 12.8°C was used for modeling.

**Results and Discussion**

Table 3-3 below shows the saturation indices (SI) for common minerals found in corrosion scale in drinking water for each of the water sources. Comparing the SI values in Table 3-3 with the summary of minerals identified in Table 3-1, there are several apparent discrepancies. Most significant is the copper oxide, cuprite, which modeling shows to be significantly undersaturated in both water sources. The thermodynamic equilibrium calculations suggest both waters should be highly aggressive to this mineral and dissolve any that is present. This is evidently not the
case since cuprite was the only mineral to be found in all meters and was also the most abundant. The SI values also indicate that the water is undersaturated in respect to brochantite, cerussite and hydrocerussite, all of which were found in at least one of the meters. There are also some minerals shown to be supersaturated which were found in some of the meters, but not all. These include goethite, hematite, malachite and tenorite.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Cincinnati Miller</th>
<th>Seattle Cedar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brochantite</td>
<td>Cu$_4$(OH)$_6$SO$_4$</td>
<td>-2.16</td>
<td>-0.16</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>0.54</td>
<td>-0.94</td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO$_3$</td>
<td>-0.90</td>
<td>-1.05</td>
</tr>
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<td>Cuprite</td>
<td>Cu$_2$O</td>
<td>-20.94</td>
<td>-18.74</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeOOH</td>
<td>4.95</td>
<td>5.72</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>12.25</td>
<td>13.79</td>
</tr>
<tr>
<td>Hydrocerussite</td>
<td>Pb(OH)$_2$:2PbCO$_3$</td>
<td>-1.98</td>
<td>-2.28</td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu$_2$(OH)$_2$CO$_3$</td>
<td>1.51</td>
<td>2.76</td>
</tr>
<tr>
<td>Plattnerite</td>
<td>PbO$_2$</td>
<td>0.11</td>
<td>-0.68</td>
</tr>
<tr>
<td>Tenorite</td>
<td>CuO</td>
<td>0.64</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Table 3-3: Saturation indices for common minerals found in drinking water corrosion scale.

The discrepancies between the calculated SI values for the water and respective compounds can be attributed to variations in water chemistry during times of stagnation. Stagnation periods allow for the water to dissolve or precipitate solids within the distribution system, leading to changes in water chemistry as the system approaches equilibrium. In order to resolve the differences between modeled SI values and the minerals which were positively identified in the corrosion scale, input values for metal...
concentration, solution pH, and redox potential were varied. For each simulation, one variable was exclusively altered while all other water chemistry parameters remained unchanged.

**Changes in metal concentration**

In chapter one, we showed that during periods of stagnation, the oxidation of metallic surfaces and the dissolution of scale minerals leads to an increase in metal concentration within the water distribution system. First, the effect of an increase in dissolved metal concentration on the saturation indices of both waters is considered. Metal concentration for copper and lead range from their 90\textsuperscript{th} percentile values up to the Environmental Protection Agency Lead and Copper Rule action levels of 1.3 mg/L and 0.015 mg/L for copper and lead, respectively (EPA 1991).

An increase up to the copper action level did not have a substantial effect upon the cuprite saturation index which was still significantly undersaturated within the water (Figure 3-2). Tenorite showed a similar trend with an increase in supersaturation (Figure 3-3).
Both water sources which were initially undersaturated with respect to the copper sulfate brochantite, saw an appreciable increase in SI values with increasing copper concentration (Figure 3-4). The small islands of brochantite might have formed with localized increases in copper concentration leading to rapid precipitation of the mineral in both water sources.
The range of modeled lead concentration covered a more confined range than that of copper due to the lower EPA action level. The difference between minimum and maximum values was 0.01 mg/L. There was still a considerable difference between water sources (Figure 3-5), especially for the lead oxide platniterite, with the Cincinnati water being supersaturated and the Seattle water undersaturated across all values. While the SI values for the waters increased in respect to the lead carbonate cerussite, it did not reach saturation for either source.
Changes in solution pH

Chemical reactions involving transfer of protons as well as the dissolution or precipitation of carbonate compounds can alter the pH of water within distribution systems. The figures below consider how changes in solution pH might influence the interaction between water and various metallic species. Figure 3-6 shows the SI values for cuprite are unaffected by changes in solution pH of 0.5 units above or below the...
measured values, and remains heavily undersaturated within both waters. The saturation index for tenorite is positively related to an increase in pH (Figure 3-6).

![Cuprite Saturation Index vs pH](image1)

![Tenorite Saturation Index vs pH](image2)

Both water sources remain supersaturated in respect to malachite across all pH ranges simulated, as shown in Figure 3-7. Surprisingly, the low alkalinity Seattle water showed higher SI values regarding the carbonate mineral when compared to the higher alkalinity Cincinnati water. The SI values are again positively related to an increase in pH.

