Effects Of Source Water Blending Following Treatment With Sodium Silicate As A Corrosion Inhibitor On Metal Release Within A Wat

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EFFECTS OF SOURCE WATER BLENDING FOLLOWING TREATMENT WITH SODIUM SILICATE AS A CORROSION INHIBITOR ON METAL RELEASE WITHIN A WATER DISTRIBUTION SYSTEM

by

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B.S. University of Central Florida, 2006

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Civil, Environmental, and Construction Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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Major Professors: Steven J. Duranceau and James S. Taylor
ABSTRACT

A study was conducted to investigate and quantify the effects of corrosion inhibitors on metal release within a pilot distribution system while varying the source water. The pilot distribution system consisted of pre-existing facilities from Taylor et al (2005). Iron, copper, and lead release data were collected during four separate phases of operation. Each phase was characterized by the particular blend ratios used during the study. A blended source water represented a water that had been derived from a consistent proportion of three different source waters. These source waters included (1) surface water treated through enhanced coagulation/sedimentation/filtration, (2) conventionally treated groundwater, and (3) finished surface water treated using reverse osmosis membranes. The corrosion inhibitors used during the study were blended orthophosphate (BOP), orthophosphate (OP), zinc orthophosphate (ZOP), and sodium silicate (Si). This document was intended to cite the findings from the study associated with corrosion treatment using various doses of sodium silicate. The doses were maintained to 3, 6, and 12 mg/L as SiO$_2$ above the blend-dependent background silica concentration.

Sources of iron release within the pilot distribution system consisted of, in the following order of entry, (1) lined cast iron, (2) un-lined cast iron, and (3) galvanized steel. Iron release data from these materials was not collected for each individual iron source. Instead, iron release data represented the measurement of iron upon exposure to the pilot distribution system in general. There was little evidence to suggest that iron release was affected by sodium silicate. Statistical analysis...
modeling of iron release suggested that iron release could be described by the water quality parameters of alkalinity, chlorides, and pH. The $R^2$ statistic implied that the model could account for only 36% of the total variation within the iron release data set (i.e. $R^2 = 0.36$). The model implies that increases in alkalinity and pH would be expected to decrease iron release on average, while an increase in chlorides would increase iron release. The surface composition of cast iron and galvanized steel coupons were analyzed using X-ray photoelectron spectroscopy (XPS). The surface analysis located binding energies consistent with Fe$_2$O$_3$, Fe$_3$O$_4$, and FeOOH for both cast iron and galvanized steel. Elemental scans detected the presence of silicon as amorphous silica; however, there was no significant difference between scans of coupons treated with sodium silicate and coupons simply exposed to the blended source water. The predominant form of zinc found on the galvanized steel coupons was ZnO. Thermodynamic modeling of the galvanized steel system suggested that zinc release was more appropriately described by Zn$_5$(CO$_3$)$_2$(OH)$_6$.

The analysis of the copper release data set suggested that treatment with sodium silicate decreased copper release during the study. On average the low, medium, and high doses decreased copper release, when compared to the original blend source water prior to sodium silicate addition, by approximately 20%, 30%, and 50%, respectively. Statistical modeling found that alkalinity, chlorides, pH, and sodium silicate dose were significant variables ($R^2 = 0.68$). The coefficients of the model implied that increases in pH and sodium silicate dose decreased copper release, while increases in alkalinity and chlorides increased copper release. XPS for copper coupons suggested that the scale composition consisted of Cu$_2$O, CuO, and Cu(OH)$_2$ for
both the coupons treated with sodium silicate and those exposed to the blended source water. Analysis of the silicon elemental scan detected amorphous silica on 3/5 copper coupons exposed to sodium silicate. Silicon was not detected on any of the 8 control coupons. This suggested that sodium silicate inhibitor varied the surface composition of the copper scale. The XPS results seemed to be validated by the visual differences of the copper coupons exposed to sodium silicate. Copper coupons treated with sodium silicate developed a blue-green scale, while control coupons were reddish-brown. Thermodynamic modeling was unsuccessful in identifying a controlling solid that consisted of a silicate-based cupric solid.

Lead release was generally decreased when treated with sodium silicate. Many of the observations were recorded below the detection limit (1 ppb as Pb) of the instrument used to measure the lead concentration of the samples during the study. The frequency of observations below the detection limit tended to increase as the dose of sodium silicate increased. An accurate quantification of the effect of sodium silicate was complicated by the observations recorded below detection limit. If the lead concentration of a sample was below detection limit, then the observation was recorded as 1 ppb. Statistical modeling suggested that temperature, alkalinity, chlorides, pH, and sodium silicate dose were important variables associated with lead release ($R^2 = 0.60$). The exponents of the non-linear model implied that an increase in temperature, alkalinity, and chlorides increased lead release, while an increase in pH and sodium silicate dose were associated with a decrease in lead release. XPS surface characterization of lead coupons indicated the presence of PbO, PbO$_2$, PbCO$_3$, and Pb$_3$(OH)$_2$(CO$_3$)$_2$. XPS also found evidence of silicate scale formation. Thermodynamic modeling did not support the
possibility of a silicate-based lead controlling solid. A solubility model assuming Pb₃(OH)₂(CO₃)₂ as the controlling solid was used to evaluate lead release data from samples in which lead coupons were incubated for long stagnation times. This thermodynamic model seemed to similarly describe the lead release of samples treated with sodium silicate and samples exposed to the blended source water. The pH of each sample was similar, thus sodium silicate, rather than the corresponding increase in pH, would appear to be responsible if a difference had been observed.

During the overall study, the effects of BOP, OP, ZOP, and Si corrosion inhibitors were described by empirical models. Statistically, the model represented the expected value, or mean average, function. If these models are to be used to predict a dose for copper release, then the relationship between the expected value function and the 90th percentile must be approximated. The USEPA Lead and Copper Rule (LCR) regulates total copper release at an action level of 1.3 mg/L. This action level represents a 90th percentile rather than a mean average. Evaluation of the complete copper release data set suggested that the standard deviation was proportional to the mean average of a particular treatment. This relationship was estimated using a linear model. It was found that most of the copper data sub-sets (represented by a given phase, inhibitor, and dose) could be described by a normal distribution. The information obtained from the standard deviation analysis and the normality assumption validated the use of a z-score to relate the empirical models to the estimated 90th percentile observations. Since an analysis of the normality and variance (essentially contains the same information as the standard deviation) are required to assess the assumptions associated with an ANOVA, an ANOVA was performed to
directly compare the effects of the inhibitors and corresponding doses. The findings suggested that phosphate-based inhibitors were consistently more effective than sodium silicate when comparing the same treatment levels (i.e. doses). Among the phosphate-based inhibitors, the effectiveness of each respective treatment level was inconsistent (i.e. there was no clear indication that any one phosphate-based inhibitor was more effective than the other). As the doses increased for each inhibitor, the results generally suggested that there was a corresponding tendency for copper release to decrease.
ACKNOWLEDGMENTS

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CHAPTER 1
LITERATURE SURVEY

Introduction

This document was written to satisfy the requirements for completion of the doctoral program from the University of Central Florida’s College of Engineering and Computer Science within the Department of Civil and Environmental Engineering. The dissertation is entitled “Effects of Source Water Blending following Treatment with Silica as a Corrosion Inhibitor on Metal Release within a Water Distribution System.”

The Department of Civil and Environmental Engineering has conducted a study with the intent of analyzing the response of a pilot distribution system upon various treatments. The different treatments included the addition of blended ortho-polyphosphate (BOP), pure ortho-phosphate (OP), zinc ortho-phosphate (ZOP), and sodium silicate (Si), and pH adjustment (pHs+0.3). The project operated over 4 phases in which data was collected weekly for approximately 12 weeks per phase. Each phase was intended to vary in water quality, with the exception of Phase III which was initially planned to be identical to Phase I to contrast seasonal effects. The water quality was varied by blending allocated ratios of different source waters. These water sources represented conventionally treated groundwater (GW), enhanced coagulation-sedimentation-filtration surface water (SW), and desalinated water by reverse osmosis (RO). A pilot distribution system that was used during a prior, affiliated research project that consisted of 18 lines (PDSs) was used. PDSs 1-14 were used for the corrosion study. Each PDS was assumed identical and was constructed with 1) PVC, 2) lined cast iron (LCI), 3) unlined cast iron (UCI),
and 4) galvanized steel (GS) pipes taken from the actual drinking water distribution system. A series of copper corrosion loops was connected to the effluent of the GS.

As part of the study, the effect of water quality and inhibitor type and dose on the release of iron, copper, and lead was evaluated. This topic is concerned with the effects surrounding the addition of sodium silicate (*silica* will be used interchangeably). The vast collection of data, consisting of several factorial arrangements (e.g. 3 doses, 3 alkalinites, 2 controls) will allow for the quantification of these effects as has yet to be recorded within the literature. Furthermore, the statistical analyses and modeling may provide several utilities of similar water qualities with a predictive basis for deciding upon silica dosages.

**Objectives**

The objectives of the proposed research are as follows:

- Evaluate the impact of the inhibitor and its dose on iron, copper, and lead release.
- Evaluate the effect of water quality for both the inhibitor and control PDSs and assess any possible interactions of the factors.
- Incorporate all of the previous information into the development of an empirical model, and provide an explanation for the terms present in the model.
- Verify that differing scale compositions exist when iron, copper, and lead surface are exposed to silica inhibitor.
- Assess the feasibility of a controlling solid mechanism from information obtained from surface characterization analyses.
Attempt to differentiate between the effect of pH and silica, and the effect of silica that was already present in the source water to that added as inhibitor.

Theory

Basic Corrosion Theory

Corrosion may be regarded as any form of degradation rendered upon the components of a distribution system. Interactions between water and the materials used for transporting in the distribution system may alter the composition of the infrastructure in an undesirable manner. These interactions can promote the deterioration of a pipe material through abrasion and/or chemical activity. During the study, hydraulic factors were not considered, providing no means of contrasting corrosion in response to changes in factors that would be surrogate of the abrasive properties of water (e.g. velocity). For this reason, any further discussion of corrosion will pertain to the chemical interactions between water and pipe material influencing the process.

The corrosion of pipe systems constructed of metals occurs when the metal participates in a reduction/oxidation reaction with constituents present in the water. These reactions proceed when the process is thermodynamically favorable, resulting in a free energy that is negative and thereby spontaneous. A generalized formulation of the oxidation process undergone by the metal is shown as Equation 1-1.

\[ Me \leftrightarrow Me^{n+} + ne^- \]  

Equation 1-1
As oxidation proceeds, the metal will endure a loss of electrons. Equation 1-1 represents only half of the corrosion process. The other half-cell will describe the acceptance of the electrons released by the metal. This complete transfer of electrons is necessary for corrosion to occur. Electrons are accepted by an oxidant from the source water. Potential oxidants supported by the distribution system can include dissolved oxygen, hydrogen with an oxidation state of +1, and, depending on the disinfection method practiced, residuals such free chlorine, chloramines, and ozone. However, in water distribution systems that are near neutral pH, the predominant oxidant will be dissolved oxygen (Montgomery 1985).

The process of corrosion was previously described as a chemical transformation of reactants with the metal representing the reactant that is oxidized and oxygen (or any other possible oxidizing agents) representing the reactant being reduced. Understanding the process with respect to half-cells does not entirely explain all of the components necessary for corrosion to occur. Terminology more appropriate for corrosion will be reviewed that describes corrosion in a manner that is analogous to an electrical circuit.

Four basic components of a corrosion cell are necessary for the process to be feasible. These components are: (1) the anode, (2) the cathode, (3) a conductor, and (4) a conducting electrolyte solution. Both the anode and cathode have been previously discussed as reactants that are oxidized and reduced. The anode (1) represents the area of the corrosion cell where oxidation takes place. Thus Equation 1-1 describes the reaction at the anode and corresponds to a loss of electrons. Electrons are carried through a conducting medium (2), the pipe material itself, to a
site near the metal surface, the cathode (3), where the electrons are accepted by the oxidant. In
order to retain electroneutrality of the solution, a sufficient amount of electrolytes are necessary
to balance the overall charge at both the anode and cathode. Since the oxidation state of the
metal at the anode is increased, anions will migrate towards the corrosion site to balance the
increase in charge. Likewise, a decrease in charge at the cathode will instigate the migration of
cations towards that particular location along the conducting surface.

If all of the components are present, corrosion will proceed provided that the potential difference
between the anode and cathode is spontaneous. Electrons will flow from the anode to the
cathode if the potential energy in the anode is higher than that at the cathode. This desire to
achieve a lower energy state corresponds to a free energy change that is spontaneous.

Basic Chemistry of Aqueous Silica

The solubility of silica, represented as SiO2 in the solid phase, is most notably defined as:

\[
\text{SiO}_2(s, \text{amorphous}) + 2\text{H}_2\text{O} \leftrightarrow \text{Si(OH)}_4(aq) \quad \log K = -2.7 \quad \text{Equation 1-2}
\]

\[
\text{Si(OH)}_4(aq) \leftrightarrow \text{SiO(OH)}_3^- + \text{H}^+ \quad \log K = -9.46 \quad \text{Equation 1-3}
\]

\[
\text{SiO(OH)}_3^- \leftrightarrow \text{SiO}_2(OH)_2^{2-} + \text{H}^+ \quad \log K = -12.56 \quad \text{Equation 1-4}
\]

\[
4\text{Si(OH)}_4 \leftrightarrow \text{Si}_4\text{O}_6(OH)_6^{2-} + 2\text{H}^+ + 4\text{H}_2\text{O} \quad \log K = -12.57 \quad \text{Equation 1-5}
\]

The equilibrium constants are based on the work of Lagerstrom (1959). Figure 1-1 shows the
theoretical log-molar concentrations of these silica species as calculated from the preceding
equilibrium constants. The hydration of silica as shown by Equation 1-2 is the most widely
accepted, as opposed to the case where SiO$_2$ forms H$_2$SiO$_3$ (Roques, 1996). H$_2$SiO$_3$ is also
known as dissolved metasilicate, whereas $Si(OH)_4$ is known as dissolved orthosilicate. $Si(OH)_4$ exists in undersaturated silica solutions and has a high tendency to polymerize if the solubility limit is reached. The polymerization of silica results in colloidal structures that stabilize to gels (Iler, 1955).

Figure 1-1  Solubility of amorphous silica using equilibrium constants previously shown

Also shown on Figure 1-1 is the boundary of a mononuclear wall as defined by Stumm et al. (1967). The mononuclear wall defines the boundary where 1% of the total silica (as silicon) exists as soluble polymeric species. Note that the line that represents the boundary between the Insoluble domain and the Mononuclear domain is at a molar concentration of $10^{-2.7}$ M. This is approximately equivalent to 120 mg/L of silica as SiO$_2$. It has been suggested that only $Si(OH)_4$
occurs within neutral and slightly alkaline pH ranges (Stumm, 1981). However, some evidence has indicated that polymeric species may be significant for such common conditions. As Davis (2002) illustrates while applying revised equilibrium constants from Svensson et al. (1986), at concentrations as low as 1.90 mg/L as SiO₂, 2% of the total Si is predicted to be in polymeric form at pH 7.5; at pH 9.5, 37% is described by polymeric species.

The geometry of silicon in an oxide form is tetrahedral to its four oxygen atoms. This allows for a potentially complicated structure from the sharing of one or more oxygen atoms, with several possible crystalline states. If precipitation occurs under drinking water conditions, silica initially precipitates as a gel that will progressively lose water and age toward a more crystalline form (Roques, 1996). In the presence of di- or trivalent cations is likely to form silicates as the pH is increased (Iler, 1979; McCutchan et al., 1978).

**Literature Review**

As early as the 1920’s soluble sodium silicates have been implemented as a corrosion inhibitor and sequestering agent in drinking water (Thresh, 1922). Addition of the chemical was generally a response to red water problems or concerns with lead. Early research on the matter has shown that silica can demonstrate similar mitigating effects on other metals such as copper and brass. Both Lehrman and Shuldener carried out experiments to assess the mechanism of silica film formation on compounds common in drinking water piping systems (Lehrman, 1952). The methods consisted of simply mixing suspensions of solid cupric, ferric, and zinc hydroxides in sodium silicate solutions. Results from the analysis suggested that there was potential for a
reaction between silica and the suspensions within the solution. Sodium silicate has been described as an anodic inhibitor at low doses and has to be potential to favor pitting corrosion (Vic et al, 1996). However, the nature of that reaction is still not completely understood.

There have been questions surrounding the inhibitor’s exact role in the control of metal release. For instance, one concern arises from the corresponding increase in pH associated with its addition. With the beneficial effect of pH already well known, it is difficult to differentiate between the effect presented from silica and that to pH without a carefully controlled experiment. Control that is not typically present when observing any treatment within a water distribution system itself. Although there have been limited studies that exhibit the experimental control necessary, promulgation of the Lead and Copper Rule in 1991 has brought attention to research in this area.

Iron Release

Although there are many studies pertaining to the effect of silica on iron corrosion rates, their effect on iron release from corrosion scale is not well documented. As recent as 2002, it was reported within a credible document discussing iron corrosion that there has yet to be a thorough evaluation of iron release in the presence of silica (Sarin, 2004).

Early documentation suggests that treatment with sodium silicate improved red water problems within a distribution system (Thresh, 1922). Speller (1926) claimed that waters with natural silica were less corrosive than water with less silica. This fact may complicate research with
which silica is naturally present. It would be nearly impossible to isolate the effects of natural silica and the added sodium silicate. Some literature has admitted to the incorporation of natural silica into the overall determination of dosage without justification (Hanson et al, 1945).

Stericker (1938) was responsible for the earliest attempt to define an inherent mechanism for the action of sodium silicate as it pertained to iron corrosion. The proposed mechanism begins with the attraction of the negatively charged silicate to the positively charged iron ions upon corrosion. A gel is then formed following the coalescence of silicate particles. Stericker personally came to believe that ferrous hydroxide reacted with silicate to form a ferrous silicate that was light green in appearance. Stericker also notes that existence of a zinc silicate when galvanized piping is treated sodium silicate. The existence of silicate-based scales is supported by Imhoff (1943).

As previous mentioned, Lehrman and Shuldener (1952) examined the possibility of silicate reacting with ferric and zinc hydroxides. The research suggested that the mechanism followed chemisorption for zinc hydroxide, while there was no conclusion for iron hydroxide. It was postulated that sodium silicate formed a film consisting of two layers; a lower layer of corrosion products and an upper layer of silica-metal hydroxide and silica gel that enmeshes compounds of iron. It has been suggested that an initial corrosion layer of iron is necessary for sodium silicate to form a film (Lehrman, 1951). Other early studies have indicated that sodium silicate was effective with decreasing corrosion rates of galvanized steel, however, there was no analysis concerned with the impact on water quality (Lehrman, 1957; Lane, 1973).
Rushing, McNeill, and Edwards (2003) conducted a 4-month long experiment in which iron coupons were treated with water containing 0.5, 10, 25, or 50 mg/L of silica as SiO$_2$. The study found that the amount of total iron suspended in the water increased as the concentration of silica had increased. Water was changed twice during the study, and each time the total suspended iron concentrations increased with time, but at a rate lower than the previous change of water. Thus as the iron samples aged, the total iron release decreased. During the experiments with silica concentrations of 25 and 50 mg/L, the silica concentration was found to decrease with time. The author explains the decrease in silica as a possible result of 1) silica becoming incorporated into the scale by sorbing to the iron surface, 2) formation of an iron-silica solid on the surface of the iron scale, and 3) catalyzing effect of iron corrosion encouraging the formation of a crystalline form of silica. It was suggested that the second scenario seems to describe the relationship observed during the study. This is evidenced by the fact that the rates of iron release and silica uptake corresponded well with each other. Although this study appears to contradict the classification of silica as a corrosion inhibitor, the author states that if the trends in iron release continued, then long term effects of silica might be beneficial.

Schock, Lytle, Sandvig, Clement, and Harmon (2005) assessed the water quality of a drinking water distribution system following treatment with sodium silicate. This was in response to the failure of a utility to meet the Lead and Copper Rule action levels, and a red water problem for the region. The case study took place from October of 1993 to July of 1995. About 4 months of base line data was collected before treating 2 of the well sources with 25-30 mg/L SiO$_2$. 

Following about 9 months of treatment with silica, the dose was increased to 45-55 mg/L SiO$_2$. Following silica addition the iron concentrations initially increased. The justification for this observation was inconclusive. It was suggested that some seasonal effect may have caused the increase in iron. However, the aesthetic concerns that are commonly attributed to iron release such as turbidity and color remained acceptable. This may be explained from the ability of silica to sequester iron. Silica has often been used as an agent to sequester iron and has been thoroughly studied (Robinson, 1992). Once again, this study is limited and does not distinguish benefits from pH increase.

MacQuarrie, Mavinic, and Neden (1997) analyzed the corrosion of cast iron coupons during a pilot study. Weight loss analyses, as expressed in terms of equivalent rates of penetration (mm/yr), suggested that differences between silica and the control were inconclusive. Scale thickness was tracked and was found to build up with time at 2.03 mm/yr. The line corresponding to no treatment with silica, but equivalent pH and alkalinity was greater at 3.81 mm/yr. Unfortunately, iron release was not monitored during this study. Other corrosion rate studies found that sodium silicate decreased the corrosion rate of iron coupons (Armstrong et al, 1994; Osterhus, 2001; Hem et al, 2001). Hem et al (2001) suggested that this reduction in iron corrosion rate was induced by an increase in pH.

Davis, Chen, and Edwards (2002) studied silica sorption at 0-200 mg/L SiO$_2$ on ferric hydroxide at pH from 5 to 9.5. They concluded that at all pH studied, sorption densities exceeding monolayer sorption were observed at silica levels typical of natural waters. The authors
proposed a soluble dimeric silica Si$_2$O$_2$(OH)$_5$ sorption model which fitted the data from zero to 0.40 mol SiO$_2$/mol Fe. They also reported that the iron surfaces become more negatively charged with increasing SiO$_2$ dose and pH.

Sodium silicate has been investigated for its properties as a sequestering agent for iron and manganese (Dart, 1970; Robinson, 1992). Silica may react with iron to form a complex that prevents the formation of iron particles associated with red water. The complexing property of silica has been used to explain another possible mechanism for inhibition of iron corrosion rates. Since ferric oxides are more porous, and thus less protective, than ferrous iron scale, deterring oxidation of ferrous to ferric iron via complexation may inhibit corrosion of iron (Benjamin, 1996).

Copper Release

Lab Studies

Pinto, McAnally, and Flora (1997) evaluated various corrosion control strategies for waters that can be characterized as having low hardness and low alkalinity. The experimental set-up consisted of several batch systems containing an assembly of copper coupons partially coated with lead/tin solder. Samples were analyzed following a 8-hour and 68-hour stagnation time for each experiment. All experiments had a control (no treatment) and also a control that was intended to match the pH of a designated line treated with silica. Silica doses ranged from 15 to 30 mg/L as SiO$_2$. 

12
The study concluded that the silicate inhibitor could be used as an effective method for reducing copper release. However, it should be noted that there was little attempt to quantify the extent of this effect. The study showed that the pH adjustment performed better than the silica treatment for the 68-hour stagnation for nearly all cases. For the 8-hour stagnation times, the silica treated systems performed either similarly or better than the pH adjustment. The copper concentrations observed during this study were nearly negligible with the control averaging 0.04 mg/L Cu for the first phase and 0.03 mg/L for the second phase.

MacQuarrie, Mavinic, and Neden (1997) conducted a study to evaluate the effectiveness of silica within a system of loops. The study attempts to simulate the plumbing system of a house. Copper concentrations were measured after a 24-hour of stagnation. The experiment included a control line and a line with pH adjusted to that of the silica treated line. Alkalinity was increased as well to a moderate concentration of approximately 20 mg/L as CaCO₃. Although both the silica and pH adjusted line out-performed the control line, the author suggests that further addition of silica would do nothing to reduce copper mobility in pH and alkalinity adjusted water. Rather, further addition of silica might make the conditions slightly worse.

Osterhus (2001) also found that copper release can be mitigated for low alkalinity and hardness source waters. However, copper release from silica treated copper loops was indistinguishable from untreated samples with similar pH. Although the raw water pH was approximately 1 to 2 units lower than that of the silica treated lines, another treatment was employed that increased the pH after CO₂-dosage/CaCO₃-filtration. This process also increases the alkalinity from
approximately 2 to 30 mg/L as CaCO₃ during this study. However, increasing alkalinity has been shown to increase copper corrosion by-product because of a corresponding contribution to copper complexes (Edwards et al., 1996). Another interesting aspect concerning the study arises from corrosion rate analyses. Electrochemical measurements indicated that the anodic and cathodic half-reactions were affected differently between the silica and pH adjusted treatment. Since the reduction of copper corrosion rate is primarily an effect of increasing pH, both the silica and pH adjusted treatment would be expected to exhibit the same measurements. The author states that the difference may suggest a contribution from silicate on the corrosion and film formation mechanisms.

Powers (2001) investigated the effect of silica on the aging of cupric hydroxide aging. The study investigated the sorption of silica on cupric hydroxide. It was found that sorption was not a strong function of pH, and at all pH values the presence of silica hindered the aging process of cupric hydroxide to the less soluble tenorite (CuO). It was initially assumed that dioptase was formed upon addition of silica as follows.

\[
Cu(OH)_2 + Si(OH)_4 \rightarrow CuH_2SiO_4(\text{dioptase}) + H_2O
\]

The molar ratios of copper to silica in the solid samples suggested that the concentration of dioptase would have, if indeed present, made up 2-29% of the total copper. However, x-ray diffraction analyses could not identify any solids located within a standard database which included dioptase. Given the lack of evidence to suggest dioptase, the author refers to the incorporation of silica within the cupric hydroxide matrix as an adsorption mechanism of monomeric or polymeric silica.
Becker (2002) tested the effect of silica using 13 test pipe rigs consisting of copper tubes and ring coupons for a one year study with relatively high alkalinity water. Silica doses ranged from 3-12 mg/L SiO$_2$. The study found that copper concentrations decreased, with the efficiency depending significantly on the silica concentration. Time series weight loss analyses on copper coupons placed within the system demonstrate the influent of silica dose as well. When comparing against the identical pH value and precipitation potential of the control line it was apparent that silica reduced copper concentrations more than adding only NaOH.

Surface layer analyses were also conducted on the copper coupons. Measurements of the mass per unit area of the copper layer indicated that increasing dose encourages this property to become smaller. The silica composition of the surface layer, reported as mass of silica per unit area, corresponded with the increase in dose. Formations of thick deposits of silica were found for concentrations of 3 and 8 mg/L SiO$_2$, while the highest 12 mg/L dose was reported to stimulate the formation of thin copper layers.

Site-Specific Studies
In 1995, a study was conducted in Wilbraham, MA to evaluate the implementation of a pilot water treatment program to control copper and lead release (Chiodini, 1998). The initial water quality of the raw water source is characterized by hardness averaging 2.7 mg/L as CaCO$_3$ and alkalinity of 5.0 mg/L as CaCO$_3$. The initial silica dose was targeted at 20 mg/L and then reduced to 12 mg/L upon equilibration of the influent concentration. Significant reductions in
copper release were observed throughout the study. The pH impact of the treatment was left confounded with the dose of silica.

Schock, Lytle, Sandvig, Clement, and Harmon (2005) included an evaluation of the effect of copper release within the water distribution system located in Hopkinton, MA (see Iron Release). The effectiveness of silica in the distribution system was apparent, and improved upon stabilization of the pH. The author notes that the observation appeared consistent with the slow formation of a protective film.

The evaluation of copper consisted of several analyses related to surface characterization that included x-ray diffraction (XRD) and scanning electron microscopy (SEM). This was done to gain some understanding of the mechanism of silica corrosion control. One of the copper pipes was analyzed before the study, while the other was analyzed afterwards. For the copper pipe removed before the study, the XRD analysis suggested that the pipe had a hard inner scale of malachite (Cu₂(OH)₂CO₃) and to a lesser extent cuprite (Cu₂O). However, the concentrations of copper observed during the study were much higher than permitted by malachite solubility characteristics. The SEM analysis suggested that the scale was inhomogeneous. Silica made up approximately 0.6-1.6% of the scale by weight. Calcium made up less than 0.2% of the scale. Following treatment with silica, coulometric inorganic carbon analysis yielded 0.2 and 0.3% as CO₂; much lower than 16% measured for the copper pipe prior to treatment. The information obtained from XRD and coulometric inorganic carbon analysis suggested that malachite was likely converted to some amorphous cupric silicate phase.
Lead Release

Lab Studies

Pinto, McAnally, and Flora (1997) monitored the effects of silica on the release of lead in the form of 50/50 lead-tin solder that partially coated the copper coupons (see Copper Release). Unlike the copper analysis, lead levels detected were relatively high, thus demonstrating a more salient contrast between treatments. During the study it was observed that silica significantly reduced lead release for both a 68 and 8-hour stagnation time. However, the reduction in lead release attained from an equivalent pH increase was more effective than the silica batches for the 68-hour stagnation time. The author states that this observation suggests that lead levels were reduced primarily because of an increase in pH and not due to the formation of a passivating layer. For the 8-hour stagnation time, the observations between the silica and pH adjusted treatments were consistent with the exception of the final month of the study. During the final month, lead levels were slightly lower for the silica treatment. This observation was described as a consequence of the slow formation of silicate surface films as suggested by previous studies (AWWARF, 1990).

MacQuarrie, Mavinic, and Neden (1997) evaluated lead release in addition to copper release (see Copper Release). Copper loops were joined together by 50/50 lead-tin solder. Another source of lead came from coils of 50/50 lead-tin solder that were installed immediately downstream of the copper loops. When a sample was taken from the copper loops, lead levels were typically higher for the silica treatment when compared with the pH adjustment. It appeared that any
further addition of silica might have actually made lead release worse than the raw water. For a 24-stagnation within the lead-tin coils, the author stated that none of the treatments (includes treatments other than silica and pH adjustment) reduced lead release.

A general theory for the action of sodium silicate on lead release suggests that a protective film on an already corroded lead surface forms via an adsorption mechanism (LaRosa-Thompson, 1997; Scheetz, 1997). It has been suggested that this film supports a diffusion barrier that slows the rate at which equilibrium of the system is attained with the bulk solution (Stericker, 1945). Schock et al (2005) states that there is no strong evidence to support this as the mechanism. An adsorption mechanism, which implies that silica could be detected on samples exposed to sodium silicate, seems to be implied by some of the results of Scheetz (1997).

The USEPA studied the effect of silicate on lead release during 1979 and 1980 (Schock et al, 1996). It was noted that lead release was not much different from the control of the experiment during the first run. During the first run the silicate doses were 10 and 20 mg/L as SiO₂. However, after refilling the experimental units with new water and allowing an incubation period of about 8 to 9 months, the amount of lead release began to decrease. The mechanism of the study was inconclusive.

Johnson et al (1993) found that sodium silicate addition was beneficial during an analysis of several corrosion control techniques. Sheiham (1981) noted that treatment with sodium silicate showed little improvement in lead control. Other researchers (Ryder, 1985) have suggested that
any benefit from sodium silicate addition is the associative effect of increasing pH. The effect of pH of lead release has been well documented (Schock, 1989).

**Site-Specific Studies**

Lytle, Schock, and Sorg (1996) performed a study in two isolated sections of a building plumbing system to determine whether lead levels could decrease without treatment. However, following 8 months and the absence of any positive results, a second study was performed to include treatment with several corrosion inhibitors. As one of the treatments 32 mg/L SiO$_2$ was maintained, then dropped to 16 mg/L after 71 days. For both doses the concentrations of silica suggested silicate deposition that caused about a 1 mg/L drop. Average alkalinity was 32 mg/L as CaCO$_3$ and average pH was 8.0 for the source water. Release of lead diminished upon silica treatment, and stabilized after 25 day. Once the original maintenance dose of 32 mg/L was dropped, there appeared to be no impact on lead release. It was mentioned that the silica doses used were much greater than manufacturer recommendations and that further reduction could be tolerated.

Chiodini (1998) analyzed lead release from a pilot performed in Wilbraham, MA (see *Copper Release*). The operation resulted in significant reductions in lead concentrations at all sampling points. With some violations exceeding 100 ppb, the maximum sample observed following treatment was 19 ppb. Control of lead release appeared to progressively improve as the silica treatment continued.
Schock, Lytle, Sandvig, Clement, and Harmon (2005) included an evaluation of the effect of lead release within the water distribution system located in Hopkinton, MA (see Iron Release). The 90th percentile lead levels declined from 77 ppb to 2 ppb during the study. Surface analyses, similar to that performed on the copper pipes (see Copper Release), were performed on lead pipes obtained from a section of service lines before treatment. These pipes had been previously exposed to polyphosphate inhibitor. The analysis found that the scale was comprised of 3 layers 1) a reddish outermost layer consisting of the very insoluble chloropyromorphite (Pb₅(PO₄)₃Cl), 2) a white layer beneath the outermost layer consisted almost entirely of cerussite (PbCO₃), and 3) below the cerussite layer was a gray-white layer containing highly soluble litharge (PbO).

Past Modeling Efforts

During the previous study (TBWI), iron, copper, and lead release was analyzed in response to changing water quality (Taylor et al., 2005). Empirical modeling efforts determined the least squares estimates for a predictive model of non-linear form for total iron (was related to color), copper, and lead. The information provided from this study provides somewhat of a control in itself. Since the pilot distribution system remained unchanged, the response of the system to changing water quality is now somewhat anticipated. This offers information surrounding the form, and the terms, of the models to be developed for the case with silica as a corrosion inhibitor.
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CHAPTER 2
EFFECTS OF SOURCE WATER BLENDING FOLLOWING TREATMENT WITH SODIUM SILICATE AS A CORROSION INHIBITOR ON IRON RELEASE

Abstract

The effects of various sodium silicate corrosion inhibitor doses, ranging from 3 to 12 mg/L-SiO₂, on iron release were investigated during a field study. The study was conducted within a pre-existing drinking water distribution pilot system. The sources of iron release consisted of 1) lined cast iron, 2) un-lined cast iron, and 3) galvanized steel. Water quality changes occurred for each phase of operation (4 phases in total). Variations in water quality were implemented through blending differing proportions from 3 different source waters; groundwater, surface water, and desalinated water. The study analyzed both total and dissolved iron release. A non-linear regression model was developed to describe total iron release in terms of water quality. A two-way ANOVA performed on the data set suggested that there was little validity for including silica dose in the empirical model. The empirical model suggested that alkalinity, chlorides, and pH had an effect on iron release ($R^2 = 0.36$). Data included within the set for regressional analysis consisted of the experimental lines treated with sodium silicate and two control lines. One of the controls was designated as treatment with pH adjustment, while the other represented the equilibrium pH. Surface compositional analyses were performed on iron and galvanized steel coupons to offer incite into the possibility of protection by scale formation. Referring to silica deposits of the coupon surface, there was insufficient evidence that the coupons were different from those of the controls.
Introduction

A pilot distribution system was analyzed over a course of approximately a year to evaluate different strategies for control of metal release. This paper is intended to discuss iron release using data that corresponded to treatment with sodium silicate. The study also included variations in water quality that were achieved through controlling the proportions of blended source waters. Seasonal variations also impacted water quality. The study attempts to quantify the effect of treatment, and also to evaluate the mechanisms associated with such an effect.

The first recorded use of sodium silicate as a corrosion inhibitor within a distribution systems occurred in 1922 (Thresh, 1922). Although this treatment was originally intended to reduce lead release, it was later reported that red water problems were improved. During an unrelated event, Speller (1926) claimed that waters with natural silica were less corrosive than water with less silica. Despite the relatively long history of sodium silicate addition, research has been somewhat inconclusive regarding the precise benefit of the sodium silicate. Research has been primarily devoted to corrosion rates of iron, while studies concerning iron release in the presence of sodium silicate are not well documented (Sarin, 2004). Other limitations have been prevalent within the research of sodium silicate. In waters where silica is naturally present it becomes nearly impossible to identify the effects of the natural silica and sodium silicate added. For this reason, some applications of sodium silicate have included the natural silica into their determination of dosage with no scientific justification (Hanlon et al, 1945). Another complication of studying the effect of sodium silicate on iron originates from the alkaline
properties of the sodium silicate solution. It has been suggested that the principal benefit of treatment with sodium silicate is pH increase associated with its use (Ryder, 1985).

Early researchers describe the action of sodium silicate inhibitor as a consequence of its ability to form a thin film (Stericker, 1938). The proposed mechanism begins with the attraction of the negatively charge silicate to the positively charge iron ions upon corrosion. A gel is then formed following the coalescence of silicate particles. Stericker suggested, because of some later experience, that ferrous hydroxide reacted with silicate to form a ferrous silicate that was light green in appearance. For galvanizing piping, Stericker documents the existence of a zinc silicate following exposure to sodium silicate.

Lehrman and Shuldener (1952) examined potential for reactions of silicate with ferric and zinc hydroxides. Both removed silica with the mechanism for zinc hydroxide suggested to be chemisorptions, while that of ferric hydroxide was undecided. It was postulated that sodium silicate formed a film consisting of two layers; a lower layer of corrosion products and an upper layer of silica – metal hydroxide and silica gel that enmeshes compounds of iron. The authors claim that the initial presence of the corrosion products is necessary for film formation (Lehrman, 1951). Other early studies indicated that sodium silicate decreased corrosion rates of galvanized steel, but did not discuss water quality impacts (Lehrman, 1957; Lane, 1973).

The literature describes the use of sodium silicate as a sequestering agent for iron and manganese (Dart, 1970; Robinson, 1992). Dissolved silica reacts with iron to form a complex that prevents
the formation of iron particles typically associated with red water problems. This property of sodium silicates has further implications in mitigating iron corrosion. Ferric oxides are considered porous, and thus a less protective scale compared to the Fe(II)-based scales. Complexing agents of ferrous ions are thought to deter the oxidation to ferric ions, and thus facilitate the formation of Fe(II) scale (Benjamin, 1996).

More recent studies have been implemented in response to the lead and copper rule. Some of these studies have taken a more comprehensive evaluation, and have extended their studies to include the water distribution system in general. Schock et al (2005), during a comprehensive field analysis, found that iron concentrations initially increased following silicate addition, with no conclusive justification for this observation offered. Rushing et al (2003) conducted a laboratory study concerning the effects of sodium silicate dose with iron release. The study found that the amount of total iron suspended in the water increased as the concentration of silica had increased. While this relationship prevailed through the course of the study, it was noted that, as the iron coupon samples aged, the total iron release steadily decreased. The study clearly showed that silica was taken out of solution during the experiments. MacQuarrie et al (1997) conducted a study that was limited to an analysis of corrosion rates for iron coupons. Sodium silicate decreased the corrosion rate of the iron coupons. Armstrong et al (1994) supported similar findings. Osterhus (2001) found the same relationship between sodium silicate treatment and iron corrosion rates. Inspection of the scale treated with sodium silicate also indicated the presence of a discontinuous iron and calcium silicate scale within the top layer. There is evidence that such silicate-based scales exist in water distribution systems (Imhoff, 1943). Hem
et al (2001) studied iron corrosion rates following sodium silicate treatment and suggested that the reduction in iron corrosion rate was induced by an increase in pH.

The dates corresponding to these studies suggest a relatively recent resurgence in the study of iron corrosion under treatment with sodium silicate. However, with the exception of Rushing et al (2003), there is a clear lack of information related to iron release following sodium silicate treatment. This paper is intended to expand the understanding of sodium silicate as it pertains to effects on water quality.

**Experimental Methods**

**Pilot Distribution System**

This project used existing facilities from a previous study examining the effects of varying water quality on metal release (Taylor et al, 2005). A description of the facilities and operations will be limited to those that were necessary for analysis of iron release. Blended source water was pumped into 14 different pilot distribution systems (PDS) labeled lines 1 to 14. Both the source water and inhibitor were fed into an influent standpipe that can be seen as the green, upright pipes on the left of Figure 2-1. Lines 1 to 14 were hybrid lines that consisted of the materials shown in Table 2-1.
Table 2-1  Description of pipe materials used in hybrid system (i.e. PDS)

<table>
<thead>
<tr>
<th>Order of Entry</th>
<th>Pipe Material</th>
<th>Length (feet)</th>
<th>Nom. Diameter (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st}</td>
<td>PVC</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>2\textsuperscript{nd}</td>
<td>Lined Cast Iron</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>3\textsuperscript{rd}</td>
<td>Unlined Cast Iron</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>4\textsuperscript{th}</td>
<td>Galvanized Steel</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

The system of pipes is displayed as the right image in Figure 2-1. The PDSs were designed to operate at a 2-day hydraulic residence time (HRT). Such operating conditions were designed to simulate characteristics of the TBW Member Government’s distribution systems. Intermediate (neither influent nor effluent) sampling ports were positioned such that a sample port was located ahead of a change in pipe material.

Figure 2-1  Inhibitor tanks, standpipes, pumps for influent (left) and PDS in flow direction (right)
Upon approaching the effluent standpipe, a portion of effluent water from each PDS line was pumped to cradles that contained iron coupons, while another portion was directed into a system of copper corrosion loops.

Blending of Source Waters

Blends were prepared from various proportions of conventionally treated groundwater (GW), enhanced coagulation-sedimentation-filtration surface water (SW), and desalinated water by reverse osmosis (RO). While the GW and RO were obtained from the project site, SW was obtained from the TBW regional surface water treatment plant. Selected average water quality parameters for each source water are shown in Table 2-2. The water quality of each source water was intended to remain unchanged throughout operation. However, some minor variations of surface water were understandably unavoidable with seasonal changes.

<table>
<thead>
<tr>
<th>Source Water</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Ca Hardness</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>TDS</th>
<th>DO</th>
<th>UV₂₅₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>mg/L as CaCO₃</td>
<td>mg/L as CaCO₃</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>GW</td>
<td>7.7</td>
<td>211</td>
<td>214</td>
<td>36</td>
<td>29</td>
<td>357</td>
<td>7.4</td>
<td>0.073</td>
</tr>
<tr>
<td>SW</td>
<td>7.8</td>
<td>79</td>
<td>210</td>
<td>51</td>
<td>184</td>
<td>428</td>
<td>8.8</td>
<td>0.058</td>
</tr>
<tr>
<td>RO</td>
<td>7.9</td>
<td>70</td>
<td>63</td>
<td>92</td>
<td>2</td>
<td>285</td>
<td>8.3</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The project duration required 4 phases of operation. Each phase generally took 3 months of data collection to complete. The phases represented a difference in blend, and thus a difference in water quality, that was obtained from predetermined ratios of source water. The corresponding
ratios of GW, SW, and RO for each phase are shown in Table 2-3. Although the ratios for Phase I and Phase III are identical, water quality was somewhat dissimilar as a consequence of seasonal variations with source waters (namely SW). The contrast between Phase I and Phase III was originally intended for the analysis of a seasonal, or, more appropriately, a temperature effect.

### Table 2-3 Blend composition for each phase of operation

<table>
<thead>
<tr>
<th>Phase</th>
<th>Time Period</th>
<th>%GW</th>
<th>%SW</th>
<th>%RO</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Feb-May 2006</td>
<td>62</td>
<td>27</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>II</td>
<td>May-Aug 2006</td>
<td>27</td>
<td>62</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>IV</td>
<td>Nov 2006-Feb 2007</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

**Silicate Addition**

During all 4 phases of operation, PDS 10, 11, and 12 were treated with silica inhibitor. The silica inhibitor used was N-type® sodium silicate solution with a SiO<sub>2</sub>/Na<sub>2</sub>O weight ratio of 3.22 (PQ Corporation, Valley Forge, Pa.). The solution was diluted and stored in 2 separate chemical storage tanks that were prepared weekly. One stock tank was designated for PDS 10 (low dose), while the other was designated for PDS 11 and PDS 12 (medium and high dose). The solutions were diluted to approximately 110 mg/L-SiO<sub>2</sub> for the low dose, and to approximately 220 mg/L-SiO<sub>2</sub> using the low alkalinity RO source water. This protocol prevented the precipitation of calcium carbonate in the stock tank. The flow of the inhibitor into the system represented about 6% of the total flow for the highest dosing condition; therefore the composition of the blend deviated only slightly. The accuracy for each dose was evaluated at least twice a week.
Originally doses were established at 10, 20, and 40 mg/L-SiO$_2$ for PDSs 10, 11, and 12, respectively. However, after the fourth week of operation during Phase I, the doses were lowered to 3, 6, and 12 mg/L-SiO$_2$ above the background silica concentration of the blended source water. Lowering the doses was necessary to prevent the precipitation of calcium carbonate in PDS 11 and PDS 12, which had impeded operations early in Phase I.

Neither PDS 13 nor PDS 14 received a corrosion inhibitor. PDS 13 represented the equilibrium condition, while PDS 14 was considered to represent an increase in pH. PDS 13 was allocated as the control, although PDS 14 represented the common blended source water that received the inhibitors. PDS 13 was fed by a separate tank that used blended source water that was similar to PDS 14 with the only difference being that hydrochloric acid was added to the tank.

**Sampling and Data Collection**

Selected water quality parameters that were considered as possible variables for the empirical modeling of iron release are shown in Table 2-4 and Table 2-5. Influent and effluent water quality data was collected weekly from PDSs 1-14 during the first phase of operation. Sampling was limited for some water quality monitoring to a biweekly schedule. For analyses conducted at both the field lab and at the UCF lab, the number of replicates assigned represented at least 10% of the samples. Blind duplicates and spikes were taken to represent at least 10% of the samples for selected water quality parameters.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method Reference</th>
<th>Method Description</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>SM 2320B</td>
<td>Titration Method</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>SM 4110</td>
<td>Ion Chromatography with Chemical Suppression of Eluent Conductivity</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Color</td>
<td>SM 2120A</td>
<td>Or Hach 8025 Cobalt-Platinate Method (with spec)</td>
<td>1 CPU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>SM 2510B</td>
<td>Laboratory Method</td>
<td>1 μmho/cm</td>
</tr>
<tr>
<td>Copper</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrogen (NH₃,TKN)</td>
<td>SM 4500-Norg</td>
<td>Macro-Kjeldahl Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrate (NO₃)</td>
<td>SM 4500-NH₄</td>
<td>Persulfate-UV Oxidation Method</td>
<td>0.1 mg C/L</td>
</tr>
<tr>
<td>pH</td>
<td>SM 4500-H⁺ B</td>
<td>Electrometric Method</td>
<td>± 0.01 pH units</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Silica</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Solids (TDS)</td>
<td>SM 1030E</td>
<td>Estimation of TDS by major ion sum</td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SM 4110</td>
<td>Suppression of Eluent Conductivity</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>SM 2130B</td>
<td>Nephelometric Method</td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>UV-254</td>
<td>SM 5910</td>
<td>UV Absorption at 254 nm</td>
<td>0.0001 cm⁻¹</td>
</tr>
<tr>
<td>Zinc</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
</tbody>
</table>
### Table 2-5  Selected water quality parameter and methods performed at field laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method Reference</th>
<th>Method Reference</th>
<th>Method Description</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>SM 2320 B</td>
<td>Titration</td>
<td></td>
<td>5 ppm</td>
</tr>
<tr>
<td>Ammonia-N</td>
<td>SM 4500-NH3 C</td>
<td>Membrane Probe Method</td>
<td></td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>SM 4500-Cl B</td>
<td>Argentometric Titration</td>
<td></td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Chlorine, free</td>
<td>SM 4500-Cl G or Hach 8021</td>
<td>DPD colorimetric</td>
<td></td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Chlorine, total</td>
<td>SM 4500-Cl-G or Hach 8167</td>
<td>DPD colorimetric</td>
<td></td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Color, apparent</td>
<td>SM 2120 B</td>
<td>Visual Comparison (by spectrometer)</td>
<td></td>
<td>1 CPU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>SM 2510 B</td>
<td>Conductivity Bridge</td>
<td></td>
<td>1 μmho/cm</td>
</tr>
<tr>
<td>Hardness (total, calcium)</td>
<td>SM 2340 C</td>
<td>EDTA Titration</td>
<td></td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Hach 8192</td>
<td>Cadmium reduction</td>
<td></td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Hach 8507</td>
<td>Diazotization</td>
<td></td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Oxygen, Dissolved (DO)</td>
<td>SM 4500-O G</td>
<td>Membrane probe</td>
<td></td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>SM 4500-H+ B</td>
<td>Electrometric</td>
<td></td>
<td>± 0.01 pH units</td>
</tr>
<tr>
<td>Phosphate-P (Reactive)</td>
<td>SM 4500-P E. or Hach 8048</td>
<td>Ascorbic Acid Method</td>
<td></td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Silica, SiO2 (reactive)</td>
<td>SM 4500-SiO2 or Hach 8185</td>
<td>Molybdsilicate Method</td>
<td></td>
<td>0.1 mg/L as SiO2</td>
</tr>
<tr>
<td>Temperature</td>
<td>SM 2550 B</td>
<td>Direct reading</td>
<td></td>
<td>0 deg C</td>
</tr>
<tr>
<td>Turbidity</td>
<td>SM 2130 B</td>
<td>Nephelometric</td>
<td></td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>UV254</td>
<td>SM 5910 A</td>
<td>UV spectrometry</td>
<td></td>
<td>0.0001 cm⁻¹</td>
</tr>
</tbody>
</table>

Iron and galvanized steel coupons were collected following every phase of operation. Iron and galvanized steel coupons had been exposed to all PDS waters, however, only medium doses and PDS 13 and PDS 14 were analyzed. Iron coupons were housed in a separate operation that received effluent water from the PDS. In contrast, galvanized steel coupons were housed within a separation operation as well, but this system received influent water from the PDS. The iron
and galvanized steel coupons were then analyzed using X-Ray Photoelectron Spectroscopy (XPS) within about 3 weeks following the end of each phase.

Results and Discussion

Performance of Si Treatment

Dose Maintenance
With the exception of the first 4 weeks of operation, silica doses were adjusted accordingly to maintenance doses of 3, 6, and 12 mg/L (all as SiO₂) representing the low, medium, and high doses. The box plots shown in Figure 2-2 illustrate the accuracy of these targets during the project as depicted by the mean, 25th and 75th percentiles, and minimum and maximum measurements. The silica concentrations represent the contribution of the inhibitor alone. These concentrations were determined as the amount of silica measured above the background from the control line, PDS 14.

It should be noted that Figure 2-2 does not include data from the first 4 weeks of sample collection. Originally the intended doses for silica were designated as 10, 20, and 40 mg/L, during which the average doses were 8.4, 21.6, and 43.1 mg/L. However, following the fourth week of operation, the accumulation of a precipitate was found to be impeding the flow for the PDS treated with the high dose. The average pH was 8.7 for the high dose, while the highest alkalinity (approximately 160 mg/L-CaCO₃) and hardness (approximately 220 mg/L-CaCO₃) occurred during Phase I. Such conditions favored the precipitation of calcium carbonate, and
following analysis of an observed reduction in calcium through the system, its presence was confirmed to be present.

With the possible exception of the medium dose, Figure 2-2 suggests that the targeted doses were maintained accurately about their intended doses with consistency. The medium dose was slightly greater than the targeted dose, operating on average at 6.7 mg/L. The medium dose still demonstrates precision in its maintenance, and may be regarded as a treatment level significantly different from the low and high doses.

Figure 2-2  Silica addition for all phases
Response of Iron to Phase and Treatment

The source of iron in the effluent consisted of a contribution from both iron present in the source water and the action of iron release within the distribution system. The average total iron of the blended source water for each phase is shown in Table 2-6. Information within Table 2-6 was generated from influent data of PDS 14. PDS 14 utilized water from which all other treatments during the study had been derived. The amount of influent iron was significant enough so as not to assume that iron release was responsible for all of the effluent iron. In some cases, influent iron accounted for approximately 30% of the total iron measured from the effluent. Phases with the largest fraction of GW exhibited the highest levels of iron within the blended source water. For this reason, Phase I and Phase III demonstrated the highest influent iron levels during the study.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Total Iron (mg/L-Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>I</td>
<td>0.029</td>
</tr>
<tr>
<td>II</td>
<td>0.020</td>
</tr>
<tr>
<td>III</td>
<td>0.030</td>
</tr>
<tr>
<td>IV</td>
<td>0.022</td>
</tr>
</tbody>
</table>

The mean average, minimum, and maximum effluent iron concentration for each treatment and phase are shown in Table 2-7. Effluent iron concentrations during the study will be simply referred to as iron release. For a more accurate description of iron release (defined here as the change in total iron for the system) the reader should refer to Table 2-6 for the initial iron present in the system. PDS 10, 11, and 12 corresponded to the low, medium, and high doses of sodium.
silicate added in the pilot distribution system, respectively. PDS 13 and PDS 14 are referred to as controls since no inhibitor was added to both lines. However, PDS 14 represents the original blend. PDS 13 was made from the same blend as PDS 14, however, the pH of PDS 13 was reduced to approximately 0.3 units and held in a separate tank.

Data used for Table 2-7 was obtained from analysis of dissolved and total iron with the ICP. The detection limit for the analysis was 0.001 mg/L-Fe. For samples detected below the detection limit, the observation was recorded as 0.001 mg/L-Fe. This method of recording would render any assessment of the treatments as conservative. Note that there was no record of total iron measured below detection limit. Issues concerning the detection were typically characteristic of the dissolved fraction of the samples, and not the total iron. Minimum values of dissolved iron within Table 2-7 allude to the recording of at least one sample below detection limit. For Phase II, III, and IV, all of the samples exhibited a measurement below detection limit. In this respect, Phase I appears to differ from the other phases. However, dissolved iron data from Phase I was obtained from samples that had been filtered with a glass fiber filter, while the other phases utilized a membrane filter. Note that the membrane filter has a smaller pore size. Even with the biased differences between Phase I and the other phases, it is still apparent that the dissolved fraction represented a relatively small, yet variable, fraction of the total iron. Due to the filtration method, dissolved iron for Phase I typically represented approximately 20% of the total iron on average; while for observations that employed the use of membrane filters (began prior to the end of Phase II) the dissolved fraction was typically less than 10%, with more observations that were recorded below detection.
Table 2-7  Summary of iron release for Si and control PDSs

<table>
<thead>
<tr>
<th>Phase</th>
<th>PDS</th>
<th>Dissolved Iron (mg/L-Fe)</th>
<th>Total Iron (mg/L-Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>Min</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.018</td>
<td>0.003</td>
</tr>
<tr>
<td>I</td>
<td>11</td>
<td>0.015</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.021</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.016</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.016</td>
<td>0.003</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>0.019</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.018</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.009</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.025</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.030</td>
<td>0.001</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>0.008</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.008</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.009</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.011</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.009</td>
<td>0.001</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Considering the data summary of total iron from Table 2-7, it appears that all the treatments (PDS 10, 11, 12, and 14) significantly reduced iron release. Based on the criteria of operating below the secondary MCL of iron, it could be argued that treatment of any sort was somewhat unnecessary. In fact, of the average, all of the treatments during all phases performed at a satisfactory level. However, PDS 13 during Phases II and III was relatively close to the iron secondary standard. Following pH adjustment, iron release had been reduced to the point that a greater than 50% increase would be necessary to exceed the secondary standard.
Shown in Figure 2-3 are boxplots depicting total iron release for each phase of operation. Each boxplot was constructed from the mean average, minimum and maximum observation, and the lower and upper quartiles of the data. The secondary standard for iron of 0.3 mg/L-Fe is shown as a dotted boundary line for each diagram as well.

As previously mentioned, all treatments reduced iron release for each phase. Contrasting the distributions between the treatments and control seem to suggest the reduction was significant. In fact, a one-way ANOVA was conducted on the data for each phase. Following Tukey’s method of pairwise contrast for each phase ($\alpha = 0.05$), the statistical analysis suggested that there was a statistical difference between all the treatments and the control for Phase I, II, and III. For Phase I, the results of the ANOVA required that the maximum observations (evidence of being outliers) of the high dose and pH adjustment be removed from the data set. Note from Figure 2-3 that those particular observations skew the distribution towards the mean of the control. The removed observations were both from the last week of Phase I. This week followed a chlorine maintenance treatment of the pilot distribution system. Generally a chlorine burn was followed by the end of a phase.

The one-way ANOVA suggested that all of the Si data was significantly different from the control for Phase IV. However, there was insufficient evidence to suggest a difference between the control and the pH adjustment. This was likely due to the conspicuously greater variance in the control data that tended to extend into the distribution (box) of the pH adjustment. Although,
the one-way ANOVA suggested insufficient evidence of a difference, it is clear that the pH adjustment provided more precise control of iron release within the system during Phase IV.

While the boxplots suggest a beneficial effect for all treatments, effects are not so clear with the effect of Si dose. Based on the averages alone, there appears to be no evidence to suggest a monotonic relationship between dose and iron release for the data set (i.e. iron release does not continue to increase or decrease in response to increasing the dose). Iron release tended to decrease slightly as the dose was increase from low to medium for all phases except Phase I where the average iron release for the low and medium doses was nearly identical. Meanwhile, as the dose was further increased from medium to high, iron release tended to increase slightly. A two-way ANOVA of the entire data set will be discussed later during the regressional analysis section to determine the validity of introducing silica as a variable.
Figure 2-3  Total iron release for silica treated and control PDSs

Investigation of Scale Formation

The following section is intended to discuss the results from experimental findings concerning the chemical identity of the scales associated with iron release. These results include surface analyses of both cast iron (UCI) and galvanized steel (GS) coupons. The remaining source for iron release in the pilot distribution system, lined cast iron (LCI), was not analyzed. During the
preceding project in which there was no application of inhibitors, it was found that the dominant source of iron release in the hybrid system was UCI, while the remaining iron could be attributed to GS (Taylor et al, 2005).

**Surface Characterization**

XPS was used to identify the chemical composition of scales that formed on both cast iron (UCI) and galvanized steel (GS) coupons. UCI coupons received effluent water, while GS were exposed to water equivalent to the influent of the system. For each phase of operation, one coupons of both UCI and GS was exposed to medium dose Si. UCI and GS exposed to PDS 13 and PDS 14 were also scanned using XPS following each phase.

**Cast Iron**

For UCI coupons, high resolution scans were produced for the elements carbon, calcium, iron, oxygen, silica, and zinc. The binding energies used for deconvolution of the elemental scan were obtained from the NIST database. Tang identified surface scales on UCI, LCI, and GS during the preceding project using both XPS and XRD surface analyses (Tang, 2003).

The data obtained from the XPS analysis of UCI suggested that Fe$_2$O$_3$, Fe$_3$O$_4$, and FeOOH were the predominant species of iron scale. The distribution of the iron scale species, represented by the mean average, minimum, and maximum observations, are shown in Figure 2-4 for both Si treatment and the controls. There is no indication from the diagram that iron scale from both the Si and controls differed significantly. Based on Figure 2-4 it appears that the addition of Si did
not change the composition of the scale. This could simply suggest that the presence any ferrous or ferric species associated with silica are sparse compared to that of the predominant iron corrosion product.

The distribution of scales supported by Figure 2-4 seems consistent with the layered structure associated with iron corrosion in distribution systems. Mechanisms of iron release seem to suggest that the process is regulated by diffusion of Fe\(^{2+}\) towards the bulk where it is oxidized to Fe\(^{3+}\) which forms more sparingly soluble solids. Thus, the mechanism seems to imply that Fe\(^{3+}\) species are expected to form on outer layers (e.g. FeOOH which is a dehydrated form of Fe(OH)\(_3\)), while Fe\(^{2+}\) species are expected to be stable near the surface (e.g. Fe\(_2\)O\(_3\)). It should be noted that Fe\(_2\)O\(_3\) has been found to be the product of FeCO\(_3\) when exposed to air (Heuer, 1999). A compound consisting of a mixture of both +2 and +3 oxidation state, known as magnetite (Fe\(_3\)O\(_4\)), has been thought to form and deter migration of Fe\(^{2+}\) at the boundary between the inner porous layer and the outer layer (Burlingame, 2006). The scale is found in a thick shell-like layer. The results of the elemental iron scan support the presence of all these iron scale components previously described.
Figure 2-4  Distribution of iron compounds for all phases (cast iron coupons)

The data obtained from all the elements during the scan are shown in Table 2-8. Carbon was used as a reference for the remaining high resolution scans (284.6 eV). For reasons unknown, carbon was not detected during Phase III. A best estimate of the position at the peak height for that particular scan was made, and the other high resolution scans for that phase were shifted accordingly.

Calcium was found during Phase I, II, and IV of the cast iron coupons exposed to Si. All of the calcium was identified as calcium carbonate. The detection of calcium carbonate was just as likely within the control PDSs (pHS and pHs+0.3). Calcium carbonate was found for all phases
except that of Phase III for pHs (PDS 13). Oxygen was detected on all the scans for both the Si treated and control iron coupons. High resolution scans of oxygen verified the presence of oxide and carbonate scales.

Silica was detected during all phases of operation for the Si treated cast iron coupons as amorphous silica. Amorphous silica was found on the control samples as well. The frequency of detection was less than that of Si (6/8), however, given the small amount of sampling that took place there is insufficient evidence to claim that addition of Si increased the likelihood of detecting silica within the surface scale. A quantitative analysis was conducted on a surrogate parameter of the deconvoluted scans. This analysis was similar to comparing the amount of silica for each group of coupons (i.e. Si treated and control). The surrogate parameter for the amount of silica within a scale was the area of each deconvolution curve. An unpaired t-test was employed to each group of areas and found that there was no evidence to claim that the two groups were different from each other. The results suggest that the silica surface concentrations for cast iron treated with Si should not be expected to be different from the blended water.

The detection of zinc on the UCI coupons was likely a consequence of exposing the coupons to the effluent. Zinc from the GS section of the PDS was the source of zinc in the bulk solution. The XPS results suggested that zinc was largely present as ZnO.
### Table 2-8  Frequency of elements detected by XPS scans (cast iron coupons)

<table>
<thead>
<tr>
<th>Element Surveyed</th>
<th>No. of Positive Detections for the Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si (4 total)</td>
</tr>
<tr>
<td>Carbon</td>
<td>3</td>
</tr>
<tr>
<td>Calcium</td>
<td>3</td>
</tr>
<tr>
<td>Iron</td>
<td>4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4</td>
</tr>
<tr>
<td>Silica</td>
<td>4</td>
</tr>
<tr>
<td>Zinc</td>
<td>1</td>
</tr>
</tbody>
</table>

**Galvanized Steel**

High resolution scans were produced for the elements carbon, calcium, iron, oxygen, silica, and zinc for galvanized steel (GS) coupons. The binding energies used for deconvolution of the elemental scan were obtained from the NIST database. Tang identified surface scales on UCI, LCI, and GS during the preceding project using both XPS and XRD surface analyses (Tang, 2003).

The data obtained from the XPS analysis of GS suggested that Fe₂O₃, Fe₃O₄, and FeOOH were the predominant species of iron scale. Similar to the results of the cast iron coupons. The distribution of the iron scale species, represented by the mean average, minimum, and maximum observations, are shown in Figure 2-5 for both Si treatment and the controls. Unlike with the cast iron coupons, it seems that there may be a difference between the Si treated GS coupons and the controls. The results suggest that Si treated GS coupons had less FeOOH within the scale.
FeOOH represents the dehydrated form of Fe(OH)$_3$. Less FeOOH present in the scale indicates that there was less of an opportunity for oxidation of Fe(II) to form Fe(III) solids near the surface.

![Distribution of iron compounds for all phases (galvanized steel coupons)](image)

Figure 2-5  Distribution of iron compounds for all phases (galvanized steel coupons)

The data obtained from all the elements during the GS scan are shown in Table 2-9. Carbon was used as a reference for the remaining high resolution scans (284.6 eV). Calcium was found for all phases for GS coupons exposed to Si as calcium carbonate. Calcium was also detected and identified as calcium carbonate for 7 of the 8 GS coupon scans for the control PDSs. There is no evidence to claim that the stabilization of calcium carbonate on the surface of GS was any more likely for Si than the controls. Oxygen was detected on all the scans for both the Si treated and
control GS coupons. Deconvolution of oxygen suggested the presence of oxide and carbonate scales.

Silica was detected during all phases of operation for the Si treated GS coupons as amorphous silica. Amorphous silica was identified on scans for GS coupons exposed to the controls. Silica was detected on 6 of the 8 GS coupons analyzed for the control PDSs. This frequency is equivalent to the results from the cast iron coupons. Still the data between the cast iron and GS coupons appear to be independent. Although the overall frequency is the same, the events when silica was not detected occurred during different phases. For the cast iron coupons silica was not detected during Phase III for pHs and during Phase II for pHs+0.3. For the GS coupons silica was not detected during Phase I and Phase IV for pHs+0.3. As with the cast iron coupons, a similar quantitative analysis was performed and yielded the same conclusions.

As previously mentioned, GS coupons were housed in a section of the piping that received influent water from its respective treatment PDS. Thus any form of zinc detected during the XPS scan would have come directly from the GS coupon itself (raw water zinc was negligible). Consequently, zinc was detected on nearly all of the GS coupons that had been analyzed for both Si and controls. A high resolution scan was not generated for pHs+0.3 during Phase I for reasons that are unknown to the author. This failure to analyze zinc accounts for the one GS coupon with which zinc was not detected. All of the samples that had detectable zinc were found to be comprised of ZnO. Zn(OH)₂ was detected on 2/4 Si treated GS coupons (Phase I and II),
2/8 control GS coupons (Phase IV for pHs and Phase II for pHs+0.3). For all these cases ZnO represented a majority relative to Zn(OH)$_2$.

Table 2-9  Frequency of elements detected by XPS scans (galvanized steel coupons)

<table>
<thead>
<tr>
<th>Element Surveyed</th>
<th>Si (4 total)</th>
<th>pH (control) (8 total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Calcium</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Iron</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Silica</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Zinc</td>
<td>4</td>
<td>7</td>
</tr>
</tbody>
</table>

Thermodynamic Implications

Cast Iron

A pe-pH diagram, shown as Figure 2-6, provides a theoretical description of the solids to be expected. The diagram was modeled using water quality from the study. Iron solids considered during the development of the model include Fe(OH)$_2$, FeCO$_3$, Fe(OH)$_3$, FeSiO$_3$, and Fe$_2$SiO$_4$. Soluble species of iron were represented as Fe$^{2+}$, Fe$^{3+}$, FeOH$^+$, FeOH$^{2+}$, Fe(OH)$_2^+$, Fe(OH)$_4^-$, FeCO$_3^0$, and FeHCO$_3^+$. Thermodynamic data had been previously referenced by Snoeyink (1980) and Benjamin (2001).

Under the conditions demonstrated during the study, the model clearly identifies Fe(OH)$_3$ (ferric hydroxide) as the favorable solid. These conditions are depicted as the shaded cube in Figure 2-6. The boundaries of this cube were derived from measurements taken from samples
representing conditions in the bulk solution during the study. As previously discussed iron scale forms as a series of layers. Oxygen does not penetrate as well into the deep layers of the scale. The lack of oxygen would encourage an environment that would be less oxidative (i.e. lower $pe$). The diffusion limitation governed by the layered system of scale suggests that solids such as FeCO$_3$ and Fe$_2$SiO$_4$ are stable within the inner layers of the iron scale. Fe(OH)$_3$ would be expected near the outer layers of the scale, and should be the dominant species in the bulk (the solubility of Fe(OH)$_3$ is relatively low).

![Iron Species Diagram](image)

Figure 2-6 $pe$-$pH$ equilibrium diagram for iron species
Galvanized Steel

The effluent iron concentration represented a contribution from the source water and all of the hybrid lines. There was no procedure implicated during the study that allowed for the analysis of iron release from the galvanized steel (GS) section of the PDS. However, since source water zinc was negligible, the source of zinc was limited to the GS.

The protective properties of zinc are generally attributed to its active potential relative to iron. Because of this property, zinc is said to act as a sacrificial anode in the presence of an oxidant. Although this view of zinc is correct, it does not describe the complete benefit of a zinc coating. Upon oxidation, zinc can form a protective scale that may limit oxygen penetration to the iron surface and may also limit diffusion of dissolved iron to the bulk solution. The limitation of oxygen penetration may be supported by Figure 2-5 in which the presence of Fe(III) scale for control GS coupons is greater than that of the Si GS coupons (due to the higher pH of Si). The limitation of iron diffusion could not be assessed because the analysis of iron release was not focused on each individual iron-based material.

Zinc release within the system was significantly affected by the treatments implemented during the study. This relationship between zinc release and experimental treatment is illustrated in Figure 2-7. Notice that the secondary standard for zinc (5 mg/L as Zn) was not exceeded during the entire study. Zinc release during the study was of little concern with respect to regulatory limits. The importance of zinc release was to provide a basis for evaluating a controlling solid phase.
Figure 2-7  Total zinc release for silica treated and control PDSs

The XPS results suggested that ZnO and Zn(OH)$_2$ were present within the scale of the GS coupons. The development of a pe-pH diagram was not utilized for analysis of zinc simply because zinc can exist as Zn(0) and Zn(II). In evaluation of the thermodynamically favorable solid for a given pH and $C_T$, the least soluble solid would be theoretically present. Constants
provided by Schindler (1967) for ZnO and Baes and Mesmer (1976) for Zn(OH)\textsubscript{2} suggested that ZnO was the least soluble between the two solids. Evidence has suggested that Zn\textsubscript{5}(CO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{6} (hydrozincite) may act as the controlling solid phase in the presence of a carbonate source (Paulson et al, 1989).

A solubility model for both zinc oxide and hydrozincite are shown in Figure 2-8. The average alkalinity, pH, and zinc release for each phase are plotted on the diagram as well. The soluble species considered in the equilibrium model were Zn(OH)^+, Zn(OH)\textsubscript{2}^0, ZnHCO\textsubscript{3}^+, and ZnCO\textsubscript{3}^o (constants as shown in Trussel, 1996). Thermodynamic data for hydrozincite was obtained from Mercy et al (1998).
The ZnO model consistently over-predicts the actual zinc release data. It is not until a pH greater than 8.0 that the $Zn_T$ concentration is less than 1 mg/L-Zn for the region shown. In contrast, the hydrozincite model seems to provide a more accurate representation of zinc release during the study. However, this appears to contradict the findings from the XPS analysis of the GS coupons in which Zn(OH)$_2$ and ZnO were identified. Tang (2003) notes that during the stage of the study when there was no addition of inhibitor that XRD (X-ray diffraction) analyses identified hydrozincite. A key observation to that finding was that the peaks (proportional to the amount)
of the XRD scan for ZnO were predominant over hydrozincite. This coexistence of ZnO and hydrozincite on a corroded galvanized steel pipe was observed during Pisigan and Singley (1985). The XPS results from this study, combined with the solubility modeling, seem to suggest a layered formation consisting of an inner layer of ZnO and an outer, less prevalent, layer of hydrozincite for GS.

Empirical Modeling of Iron Release

Water Quality Available for Regressional Analysis

All variables that were considered for regressive analysis are shown in Table 2-10. The quantities shown in Table 2-10 represent the average of the blended source water for a given phase. The water quality associated with the blended source water was likely to be better described using the data from the pH adjusted PDS.

<table>
<thead>
<tr>
<th>Water Quality Parameters</th>
<th>Phase I</th>
<th>Phase II</th>
<th>Phase III</th>
<th>Phase IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (mg/L as SiO₂)</td>
<td>11</td>
<td>5</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>164</td>
<td>106</td>
<td>151</td>
<td>125</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>7.9</td>
<td>8.1</td>
<td>7.9</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>43</td>
<td>65</td>
<td>65</td>
<td>58</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>62</td>
<td>102</td>
<td>67</td>
<td>76</td>
</tr>
<tr>
<td>Influent Iron (mg/L)</td>
<td>0.029</td>
<td>0.020</td>
<td>0.030</td>
<td>0.022</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>77</td>
<td>72</td>
<td>78</td>
<td>58</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>7</td>
<td>36</td>
<td>41</td>
<td>32</td>
</tr>
<tr>
<td>UV-254 (cm⁻¹)</td>
<td>0.073</td>
<td>0.076</td>
<td>0.079</td>
<td>0.065</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>8.8</td>
<td>7.6</td>
<td>7.7</td>
<td>8.9</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.2</td>
<td>26.5</td>
<td>25.6</td>
<td>21.3</td>
</tr>
</tbody>
</table>
Model Evaluation

An empirical model, shown as Equation 2-1, was developed for the total iron release. A non-linear power model was used to describe total iron release. A stepwise approach was utilized to systematically reject variables upon exceeding a predetermined significance level (α = 0.05). The overall ANOVA for the model and all of the variables shown in Equation 2-1 were strongly significant (p-values < 0.0008). The $R^2$ value for the model was 0.36.

$$Total \text{ Fe} = 1.01^{(T-25)}\left(\text{Alk}\right)^{-0.57}\left(p\text{H}\right)^{-1.58}\left(\text{Cl}\right)^{0.98} + \text{Fe}_{\text{Inf}}$$  \hspace{1cm} \text{Equation 2-1}

where

- $Total \text{ Fe} = \text{total iron, mg/L-Fe}$
- $p\text{H} = -\log[H^+]$
- $\text{Alk} = \text{alkalinity, mg/L as CaCO}_3$
- $\text{Cl} = \text{chloride, mg/L}$
- $T = \text{temperature, \celsius}$
- $\text{Fe}_{\text{Inf}} = \text{influent iron, mg/L-Fe}$

Equation 2-1 suggests that iron release was unaffected by silicate addition. However, the relationships shown in Figure 2-3 clearly demonstrate that silicate had some effect on iron release. While the addition of silicate appeared to reduce iron release when compared to the control, there was no evidence that an increasing dosage continued to mitigate iron release. For this reason, silicate was not forced into the final model.

A two-way ANOVA was applied to the entire data set to further analyze the effect of treatment and phase on iron release. There was no evidence to suggest that an interaction existed between the treatment and phase. The two-way ANOVA found, using Tukey’s method of pairwise contrast at a significance level of 0.05, that there was a significant difference between all
treatments and the control (PDS 13). This indicates that an increase in pH of approximately >0.30 was sufficient in reducing iron release relative to the control for each phase. Not only were the treatments statistically different from the control, but the confidence limits to the contrast intervals suggested that there was a practical difference as well. For instance, the contrast between PDS 13 and PDS 14 (i.e. PDS 13 minus PDS 14) had a 95% confidence interval of [0.07, 0.11]. Note that even the lower limit of this 95% confidence interval could be considered significant in a practical sense. Of all of the contrasts against PDS 13, that of PDS 14 had the lowest mean difference and lowest lower confidence limit.

The only other pairwise contrast that was identified as statistically significant was the contrast between PDS 14 and PDS 11 (i.e. PDS 14 minus PDS 11). The 95% confidence interval for this contrast was [0.01, 0.06]. PDS 11 represents the medium dose of the study. The fact that PDS 12, the high dose, was not found to be significantly different from PDS 14 lends absolutely no support for a monotonic relationship between dose and iron release. Had the contrast between PDS 12 and PDS 14 been significant rather than that of PDS 11 and PDS 14, then it could be speculated that there was some lower limit necessary to notice a significant change when treating with Si. Rather than proposing some polynomial effect of silicate for this limited range of data, and since the difference between PDS 11 and PDS 14 was relatively small, silicate was not forced into the final model. To the author’s knowledge during writing there was no evidence of an effect that was anything other than monotonic within this range of dosing (assuming there was an effect).
The effect of phase when evaluated suggested that Phase II differed significantly from all of the other phases. From Equation 2-1, temperature, chlorides, alkalinity, and pH were sufficient in describing iron release for the study. The exponents imply that increases in both alkalinity and pH were benefit to the control of iron release. In contrast, the exponents of the model suggest that increases in chlorides and, to a lesser extent, temperature caused an increase in iron release on average. Phase II was characterized by low alkalinity and pH, and high chlorides and temperature. The only other significant contrast was between Phase I and Phase III. Although these two phases were initially intended to have identical water quality, excluding temperature, there were other significant differences. Chlorides were much higher for Phase III, while alkalinity decreased by approximately 5%. Another difference between Phase I and Phase III was a consequence of operational procedure rather than changes in source water. From Figure 2-3 it can be seen that the difference between the control and pH adjusted line was much less for Phase I than for Phase III. The likely cause for this was that the intended pH difference of 0.3 between PDS 13 and PDS 14 was much more precise during Phase III than during Phase I. In addition, Phase III exhibited, on average, a larger difference between PDS 13 and PDS 14 by approximately 0.2 pH units.

The performance of Equation 2-1 can be assessed from the diagram shown as Figure 2-9. The diagram represents a comparison of average predictions and average measurements of total iron release from the study. The upper limit whiskers represent the maximum observation, while the lower limit whiskers represent the minimum total iron release value from the predicted and measured data.
The model appears to do nothing more than predict the average between all the dose levels for a given phase. There is a slight decreasing trend associated with the predicted data. This relationship is a result of the confounding effect between silicate dose and pH increase. Since the water quality for each phase can be regarded as remaining relatively constant, the variation associated with the predicted data is a result of the pH term in Equation 2-1.
Conclusions

The study suggests that the use of sodium silicate during this study was relatively ineffective in reducing iron release beyond that of pH adjustment. A list of specific findings from the study are as follows:

- Data from the study did not offer any indication that iron release was reduced as the silicate dose was increased. However, a two-way ANOVA on the data set suggested that the medium dose exhibited significantly less iron release than the blended source water (PDS 14). The low and high doses were not significantly different from the blended source water.

- With respect to the control (PDS 13), sodium silicate was effective in reducing iron release. However, there was essentially no additional benefit, for practical considerations, from the blended source water (PDS 14). As a reminder, the blended source water represented the pH adjustment treatment or pHs+0.3, whereas the control was simply pHs.

- Average iron release did not exceed the secondary MCL for any combination of treatment and phase during the study. Sodium silicate was unnecessary to maintain compliance with the iron secondary standard for all phases.

- There was insufficient evidence that the XPS scans of silica were different between the control and silicate treated coupons (i.e. further investigation would be necessary to claim that silica deposits were different from controls when treating with sodium silicate). This conclusion applies to both the cast iron (UCI) and galvanized steel (GS) coupons.

- The deconvoluted XPS scans of iron identified Fe₂O₃, Fe₃O₄, and FeOOH as predominant corrosion scales for both UCI and GS coupons. There was no indication that the distribution
of iron corrosion products differed from control following the addition of silicate for UCI coupons. However, for GS coupons, the distribution of scales shifted towards iron species of lower oxidation states when treating with silicate (likely due to a pH benefit).

- XPS scans of zinc for GS coupons identified ZnO as the predominant zinc corrosion scale. However, equilibrium modeling of zinc did not suggest that ZnO governed zinc release during the study. Zinc release was reduced by treatment with silicate. An equilibrium model assuming Zn₅(CO₃)₂(OH)₆ (hydrozincite) as a controlling solid phase appeared to describe the data for both the controls and the Si lines. Whereas a MSE for ZnO was calculated to be 11.4, the MSE for the hydrozincite model was much less at 0.04.

- Empirical modeling suggested that alkalinity, chlorides, and pH were the statistically significant variables for describing iron release during the study. Temperature (°C) was incorporated into the model as $K(T^{25})$, however, the estimate of $K$ was found to be nearly 1 ($K = 1.01$). This suggests only a slight change in iron release during the study due to the temperature. This change was unlikely to be separate from the random variation exhibited by the data. An increase in either alkalinity or pH would have decreased iron release on average, while an increase in chlorides would have encouraged iron release.

- Silica was not included as a term in the final empirical model describing iron release. Support for this decision was drawn from the two-way ANOVA results that did not indicate a significant difference amongst the dosages (between PDS 10, PDS 11, and PDS 12).
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CHAPTER 3
EFFECTS OF SOURCE WATER BLENDING FOLLOWING TREATMENT WITH SODIUM SILICATE AS A CORROSION INHIBITOR ON COPPER RELEASE

Abstract

The effects of various sodium silicate corrosion inhibitor doses, ranging from 3 to 12 mg/L-SiO₂, on copper release were investigated during a field study. The study was conducted within a pre-existing drinking water distribution pilot system where samples were drawn from a system of copper loops. Water quality changes occurred for each phase of operation (4 phases in total). Variations in water quality were implemented through blending differing proportions from 3 different source waters; groundwater, surface water, and desalinated water. The study analyzed both total and dissolved copper release. A linear regression model was developed to describe total copper release in terms of dose and water quality ($R^2 = 0.68$). The model suggested that the dose, alkalinity, chlorides, and pH had an effect on copper release. Data included within the set for regressional analysis consisted of the experimental lines treated with sodium silicate and two control loops. One of the controls was designated as treatment with pH adjustment, while the other represented the equilibrium pH. Total copper release demonstrated a beneficial response (i.e. decreasing copper release) after increasing the dose of sodium silicate. Surface compositional analyses were performed on copper coupons to offer incite into the possibility of protection by scale formation. The findings found evidence of a silicate-based surface film. Differences in scale were also confirmed visually as the color of the treated copper coupons produced a light green compound. Thermodynamic modeling was unsuccessful in alluding to the definite composition of the silicate-based scale.
Introduction

A study was conducted to study the response of a pre-existing pilot distribution system carried out from the facilities utilized during Taylor et al (2005), referred to as TBW I. As part of the project, metal release was evaluated throughout the course of operations. Different treatments, in the form of corrosion inhibitors, were implemented during the study to quantify the effectiveness on mitigating metal release. The topic of this paper refers to the response of copper tubes within the system when exposed to sodium silicate as the corrosion inhibitor.

There have been several studies documenting the effect of silicate treatment, however, the mechanism of describing the protection process is not well known. Studies influenced by differing water qualities tend to agree on a beneficial effect upon the addition of silicate inhibitor in decreasing copper levels (Schock, 2005; Chiodini, 1998; Pinto, 1997; Lytle, 1996; MacQuarrie, 1997; Osterhus, 2001; Lane, 1973). However, prior research has rendered some limitations to subsequent application and understanding of the silicate control of copper. Most of the literature consists of treatment of waters that are of relatively low in alkalinity while incorporating silicate addition (<30 mg/L as CaCO₃). The study following TBW I, referred to as TBW II, operated with blends that were considerably higher, ranging from approximately 100-160 mg/L as CaCO₃. It has been established that alkalinity has an undesirable effect of the release of copper (Pinto, 1997). This effect has been attributed to complex formation contributing to the soluble portion of copper species (Edwards, 1996; Xiao, 2004).
Aside from the lack of disparity in alkalinity, there has been little research devoted to other potentially influential water quality parameters in the presence of silicate inhibitor. This aspect of literature impedes the identification of an optimum silicate dosing requirements for the general utility. Operating under a variety of blended source waters during the study allowed for the assessment of copper control for systems of diverse water quality. Results presented in the literature have yet to elegantly quantify the effects of silicate addition. Regression techniques employed during the project provided a more quantitative representation of the main effect of silicate inhibitor along with the investigation of possible interactions with water quality.

The mechanism describing how the silicate inhibitor protects against copper release is currently questionable (Schock et al, 2005). The literature alludes to a disagreement between many researchers concerning the mode of inhibition. Part of this disparity may result from the pH response to the addition of a silicate solution. Since the silicate inhibitor is itself a highly alkaline solution, an increase in silicate dose is directly associated with an increase in pH. Thus, unless the pH is adjusted to that of the control, the silicate dose and pH are confounded. Research has well established that increasing pH is beneficial to the control of copper (Ferguson, 1996; Schock, 1995). Some research has suggested that the benefit of silicate addition may be explained by the pH contribution (Ryder, 1985; MacQuarrie, 1997).

Others suggest that the silicates may act as an anodic inhibitor forming a protective film on the metal surface where the positively charged metal species is released (Katanis, 1986; Schock, 2005; LaRosa-Thompson, 1997). Pinto conducted batch studies and observed the release from
copper coupons while varying silicate dose and compared these to control units with similar water quality and pH for each dose (Pinto, 1997). The results found that silicate addition performed either similarly or better than the pH adjustment for an 8-hour stagnation period. In contrast, Becker (2002) found that the effect of silicate was apparent of the sole effect of pH adjustment via base addition. Earlier work from Lehrman focused, in part, on the action of dilute solutions of silicate in hope of determining the mechanism of corrosion protection (Lehrman, 1952). The findings indicated that a reaction between a cupric hydroxide suspensions were possible under drinking water conditions. The study also suggested the importance of a pre-formed corrosion scale for silica to be taken up. Additional research has also suggested the incorporation of silica into the copper scale (Becker, 2002; Schock, 2005).

**Experimental methods**

**Pilot Distribution System**

This project used existing facilities from a previous study examining the effects of varying water quality on metal release (Taylor et al, 2005). A description of the facilities and operations will be limited to those that were necessary for analysis of copper corrosion. Blended source water was pumped into 14 different pilot distribution systems (PDS) labeled lines 1 to 14. Both the source water and inhibitor were fed into an influent standpipe that can be seen as the green, upright pipes on the left of Figure 3-1. Lines 1 to 14 were hybrid lines that consisted of pipe materials as described by Table 3-1.
Table 3-1  Description of pipe materials used in hybrid system (i.e. PDS)

<table>
<thead>
<tr>
<th>Order of Entry</th>
<th>Pipe Material</th>
<th>Length (feet)</th>
<th>Nom. Diameter (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>PVC</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>2nd</td>
<td>Lined Cast Iron</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>3rd</td>
<td>Unlined Cast Iron</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>4th</td>
<td>Galvanized Steel</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

The system of pipes is displayed as the right image in Figure 3-1. The PDSs were designed to operator at a 2-day hydraulic residence time (HRT). Such operating conditions were designed to simulate characteristics of the TBW Member Government’s distribution systems. Intermediate (neither influent nor effluent) sampling ports were positioned such that a sample port was located ahead of a change in pipe material.

Upon approaching the effluent standpipe, a portion of effluent water from each PDS line was pumped to cradles that contained copper coupons, while another portion was directed into a system of copper corrosion loops. These corrosion loops were housed within a non-air

Figure 3-1  Inhibitor tanks, standpipes, pumps for influent (left) and PDS in flow direction (right)
conditioned shed. Each copper loop was 30 feet in length and 5/8 inch in diameter, thus was able to hold approximately 1.8 L of water. One lead-tin coupon was placed within the copper tubing to simulate the presence of solders. To further simulate the hydraulic conditions of common household water usage by consumers, the corrosion loops were flushed with approximately 2 gallons of water every morning. Both the corrosion shed and copper loops are shown in Figure 3-2.

![Corrosion shed and copper loops](image)

Figure 3-2  Corrosion shed (left) and copper loops (right)

**Blending of Source Waters**

Blends were prepared from various proportions of conventionally treated groundwater (GW), enhanced coagulation-sedimentation-filtration surface water (SW), and desalinated water by reverse osmosis (RO). While the GW and RO were obtained from the project site, SW was obtained from the TBW regional surface water treatment plant. Selected average water quality parameters for each source water are shown in Table 3-2. The water quality of each source water was intended to remain unchanged throughout operation. However, some minor variations of surface water were understandably unavoidable with seasonal changes.
Table 3-2  Average source water quality

<table>
<thead>
<tr>
<th>Source Water</th>
<th>pH</th>
<th>Alkalinity (mg/L as CaCO3)</th>
<th>Ca Hardness (mg/L as CaCO3)</th>
<th>Cl^- (mg/L)</th>
<th>SO_4^{2-} (mg/L)</th>
<th>TDS (mg/L)</th>
<th>DO (mg/L)</th>
<th>UV_{254} cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW</td>
<td>7.7</td>
<td>211</td>
<td>214</td>
<td>36</td>
<td>29</td>
<td>357</td>
<td>7.4</td>
<td>0.073</td>
</tr>
<tr>
<td>SW</td>
<td>7.8</td>
<td>79</td>
<td>210</td>
<td>51</td>
<td>184</td>
<td>428</td>
<td>8.8</td>
<td>0.058</td>
</tr>
<tr>
<td>RO</td>
<td>7.9</td>
<td>70</td>
<td>63</td>
<td>92</td>
<td>2</td>
<td>285</td>
<td>8.3</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The project duration required 4 phases of operation. Each phase generally took 3 months of data collection to complete. The phases represented a difference in blend, and thus a difference in water quality, that was obtained from predetermined ratios of source water. The corresponding ratios of GW, SW, and RO for each phase are shown in Table 3-3. Although the ratios for Phase I and Phase III are identical, water quality was somewhat dissimilar as a consequence of seasonal variations with source waters (namely SW). The contrast between Phase I and Phase III was originally intended for the analysis of a seasonal, or, more appropriately, a temperature effect.

Table 3-3  Blend composition for each phase of operation

<table>
<thead>
<tr>
<th>Phase</th>
<th>Time Period</th>
<th>%GW</th>
<th>%SW</th>
<th>%RO</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Feb-May 2006</td>
<td>62</td>
<td>27</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>II</td>
<td>May-Aug 2006</td>
<td>27</td>
<td>62</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>IV</td>
<td>Nov 2006-Feb 2007</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

Silicate Addition

During all 4 phases of operation, PDS 10, 11, and 12 were treated with silica inhibitor. The silica inhibitor used was N-type® sodium silicate solution with a SiO_2/Na_2O weight ratio of 3.22 (PQ Corporation, Valley Forge, Pa.). The solution was diluted and stored in 2 separate chemical storage tanks that were prepared weekly. One stock tank was designated for PDS 10 (low dose),
while the other was designated for PDS 11 and PDS 12 (medium and high dose). The solutions were diluted to approximately 110 mg/L-SiO$_2$ for the low dose, and to approximately 220 mg/L-SiO$_2$ using the low alkalinity RO source water. This protocol prevented the precipitation of calcium carbonate in the stock tank. The flow of the inhibitor into the system represented about 6% of the total flow for the highest dosing condition; therefore the composition of the blend deviated only slightly. The accuracy for each dose was evaluated at least twice a week.

Originally doses were established at 10, 20, and 40 mg/L-SiO$_2$ for PDSs 10, 11, and 12, respectively. However, after the fourth week of operation during Phase I, the doses were lowered to 3, 6, and 12 mg/L-SiO$_2$ above the background silica concentration of the blended source water. Lowering the doses was necessary to prevent the precipitation of calcium carbonate in PDS 11 and PDS 12, which had impeded operations early in Phase I.

Neither PDS 13 nor PDS 14 received a corrosion inhibitor. PDS 13 represented the equilibrium condition, while PDS 14 was considered to represent an increase in pH. PDS 13 was allocated as the control, although PDS 14 represented the common blended source water that received the inhibitors. PDS 13 was fed by a separate tank that used blended source water that was similar to PDS 14 with the only difference being that hydrochloric acid was added to the tank.

**Sampling and Data Collection**

Selected water quality parameters that were considered as possible variables for the empirical modeling of copper release are shown in Table 3-4 and Table 3-5. Influent and effluent water
quality data was collected weekly from PDSs 1-14 during the first phase of operation. Sampling was limited for some water quality monitoring to a biweekly schedule. For analyses conducted at both the field lab and at the UCF lab, the number of replicates assigned represented at least 10% of the samples. Blind duplicates and spikes were taken to represent at least 10% of the samples for selected water quality parameters.

Table 3-4  Selected water quality parameters and methods at university laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method Reference</th>
<th>Method Description</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>SM 2320B</td>
<td>Titration Method</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>SM 4110</td>
<td>Ion Chromatography with Chemical Suppression of Eluent Conductivity</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Color</td>
<td>SM 2120A</td>
<td>Or Hach 8025 Cobalt-Platinate Method (with spec)</td>
<td>1 CPU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>SM 2510B</td>
<td>Laboratory Method</td>
<td>1 μmho/cm</td>
</tr>
<tr>
<td>Copper</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrogen (NH₃,TKN)</td>
<td>SM 4500-Norg</td>
<td>Macro-Kjeldahl Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>NPDOC</td>
<td>SM 5310C</td>
<td>Persulfate-UV Oxidation Method</td>
<td>± 0.01 mg C/L</td>
</tr>
<tr>
<td>pH</td>
<td>SM 4500-H⁺ B</td>
<td>Electrometric Method</td>
<td>± 0.01 pH units</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Silica</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Solids (TDS)</td>
<td>SM 1030E</td>
<td>Estimation of TDS by major ion sum</td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SM 4110</td>
<td>Ion Chromatography with Chemical Suppression of Eluent Conductivity</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>SM 2130B</td>
<td>Nephelometric Method</td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>UV-254</td>
<td>SM 5910</td>
<td>UV Absorption at 254 nm</td>
<td>0.0001 cm⁻¹</td>
</tr>
<tr>
<td>Zinc</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
</tbody>
</table>
Table 3-5  Selected water quality parameters and methods at field laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method Reference</th>
<th>Method Description</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>SM 2320 B</td>
<td>Titration</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Ammonia-N</td>
<td>SM 4500-NH3 C</td>
<td>Membrane Probe Method</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>SM 4500-Cl B</td>
<td>Argentometric Titration</td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Chlorine, free</td>
<td>SM 4500-Cl G or Hach 8021</td>
<td>DPD colorimetric</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Chlorine, total</td>
<td>SM 4500-Cl-G or Hach 8167</td>
<td>DPD colorimetric</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Color, apparent</td>
<td>SM 2120 B</td>
<td>Visual Comparison (by spectrometer)</td>
<td>1 CPU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>SM 2510 B</td>
<td>Conductivity Bridge</td>
<td>1 μmho/cm</td>
</tr>
<tr>
<td>Hardness (total, calcium)</td>
<td>SM 2340 C</td>
<td>EDTA Titration</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Hach 8192</td>
<td>Cadmium reduction</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Hach 8507</td>
<td>Diazotization</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Oxygen, Dissolved (DO)</td>
<td>SM 4500-O G</td>
<td>Membrane probe</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>SM 4500-H+ B</td>
<td>Electrometric</td>
<td>± 0.01 pH units</td>
</tr>
<tr>
<td>Phosphate-P (Reactive)</td>
<td>SM 4500-P E. or Hach 8048</td>
<td>Ascorbic Acid Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Silica, SiO₂ (reactive)</td>
<td>SM 4500-SiO₂ or Hach 8185</td>
<td>Molybdosilicate Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Temperature</td>
<td>SM 2550 B</td>
<td>Direct reading</td>
<td>0 deg C</td>
</tr>
<tr>
<td>Turbidity</td>
<td>SM 2130 B</td>
<td>Nephelometric</td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>UV254</td>
<td>SM 5910 A</td>
<td>UV spectrometry</td>
<td>0.0001 cm⁻¹</td>
</tr>
</tbody>
</table>

Copper release data was obtained from samples taken directly from the outlet port of the copper corrosion loops. During Phase I other water quality parameters were collected from the corrosion loops as well. Following Phase I it was determined that for the water quality parameters of interest, such as pH, alkalinity, and inhibitor dose, the differences between the effluent PDS ports and the corrosion loop outlet ports were insignificant. Thus following Phase I only total and dissolved copper, and total and dissolved lead were monitored from the corrosion
loops. These samples were collected following a 6-hour stagnation time that began at approximately 7:00 a.m.

Copper coupons were collected following every phase of operation. Copper coupons had been exposed to all PDS waters, however only medium doses and PDS 13 and PDS 14 were analyzed. For copper coupons exposed to silica inhibitor, there was one copper coupon that was exposed to the high dose of Phase III that was analyzed as well. The copper coupons were then analyzed using X-Ray Photoelectron Spectroscopy (XPS) within about 3 weeks following the end of each phase.

Results and Discussion

Dose Maintenance

With the exception of the first 4 weeks of operation, silica doses were adjusted accordingly to maintenance doses of 3, 6, and 12 mg/L (all as SiO$_2$) representing the low, medium, and high doses. The box plots shown in Figure 3-3 illustrate the accuracy of these targets during the project as depicted by the mean, 25$^{th}$ and 75$^{th}$ percentiles, and minimum and maximum measurements. The silica concentrations represent the contribution of the inhibitor alone. These concentrations were determined as the amount of silica measured above the background from the control line PDS 14.

It should be noted that Figure 3-3 does not include data from the first 4 weeks of sample collection. Originally the intended doses for silica were designated as 10, 20, and 40 mg/L,
during which the average doses were 8.4, 21.6, and 43.1 mg/L. However, following the fourth week of operation, the accumulation of a precipitate was found to be impeding the flow for the PDS treated with the high dose. The average pH was 8.7 for the high dose, while the highest alkalinity and hardness occurred during Phase I. Such conditions favored the precipitation of calcium carbonate, and following analysis of an observed reduction in calcium through the system, its presence was confirmed.

With the possible exception of the medium dose, Figure 3-3 suggests that the targeted doses were maintained accurately about their intended doses with consistency. The medium dose was slightly greater than the targeted dose, operating on average at 6.7 mg/L. The medium dose still demonstrates precision in its maintenance.
The effect of silica on the total release of copper can be demonstrated from the series of box plots in Figure 3-4. The data used did not include the sampling dates that occurred before the alteration of the silica inhibitor dose to 3/6/12 mg/L-SiO₂. Each box plot displays the average, lower and upper quartiles, and the minimum and maximum concentrations of total copper observed during the study. Each phase is shown separately to enhance any effect from varying water quality, while the controls are shown to illustrate the effect of silica addition. The results are shown tabulated below in Table 3-6 as well.
Table 3-6  Summary of copper release data for Si and control PDSs

<table>
<thead>
<tr>
<th>Phase</th>
<th>PDS</th>
<th>Dissolved Copper (mg/L-Cu)</th>
<th>Total Copper (mg/L-Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>Min</td>
</tr>
<tr>
<td>I</td>
<td>10</td>
<td>0.68</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.69</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.46</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.99</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.99</td>
<td>0.79</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>0.59</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.51</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.35</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.04</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.73</td>
<td>0.13</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>0.61</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.58</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.45</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.32</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.79</td>
<td>0.62</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>0.62</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.51</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.37</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.14</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.83</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Throughout the project, source water feeding the silica treated PDSs was also fed into the pH+0.3 (pH increase treatment) PDS. The pH+0.3 was not adjusted by increasing the pH, rather a second identical source water was placed in a separate tank where the pH was lowered (control PDS). Thus comparison with the pH adjusted PDS in Figure 3-4, rather than to the control, suggests the more representative effect of silica addition during the study.
During the study there was a clear mitigating effect when the source water was treated with silica. Of the 155 observations treated with silica inhibitor there were no violations of the action level of 1.3 mg/L for total copper. As can be seen from the plots, exceeding the action level was much more likely with no treatment being employed. Increasing the dose seemed to enhance the effect of silica. With the exception of Phase I, there was a consistent decreasing trend as the concentration of the inhibitor was increased. The differences observed in Phase I were likely attributed to the sudden change in operations following the first month of the study. Because of the change in dose, copper loops in the low dose PDS had actually been exposed to silica concentrations that were near the altered high dose of 12 mg/L-SiO₂. Although the data corresponding to this event was not included in the fabrication of these plots, the action of changing the dose and shifting equilibrium could have affected total copper release towards the end of Phase I.
Figure 3-4 Total copper release for silica treated and control PDSs

Total Copper Release in Response to Water Quality Changes

Factors other than silica dose were also incorporated into the study to examine any possible variation in the effect of silica inhibitor on total copper release with differing water quality. Figure 3-4 provides a qualitative tool for evaluating these effects.
If each treatment level is analyzed individually for each phase, then the effect of each phase becomes clear. Beginning with the lowest dose of the study, there is no indication that total copper release varied from phase to phase. In fact, the average copper release during each phase was nearly identical at 0.7 mg/L-Cu.

In contrast, the medium dose appears to have been influenced by changes in water quality. The highest copper release averages occurred during Phase I and Phase III for the medium dose. The average copper release was 0.8 and 0.7 mg/L-Cu for Phase I and Phase III, respectively, as opposed to 0.6 mg/L-Cu observed during both Phase II and Phase IV. Both Phase I and Phase III are characterized by high alkalinity and were intended to be identical for the analysis of a seasonal effect. Alkalinity for Phase II and Phase IV was considerably lower, on average 50 and 30 mg/L as CaCO₃ less, respectively.

Copper release for the high dose treatment was similar to the medium dose. Once again the highest copper release was observed during Phase I and Phase III, though with differing concentrations of 0.6 and 0.5 mg/L-Cu, respectively. Also, copper release for Phase II and Phase IV were nearly identical with average concentrations of 0.4 mg/L-Cu.

The effect of each phase, along with its associated water quality, becomes much more complicated when evaluating both of the control PDSs. This is partly due to the increased variability in copper release, which suggested a greater sensitivity to water quality changes than silica treated PDSs. The silica treatment appeared to dampen the effect of quality changes as
evidenced by the relatively narrower length of the boxes in Figure 3-4. The dampening effect of the silica inhibitor was likely a result of the relatively high pH sustained in a region where the solubility of the controlling solid was less affected by changes in pH.

When total copper release is analyzed for the control PDSs it is clear that Phase I and Phase III are much greater than Phase II which is characterized as having the lowest alkalinity of the phases. Similar observations were made regarding the silica inhibitor treated PDSs. However, unlike the Si PDSs, copper release for Phase IV differs from that of Phase II and is in fact similar to Phase III. This occurs because there is no dampening of the pH effect in this case, and thus the lower pH of Phase IV has a more salient effect on copper release. Figure 3-5 demonstrates how the pH behaved following the addition of Si. To further illustrate the prior discussion, consider the comparison of pH between Phase II and Phase III. On average the source water was of pH 7.9 and 8.1 for Phase II and Phase III, respectively. While for the high dose the average pH was approximately 8.6 for both phases. If the difference between each is compared directly and converted from a logarithm to standard scale, the result is that the difference between the pH for Phase II and Phase III, or more appropriately the decrease in \([H^+]\), is some 60 times greater than the high dose observations.
Figure 3-5  Average pH for Si and controls

Empirical Modeling of Total Copper

Water Quality Available for Regressional Analysis

All variables that were considered for regressed analysis are shown in Table 3-7. The quantities shown in Table 3-7 represent the average of the blended source water for a given. The water quality associated with the blended source water was likely to be better described using the data from the pH adjusted PDS.
Table 3-7  Average water quality parameters for blend source water by phase

<table>
<thead>
<tr>
<th>Water Quality Parameters</th>
<th>Phase I</th>
<th>Phase II</th>
<th>Phase III</th>
<th>Phase IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (mg/L as SiO₂)</td>
<td>11</td>
<td>5</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>164</td>
<td>106</td>
<td>151</td>
<td>125</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>7.9</td>
<td>8.1</td>
<td>7.9</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>43</td>
<td>65</td>
<td>65</td>
<td>58</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>62</td>
<td>102</td>
<td>67</td>
<td>76</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>77</td>
<td>72</td>
<td>78</td>
<td>58</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>7</td>
<td>36</td>
<td>41</td>
<td>32</td>
</tr>
<tr>
<td>UV-254 (cm⁻¹)</td>
<td>0.073</td>
<td>0.076</td>
<td>0.079</td>
<td>0.065</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>8.8</td>
<td>7.6</td>
<td>7.7</td>
<td>8.9</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.2</td>
<td>26.5</td>
<td>25.6</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Confounding Effects

The possibility for confounding effects amongst some of the variables should be addressed prior to introduction of the model. While some of the confounding effects may be obvious, a discussion is in order to explain why certain confounding effects could not be prevented during modeling. Referring back to the pH of each treatment shown in Figure 3-5, it is clear that any benefit associated with an increase in silica dose would be confounded with a pH effect. This relationship between the two variables implies that the individual effects will be indistinguishable from each other. Though the confounding effect may have complicated the regression if the data were limited to Si, the pH effect must be considered when including data to represent the zero dose (the control PDSs).
A particular water quality parameter would be confounded with other parameters that were associated with one another because of source water characteristics. Both alkalinity and silica were predominant in groundwater, while high sulfates were characteristic of surface water. The association between alkalinity and silica can be seen in Table 3-7. During Phase I and Phase III, when the highest proportion of groundwater was used, both alkalinity and silica experienced their highest concentrations.

Defining Silica as a Variable

From the previous discussion it is evident that silica had a salient effect on the release of copper. Including silica in the empirical model is clearly necessary to describe the trends in copper release. However, two methods were possible for defining a term for silica, (1) a silica term could be defined as a term that represents the total silica concentration of the sample, or (2) the silica term could be defined as the concentration of silica that had been added. The first method implies that the effect of Si is equivalent to the silica originally present in the source water. However, there have been claims within the literature that the silica already present in the source water has reacted with constituents within the water, rendering it unfit from interacting with a pipe surface (PQ, 2001).

The project did not include an experimental study to offer any insight into this dilemma. However, data of similar water quality was available from a preceding project that did not utilize inhibitors. This data allowed for a comparison with a water source that was not treated with Si. Ideally copper release data from the preceding study would be collected and then paired with
events from the current study that experienced the same water quality, including the concentration of silica (includes added Si for the current study). Assuming that the effect of Si is equivalent to that of background silica, there should be no significant difference between the data sets. However, this analysis was not performed since there were few samples with such ideal similarities. For this reason, a regresional approach was taken to compare copper release from the two studies.

Data from the preceding study was selected such that alkalinity, silica, and temperature were within the respective minimum and maximum ranges observed during the current study. A linear step-wise regression procedure was used to develop a model that would describe the response of copper within the PDSs treated with Si during the current study, while defining the silica term as the contribution from Si and the background silica concentration. The resulting model had an $R^2$ statistic of 0.43 and included alkalinity and silica as the only terms. All other terms presented in Table 3-2 were found to be insignificant at $\alpha = 0.05$. Data from the preceding study was then input into this model. The results from this analysis are shown in Figure 3-6.
Had the model provided an accurate representation of copper release for the preceding study, then the observed measurements would be expected to be randomly distributed about the one-to-one line shown in Figure 3-6. Instead, there is an overwhelming under prediction for the data set from the preceding study. The analysis suggests that under similar conditions (referring to water quality), the current study experienced less copper release than the preceding study, implying that the difference must have been due to the presence of Si inhibitor rather than simply total silica. For the final modeling effort, the term associated with silica was represented as the addition of Si rather the total silica concentration.
Model Evaluation

The release of total copper may be described by Equation 3-1. A series of stepwise methods was used to identify variables that were significant to at least $\alpha = 0.05$. All of the water quality parameters shown in Table 3-7 were investigated on a stepwise basis. A linear model was used because of complications that may have occurred when inputting a zero value associated with a PDS that did not receive Si. Referring back to Figure 3-4 it is evident that the variance function is not constant along the different treatments. Applying a logarithmic transformation on total copper stabilized the variance across all treatments.

$$\log_{10}\left[\text{Total Cu}\right] = \{-12.2[Dose_{SiO_2}] - 266[pH] + 1.9[Alk] + 2.6[Cl]\} \times 10^{-3} + 1.66 \quad \text{Equation 3-1}$$

where

- Total Cu = total copper, mg/L
- $Dose_{SiO_2}$ = silica concentration above background, mg/L-SiO$_2$
- pH = -log[H$^+$]
- Alk = alkalinity, mg/L as CaCO$_3$
- Cl = chloride, mg/L

The overall performance of Equation 3-1 can be seen from the assessment of Figure 3-7 (note, $R^2 = 0.68$). The model predicts the mitigating trends seen as the dose is increased as indicated by the negative coefficient on the dose term. The trend is apparent from Figure 3-7. It would appear that the model is somewhat conservative on the average; more so for the lowest dose. Such a property is encouraging for any utility planning for treatment using Si. However, the model fails to account for extreme events as evidenced by the large discrepancy in variations exhibited in Phase IV.
Figure 3-7  Total copper release summary for Si treated samples by phase

Less obvious than the effect of silica are the effects associated with water quality changes that should be conspicuous between phases. These trends between different phases were discussed earlier. Equation 3-1 allows for the identification of an association between total copper release and various water quality parameters present in the model.

Equation 3-1 identifies the effect of alkalinity as a significant water quality parameter that has the potential to promote total copper release. An apparent interaction that would be expected from the addition of the highly alkaline sodium silicate solution would be between Si dose and
alkalinity. However, insignificant differences in alkalinity were observed between Si and control PDSs. The model also suggests that chlorides are significant as well. Its effect may be illustrated from Phase II and Phase IV. Alkalinity was approximately 100 mg/L as CaCO$_3$ during Phase II, whereas it was increased to 125 mg/L as CaCO$_3$ for Phase IV. However, it can be seen from Figure 3-7 that both phases exhibit similar copper release among those treated with Si. The most conspicuous difference between Phase II and Phase IV other than alkalinity was the higher chloride concentrations of Phase II (the pH differed as well, however, when focusing on PDSs treated with Si the pH difference between phases was diminished as suggested by Figure 3-5). Thus the offset in the effect of alkalinity was likely a result of the lower chlorides in Phase IV.

Equation 3-1 suggests that increasing pH was associated with lower copper release. The effect was pH is difficult to discern from the data concerning silica treated PDSs due to the small differences in pH between phases (Figure 3-5). This effect is further complicated from the interaction of silica and pH. However, the pH effect can be analyzed by contrasting copper release between the pH adjusted PDS and the control PDS.

Surface Characterization of Copper Coupons

XPS was used to identify the chemical composition of scales that formed on copper coupons incubated within the pilot distribution system. For each phase of operation, one copper coupon was exposed to medium dose Si and was incubated during operation for Phases I, II, and IV. During Phase III, two copper coupons were exposed to Si; one was exposed to the medium dose
and the other to the high dose. Both were incubated for the duration of the phase. These coupons were then scanned following each phase to limit any possibility of contamination of the original scale. Scans for the pH control PDSs were also completed following each phase. One copper coupon was analyzed for each phase providing a total of 8 copper coupons that were not exposed to inhibitor.

The standard procedure for XPS scanning of the copper coupons exposed to Si was to develop high resolution scans for the elements copper, carbon, oxygen, calcium, silica, and zinc. The high resolution scans were then deconvoluted to identify the chemical composition relative to a particular element. The deconvolution of copper would provide the identity and relative abundance of the corrosion products that had formed. Published binding energies for the compounds analyzed were obtained for the NIST database. The method for detecting copper corrosion products was consistent with the work of Xiao, who used XPS to identify copper surface scales that had been incubated within the very same pilot distribution system (Xiao, 2004).

Deconvolution of the copper scans suggested the presence of Cu$_2$O, CuO, and Cu(OH)$_2$. A curve was designated as Cu(II) which represented possible cupric salts. The distribution of the copper corrosion products for the coupons exposed to Si and the control lines are shown in Figure 3-6. The relative proportions of each copper compound between Si and the control samples are similar. On average copper hydroxide was the predominant corrosion product identified by XPS. As evidenced by the results for XPS scans and equilibrium calculations, it was suggested
following TBWI that cupric hydroxide was the most probable controlling solid (Taylor et. al 2005). The copper coupons from TBWI would have been exposed to conditions similar to the pH control samples shown in Figure 3-6. Thus it would be expected that the surface characterization results for the pH controls would be consistent with the conclusions from TBWI. In fact, the results from the pH controls seem to well support the persistence of cupric hydroxide as the controlling solid.

Salient from Figure 3-8 are the similarities between the copper corrosion products identified for Si and pH control samples. Such similarities seem counterintuitive given the significant

Figure 3-8  Distribution of copper compounds for all phases
reductions of copper release were observed when applying Si. However, it is possible that the differences between the treatments corresponded to the compounds associated with the Cu(II). Differences become more apparent when the high resolution scan for silica is evaluated. It should be noted that each coupon introduced into the pilot distribution system consisted of copper that had undergone significant corrosion. In contrast, the copper tubing section that was responsible for metal release was given years to develop a surface scale before being treated with an inhibitor. Some research has indicated that the initial stages of corrosion form a series of layered films, where Cu₂O is located near the elemental surface below Cu(OH)₂ (Le Gal La Salle et. al, 1992). The observation of similar corrosion products between Si and pH control coupons seems to suggest that a protective scale resulting from Si treatment forms on the top layers of original corrosion by-products. This is also consistent with Si manufacturer suggestions that Si is recommended for systems in which a corrosion scale has previously formed.

As previously mentioned, XPS scans were also used for the analysis of elements other than copper. Table 3-3 provides a summary of the findings for all copper coupons exposed to Si and pH control treatments. Carbon and oxygen scans positively identified their presence for all samples analyzed. Carbon was found to be in the form of carbonate, while oxygen was present as a mixture of oxides, hydroxides, and carbonates. Calcium was detected during Phase III (only for the high dose) as CaO and Phase IV as CaCO₃ for Si coupons. Calcium was detected only once for the 8 pH control coupons, and was identified as CaCO₃ during Phase IV. The higher frequency of calcium deposits for Si PDSs is certainly expected to be favored over the pH control PDSs due to the alkaline properties of the inhibitor. These observations, however, do not
provide overwhelmingly conclusive evidence. Zinc was not found on any of the samples. A significant disparity between the occurrences of silica is shown in Table 3-3.

<table>
<thead>
<tr>
<th>Element Surveyed</th>
<th>No. of Positive Detections for the Element</th>
<th>Si (5 total)</th>
<th>pH (controls) (8 total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>5</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>5</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Silica was detected on 3 of the 5 coupons that were scanned. Silica was not detected for any of the 8 pH control coupons. This suggests that the presence of silica was attributed to the addition of Si, rather than to the silica concentration that was initially present. These finding support the decision not to include the background silica as part of the term for silica dose during empirical model development. In all cases Si was found as the generic composition, SiO₅. The 2 Si coupons with which silica was not detected were from Phase II and Phase III (medium dose). The absence of silica does not necessarily suggest that Si had no effect on the scale composition for those phases or doses. The observation was likely a consequence of the non-uniform properties of corrosion scales.
Thermodynamic Modeling

The copper products identified from the XPS analysis seem to suggest that treatment with Si renders a distribution of copper corrosion products similar to coupons that were not exposed to Si. Assuming a controlling solid mechanism for copper release, the similarities in copper corrosion products would imply that the beneficial effect of Si was attributed to the pH increase with Si dosing. However, silica was found to contribute to the composition of scale for 3 of the 5 coupons exposed to Si. This finding suggests the possibility that under a controlling solid mechanism, a layer of cupric silicate has formed. Both possibilities were modeled through solubility and complexation considerations under two different controlling control phases. All dissolved species that were modeled are shown within Equation 3-2. Cupric hydroxide was modeled, as it is the most probable controlling solid phase in the control PDSs. Dioptase was modeled as a possible controlling solid present in water distribution systems when treated with Si (Ferguson, 1996).

\[
\begin{align*}
[Cu]_{\text{Total}} &= [Cu^{2+}] + [Cu^{OH\cdot}] + [Cu(OH)_2^{\circ}] + [Cu(OH)_3^{-}] \\
&+ [CuHCO_3^{\circ}] + [CuCO_3^{\circ}] + [Cu(CO_3)_2^{2-}] \\
&+ [Cu(OH)CO_3^{-}] + [Cu(OH)_2CO_3^{2-}] + [CuSO_4^{\circ}]
\end{align*}
\]

Equation 3-2

The equilibrium relationships for both cupric hydroxide and dioptase are shown as Equation 3-3 and Equation 3-4. Although dioptase has not been cited in the literature as the solid responsible for mitigating copper release while undergoing treatment with Si, its equilibrium relationship incorporates all of the variables that would be expected to influence copper release at the surface of a copper/silicate layer. For example, if the addition of Si indeed resulted in a controlling solid
phase that differed from the control lines, then the silica component from its addition would be expected to deter copper release. Equation 3-4 demonstrates this as $Si(OH)_4$. The equilibrium relationship also accounts for pH effects associated with the acid-base properties of the dissolved silica system.

It has been cited that the benefit of Si addition can simply be attributed to the pH increase caused by the alkaline Si solution. This implies that the addition of Si may not result in the formation of a differing controlling solid (at least not one of copper/silicate composition). Under these presumptions cupric hydroxide would be expected to exist as the controlling solid phase. Thus copper release was predicted as though cupric hydroxide were predominant to test the possibility of its presence.

\[
\text{Cupric Hydroxide} \quad Cu(OH)_2 + 2H^+ \Leftrightarrow Cu^{2+} + 2H_2O \quad pK = -8.6 \quad \text{Equation 3-3}
\]

\[
\text{Dioptase} \quad CuSiO_2(OH)_2 + 2H^+ \Leftrightarrow Cu^{2+} + Si(OH)_4 \quad pK = -6.1 \quad \text{Equation 3-4}
\]

The typical conditions observed for each phase and dose were used to calculate an expected equilibrium concentration. Factors affecting the equilibrium model included alkalinity, pH, and sulfates. These water quality parameters contributed to the complexation portion of dissolved copper in the equilibrium model. Factors directly affecting the controlling solid were pH for cupric hydroxide, and pH and silica for dioptase. The results from the simulation as well as from the observed copper release are presented in Table 3-9 and Table 3-10.

Clearly the magnitude of copper release for dioptase is much greater than what was observed. The dioptase model demonstrates the sensitivity of copper release in response to the addition of
silica. Assuming that the thermodynamic data used to determine the equilibrium constant are accurate, then the predicted copper release is simply too high to corroborate the existence of dioptase as a controlling solid phase.

Table 3-9 Thermodynamic copper modeling of Si

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Phase</th>
<th>Actual Copper Release (mg/L)</th>
<th>Modeled Copper Release (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diss Cu</td>
<td>Total Cu</td>
</tr>
<tr>
<td>Si</td>
<td>I</td>
<td>Low</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Med.</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>Low</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Med.</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>Low</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Med.</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>Low</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Med.</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Modeling of cupric hydroxide appears to under predict the copper release that was observed in Si PDSs. However, this is consistently the case for the control PDS as well. Conditions within this PDS were nearly identical to that of the preceding study during which observation supported the presence of cupric hydroxide as the controlling solid. Perhaps simply a coincidence, the percent reduction among predicted and actual copper release is similar. However, this analysis should not be regarded as conclusive evidence to the mechanism of Si on its mitigation of copper release. There are still inconsistencies between different analyses performed on the Si PDS data.
For instance, the detection of silica on 3 of the 5 Si exposed to coupons seems to suggest some connection other than the pH benefit of Si addition.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Phase</th>
<th>Actual Copper Release (mg/L)</th>
<th>Modeled Copper Release (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diss Cu</td>
<td>Total Cu</td>
</tr>
<tr>
<td>pHs+0.3</td>
<td>I</td>
<td>0.99</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.73</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0.79</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>0.83</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Visual Inspection of Copper Coupons

Assessing the appearance of the scales shown in Figure 3-9 suggests that the scales between treatments do indeed differ from the control. This is contrary to the equilibrium modeling which seemed to describe the data somewhat well. The images of the copper coupons shown in Figure 3-9 were taken 14 months following their removal from the pilot distribution system. These particular copper coupons were exposed to Si during Phase III. XPS analysis identified the presence of amorphous silica for the high dose shown in Figure 3-9. However, the same analysis was done for the medium dose in which silicon bond energies were not detected. This comes as somewhat of a surprise considering that the medium dose copper coupon is marked with patches of blue-green scale. However, this specious contradiction more likely demonstrates the non-uniform properties of the scale. This blue-green scale appears to intensify as the Si dose is increased (note that the differences appearing as lightly colored “semi-circles” on the low dose coupon are actually remnants of an adhesive that was used to secure the coupon into position).
This same scale is absent from the control (pHs+0.3; though the scale was absent from pHs as well).

Figure 3-9  Scale appearance following nearly one year of incubation

Copper release was measured within the solution in which these copper coupons had been stored. The solution was collected from the water within which the coupons were originally treated. The pH for each of the solutions corresponding to Figure 3-9 (low, medium, high and pHs+0.3) were identical at approximately 8.3. Dissolved copper (measured, instead of total, to minimize the likelihood of bias due to scale particulate suspensions in the solution) measurements indicated that the Si treated coupons released less copper than that of the controls (both pHs and pHs+0.3
were analyzed). Both pHs and pHs+0.3 were measured to release 0.74 and 0.76 mg/L Cu, respectively, while the Si treated coupons released approximately 0.5 mg/L Cu. It should be mentioned that the response to silica dose was not quite as conspicuous as that observed during operations. The low, medium, and high doses were measured to release 0.50, 0.51, and 0.45 mg/L Cu, respectively. Since the difference in pH was essentially insignificant between the Si treatments and controls, the differences measured in copper release strongly support the presence of a controlling solid different from that of cupric hydroxide.

Conclusions

Total copper release data collected during this study indicate that copper release can be effectively controlled with proper dosing of sodium silicate. Specific findings from the study are provided below.

- Increased dosing of sodium silicate tended to further control the release of total copper for all phases with the possible exception of Phase I. During Phase I, the low dose seemed to control copper release just as effectively as the medium dose. However, these observations occurred during the initial stages of the study, during which the dosing protocol had been altered. The sudden change in dosages could possibly be responsible for the anomalous trend in copper release during Phase I.

- Copper release data from the preceding project, in which inhibitors were not added, was used to evaluate whether background silica should be included within the silica term for empirical modeling. The analysis conducted implied that there was no evidence to suggest that the
background silica and silica added from the inhibitor had similar effects on the release of copper.

• Empirical modeling of the data set suggested that alkalinity, chlorides, and pH had an effect on the release of copper during the study. However, as indicated by the differences between phases for Si treated PDSs, copper release appeared to be predominantly influenced by dose rather than water quality.

• PDSs treated with Si demonstrated more narrow fluctuations in extreme events. The frequency of these events appeared to decrease as well. This may be attributed to the pH stability when treating with Si.

• Surface composition analyses found that silica was more likely to be found on copper coupons treated with Si. In fact, of the 8 control coupons, no silica was detected.

• Deconvolution of high resolution scans (XPS) for Cu suggested that scale composition between Si and the control coupons were not significantly different. Cupric hydroxide was the candidate for the controlling solid given information from prior research.

• Equilibrium modeling results contradicted other analyses, and was essentially inconclusive. XPS (with respect to silicon deconvolution) and visual inspections of the scale on the Si copper coupons support the existence of a copper scale incorporating silica.

• Measurements of copper release following a long period of equilibration added further evidence that the effect of silica is the acting reagent for the control of copper during the study. All coupons treated with Si released significantly less copper than the controls, even though the pH for each treatment was similar.
References


CHAPTER 4
EFFECTS OF SOURCE WATER BLENDING FOLLOWING TREATMENT WITH SODIUM SILICATE AS A CORROSION INHIBITOR ON LEAD RELEASE

Abstract

The effects of various sodium silicate corrosion inhibitor doses, ranging from 3 to 12 mg/L-SiO₂, on lead release were investigated during a field study. The study was conducted within a pre-existing drinking water distribution pilot system where samples were drawn from a system of copper loops. Within each copper loop was a 50/50 lead/tin that was intended to simulate lead release from solders within typical house plumbing. Water quality changes occurred for each phase of operation (4 phases in total). Variations in water quality were implemented through blending differing proportions from 3 different source waters; groundwater, surface water, and desalinated water. The study analyzed both total and dissolved lead release. A non-linear regression model was developed to describe total lead release in terms of dose and water quality. The model suggested that the dose, temperature, alkalinity, chlorides, and pH had an effect on lead release ($R^2 = 0.60$). Data included within the set for regresional analysis consisted of the experimental lines treated with sodium silicate and two control lines. One of the controls was designated as treatment with pH adjustment, while the other represented the equilibrium pH. Total lead release demonstrated a beneficial response (i.e. decreasing lead release) to increasing the dose of sodium silicate. Surface compositional analyses were performed on lead coupons to offer incite into the possibility of protection by scale formation. The findings found evidence of a silicate-based surface film. Thermodynamic modeling seemed
to contradict this finding in suggesting that hydrocerussite could be used to model the dissolution behavior of lead.

Introduction

For approximately one year, weekly samples were collected during a pilot distribution system study that was intended to evaluate the performance of several treatments for controlling metal release. The study utilized a pilot distribution system that had been previously constructed and operated by Taylor et al (2005). This prior study, referred to as Tampa Bay Water I (TBW I), was intended to analyze the effects of variable water quality on metal release. The follow-up study, referred to as TBW II, included treatments using corrosion inhibitors that are commonly accepted by utilities. This paper will focus on the evaluation of lead release when applying sodium silicate (Si) corrosion inhibitor.

Successful attempts of mitigating lead release with Si have been documented as early as the 1920’s (Thresh, 1922). Despite its history of application, there have been few studies documenting quantitative relationships between silica and lead release. Of the few studies, there remains a general uncertainty surrounding the nature by which Si effects lead release. Early studies were carried out by Lehrman and Shuldener that assessed the possible mechanism of silica film formations in distribution systems (Lehrman, 1952). However, the solid suspensions used during the study did not include lead compounds.
Relatively recent studies have had mixed implications on the effectiveness and role of Si. Generally, Si addition has been documented within the literature as beneficial (Schock, 1985; Johnson, 1993; Lytle, 1996; Pinto, 1997; Chiodini, 1998; Schock, 2005). However, the association between silica dose and pH has proven to present difficulties when comparing with a control. In some cases, the pH of the control will remain unadjusted, implying that the difference between the control and Si treated experimental unit will consist of an effect from pH and silica. The beneficial effect of pH increase for lead control was been well documented (Schock, 1989). Because of the increase in pH associated with Si addition, some researchers have suggested that the effect of Si is essentially equivalent to pH adjustment (Ryder, 1985). It should be noted that some studies have indicated that Si showed little to no improvement in lead control when comparing to a system in which sodium silicate was not added (Sheiham, 1981; MacQuarrie, 1997).

Some research has been conducted during which a pH adjusted control was established (MacQuarrie, 1997; Pinto, 1997). Pinto suggests that, initially, lead levels were reduced primarily because of the increase in pH. However, the author eventually states that later observations were described as a consequence of the slow formation of a surface film as suggested by previous studies (AWWARF, 1990). MacQuarrie actually found that lead levels were typically higher for the silica treatment when compared to the pH adjustment.

Although the mechanism of Si addition regarding its ability to control lead release has not been clearly identified, a general theory of Si inhibition properties suggests that silica forms a
protective film on already corroded metal layers through an adsorption mechanism (LaRosa-Thompson, 1997; Scheetz, 1997). This film supports a diffusion barrier that slows the rate at which the equilibrium of the system is attained with the bulk solution (Stericker, 1945). Schock (2005) sites that there exists no strong evidence that suggests this as the mechanism. An adsorption mechanism would suggest that silica would be detected on samples exposed to lead surfaces. Although there have been limited studies that attempt to analyze the surfaces of these Si treated lead, some of the results of those studies seem to imply that a silica film may be stable (Scheetz, 1997).

This study further investigates the use of water quality and corrosion inhibition impacts of Si addition in drinking water systems. The study approach employs the use of XPS for surface compositional analysis in order to compare performance. Using information collected from the surface analysis, equilibrium models were developed to identify possible mechanisms to explain sodium silicate inhibition behavior more fully. Also, an empirical modeling approach to predicting lead release in Si treated systems was developed. Implications of the empirical model regarding water quality, Si dose, and accuracy are discussed.

**Experimental methods**

**Pilot Distribution System**

This project used existing facilities from a previous study examining the effects of varying water quality on metal release (Taylor et al, 2005). A description of the facilities and operations will be limited to those that were necessary for analysis of lead release. Blended source water was
pumped into 14 different pilot distribution systems (PDS) labeled lines 1 to 14. Both the source water and inhibitor were fed into an influent standpipe that can be seen as the green, upright pipes on the left of Figure 4-1. Lines 1 to 14 were hybrid lines that consisted of the pipe materials shown in Table 4-1.

Table 4-1 Description of pipe materials used in hybrid system (i.e. PDS)

<table>
<thead>
<tr>
<th>Order of Entry</th>
<th>Pipe Material</th>
<th>Length (feet)</th>
<th>Nom. Diameter (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>PVC</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>2nd</td>
<td>Lined Cast Iron</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>3rd</td>
<td>Unlined Cast Iron</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>4th</td>
<td>Galvanized Steel</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

The system of pipes is displayed as the right image in Figure 4-1. The PDSs were designed to operator at a 2-day hydraulic residence time (HRT). Such operating conditions were designed to simulate characteristics of the TBW Member Government’s distribution systems. Intermediate (neither influent nor effluent) sampling ports were positioned such that a sample port was located ahead of a change in pipe material.
Upon approaching the effluent standpipe, a portion of effluent water from each PDS line was pumped to cradles that contained lead coupons, while another portion was directed into a system of copper corrosion loops. These corrosion loops were housed within a non-air conditioned shed. Each copper loop was 30 feet in length and 5/8 inch in diameter, thus was able to hold approximately 1.8 L of water. One lead-tin coupon was placed within the copper tubing to simulate the presence of solders. These lead-tin coupons were located approximately 1 ft from the outlet port (sampling port) of the copper loop system. To further simulate the hydraulic conditions of common household water usage by consumers, the corrosion loops were flushed with approximately 2 gallons of water every morning. Both the corrosion shed and copper loops are shown in Figure 4-2.
Blending of Source Waters

Blends were prepared from various proportions of conventionally treated groundwater (GW), enhanced coagulation-sedimentation-filtration surface water (SW), and desalinated water by reverse osmosis (RO). While the GW and RO were obtained from the project site, SW was obtained from the TBW regional surface water treatment plant. Selected average water quality parameters for each source water are shown in Table 4-2. The water quality of each source water was intended to remain unchanged throughout operation. However, some minor variations of surface water were understandably unavoidable with seasonal changes.

Table 4-2  Average source water quality

<table>
<thead>
<tr>
<th>Source Water</th>
<th>pH</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Ca Hardness (mg/L as CaCO₃)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>TDS (mg/L)</th>
<th>DO (mg/L)</th>
<th>UV₂₅₄ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW</td>
<td>7.7</td>
<td>211</td>
<td>214</td>
<td>36</td>
<td>29</td>
<td>357</td>
<td>7.4</td>
<td>0.073</td>
</tr>
<tr>
<td>SW</td>
<td>7.8</td>
<td>79</td>
<td>210</td>
<td>51</td>
<td>184</td>
<td>428</td>
<td>8.8</td>
<td>0.058</td>
</tr>
<tr>
<td>RO</td>
<td>7.9</td>
<td>70</td>
<td>63</td>
<td>92</td>
<td>2</td>
<td>285</td>
<td>8.3</td>
<td>0.029</td>
</tr>
</tbody>
</table>
The project duration required 4 phases of operation. Each phase generally took 3 months of data collection to complete. The phases represented a difference in blend, and thus a difference in water quality, that was obtained from predetermined ratios of source water. The corresponding ratios of GW, SW, and RO for each phase are shown in Table 4-3. Although the ratios for Phase I and Phase III are identical, water quality was somewhat dissimilar as a consequence of seasonal variations with source waters (namely SW). The contrast between Phase I and Phase III was originally intended for the analysis of a seasonal, or, more appropriately, a temperature effect.

Table 4-3  Blend composition for each phase of operation

<table>
<thead>
<tr>
<th>Phase</th>
<th>Time Period</th>
<th>%GW</th>
<th>%SW</th>
<th>%RO</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Feb-May 2006</td>
<td>62</td>
<td>27</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>II</td>
<td>May-Aug 2006</td>
<td>27</td>
<td>62</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>IV</td>
<td>Nov 2006-Feb 2007</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

Silicate Addition

During all 4 phases of operation, PDS 10, 11, and 12 were treated with silica inhibitor. The silica inhibitor used was N-type® sodium silicate solution with a SiO₂/Na₂O weight ratio of 3.22 (PQ Corporation, Valley Forge, Pa.). The solution was diluted and stored in 2 separate chemical storage tanks that were prepared weekly. One stock tank was designated for PDS 10 (low dose), while the other was designated for PDS 11 and PDS 12 (medium and high dose). The solutions were diluted to approximately 110 mg/L-SiO₂ for the low dose, and to approximately 220 mg/L-SiO₂ using the low alkalinity RO source water. This protocol prevented the precipitation of calcium carbonate in the stock tank. The flow of the inhibitor into the system represented about
6% of the total flow for the highest dosing condition; therefore the composition of the blend deviated only slightly. The accuracy for each dose was evaluated at least twice a week.

Originally doses were established at 10, 20, and 40 mg/L-SiO₂ for PDSs 10, 11, and 12, respectively. However, after the fourth week of operation during Phase I, the doses were lowered to 3, 6, and 12 mg/L-SiO₂ above the background silica concentration of the blended source water. Lowering the doses was necessary to prevent the precipitation of calcium carbonate in PDS 11 and PDS 12, which had impeded operations early in Phase I.

Neither PDS 13 nor PDS 14 received a corrosion inhibitor. PDS 13 represented the equilibrium condition, while PDS 14 was considered to represent an increase in pH. PDS 13 was allocated as the control, although PDS 14 represented the common blended source water that received the inhibitors. PDS 13 was fed by a separate tank that used blended source water that was similar to PDS 14 with the only difference being that hydrochloric acid was added to the tank.

Sampling and Data Collection
Selected water quality parameters that were considered as possible variables for the empirical modeling of lead release are shown in Table 4-4 and Table 4-5. Influent and effluent water quality data was collected weekly from PDSs 1-14 during the first phase of operation. Sampling was limited for some water quality monitoring to a biweekly schedule. For analyses conducted at both the field lab and at the UCF lab, the number of replicates assigned represented at least
10% of the samples. Blind duplicates and spikes were taken to represent at least 10% of the samples for selected water quality parameters.

Table 4-4  Selected water quality parameters and methods performed at university laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method Reference</th>
<th>Method Description</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>SM 2320B</td>
<td>Titration Method</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>SM 4110</td>
<td>Ion Chromatography with Chemical Suppression of Eluent Conductivity or Hach 8025 Cobalt-Platinate Method (with spec)</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Color</td>
<td>SM 2120A</td>
<td>Laboratory Method</td>
<td>1 CPU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>SM 2510B</td>
<td>Laboratory Method</td>
<td>1 μmho/cm</td>
</tr>
<tr>
<td>Copper</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrogen (NH₃,TKN)</td>
<td>SM 4500-Norg</td>
<td>Macro-Kjeldahl Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Nitrite (NO₂⁻)</td>
<td>SM 4510A</td>
<td>Persulfate-UV Oxidation Method</td>
<td>0.1 mg C/L</td>
</tr>
<tr>
<td>pH</td>
<td>SM 4500-H⁺ B</td>
<td>Electrometric Method</td>
<td>± 0.01 pH units</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Silica</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Solids (TDS)</td>
<td>SM 1030E</td>
<td>Estimation of TDS by major ion sum</td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SM 4110</td>
<td>Ion Chromatography with Chemical Suppression of Eluent Conductivity</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Turbidity</td>
<td>SM 2130B</td>
<td>Nephelometric Method</td>
<td>0.01 NTU</td>
</tr>
<tr>
<td>UV-254</td>
<td>SM 5910</td>
<td>UV Absorption at 254 nm</td>
<td>0.0001 cm⁻¹</td>
</tr>
<tr>
<td>Zinc</td>
<td>SM 3120B</td>
<td>ICP Method</td>
<td>0.001 mg/L</td>
</tr>
</tbody>
</table>
Lead release data was obtained from samples taken directly from the outlet port of the copper corrosion loops. During Phase I other water quality parameters were collected from the corrosion loops as well. Following Phase I it was determined that for the water quality parameters of interest, such as pH, alkalinity, and inhibitor dose, the differences between the effluent PDS ports and the corrosion loop outlet ports were insignificant. Thus following Phase I only total and dissolved copper, and total and dissolved lead were monitored from the corrosion
loops. These samples were collected following a 6-hour stagnation time that began at approximately 7:00 a.m.

Lead coupons were collected following every phase of operation. Lead coupons had been exposed to all PDS waters, however only medium doses and PDS 13 and PDS 14 were analyzed. The lead coupons were then analyzed using X-Ray Photoelectron