Figure 3-6: Saturation indices for cuprite and tenorite vs. pH. Boxes indicate measured pH values (SPU 2010, GCWW 2010).

pE = 13.52
The SI values for brochantite and plattnerite were most predisposed to changes in pH of all the minerals considered (Figure 3-8). A slight increase in solution pH could lead to the precipitation of brochantite in the Seattle meters. Changes of 0.5 pH units, plus or minus from measured values, caused each water to become supersaturated or undersaturated in regard to the lead oxide, respectively. Theoretically, if the Seattle water had the same pH as the Cincinnati water, it is plausible that plattnerite would have been found in greater abundance within the corrosion scale.
Changes in oxidation reduction potential

During periods of extended stagnation, chlorine levels within the water will drop through the oxidation of metallic species. Dissolved oxygen will also oxidize metals subsequently reducing redox potential. In the following figures, the redox potential (pE) scale has been reversed to better simulate a drop in redox potential as chlorine levels decrease (i.e. with time). Figure 3-9 shows the saturation index of the copper oxides cuprite and tenorite versus pE. It is apparent that the monovalent copper oxide, cuprite
and the bivalent tenorite form under decidedly different redox conditions. In both waters, tenorite formation is favorable until the redox potential reaches relatively low values, then cuprite formation is more likely. This could indicate that tenorite precipitation occurs during periods of flow and brief stagnation while cuprite, the most dominant scale mineral, forms during extended stagnation periods.

**Figure 3-9:** Saturation Indices for cuprite and tenorite versus redox potential.  
\[ pH = 8.6 \text{ Cincinnati; } pH = 8.2 \text{ Seattle} \]
The change in SI for the copper carbonate malachite showed a similar trend (Figure 3-10) to that of tenorite, with precipitation favorable across most redox potentials and dissolution only at low values. Both of these minerals consist of cupric copper.

Although plattnerite was found extensively in the Cincinnati meters and less frequently in the Seattle set, the SI values for this lead oxide indicate both waters would have been relatively aggressive to the mineral. In fact, the waters were initially near equilibrium with respect to plattnerite but SI values would decrease significantly with a drop in redox potential as seen in Figure 3-11. This suggests plattnerite formation is only favorable during periods of flow or extremely short stagnation with sufficient pE conditions. All of the modeled waters were found to be undersaturated with respect to the lead carbonates cerussite and hydrocerrusite. This is explained by the reduction of the lead(IV) oxide plattnerite to the more soluble lead(II) carbonates as explained by Lytle (2005). This reduction can lead to a pronounced increase in lead concentration within the water.
Conclusion

In the present study, it has been shown through geochemical modeling, that changes in metal concentration, solution pH and redox potential during periods of stagnation, can significantly impact scale formation, dissolution and subsequent metal release. As expected, metal concentration was positively related to the saturation indices of all respective minerals. pH was also positively related except in the case of cuprite which was unaffected. Changes in redox potential had the most appreciable effect upon the equilibrium saturation of species within the water with some minerals only showing favorable formation at pE extremes.

Cuprite was found to be undersaturated in all simulations except those with low redox potentials (pE < 4), suggesting formation to occur during periods of extended stagnation. Tenorite and malachite followed an inverse trend, showing to be
supersaturated under all conditions except at low pE (≤ 2). The saturation indices suggest that during periods of extended stagnation, when redox conditions approach zero, copper concentration will be determined by equilibrium with both malachite and tenorite. Brochantite formation was favorable with an increase in copper concentration and in the case of Seattle, a slight increase in pH. The solubility index of plattnerite was most significantly affected by variations in solution pH and redox potential. An increase in pH of 0.2 units lead to saturation in the Seattle water. The SI values of the lead oxide shows a strong inverse relationship to the oxidation reduction potential. A slight decrease in pE results in both waters being highly aggressive to the mineral suggesting formation to occur during flow or brief stagnation when redox conditions are sufficient. In all simulations, the iron oxides goethite and hematite were found to be supersaturated, whereas the lead minerals cerussite and hydrocerussite were undersaturated.

It is not fully understood why minerals which are predicted to form under markedly different conditions are simultaneously present within the corrosion scale (i.e. tenorite and cuprite). In some areas, divergent minerals are present exclusively at different depths within the scale, indicating temporal variance. This study has shown that changes in redox conditions during cycles of stagnation and flow can lead to favorable formation of different minerals. These fluctuations combined with limitations of dissolution and precipitation rates might account for the diverse mineralogy. Seasonal variations in temperature might also play a role since both water sources are surface derived. Some minerals may also form in highly localized areas of inconsistent water
chemistries due to pitting corrosion or chemical sinks. It is important to remember that changes in the modeled variables (among others) occur simultaneously within the system for a combined effect. For instance, the reaction of disinfectants and oxygen with metals will drive down redox potential while increasing metal concentration over time. The continual interaction of dissolved species and solids in their relation to thermodynamic equilibrium within the water makes for a highly dynamic system.

Reference


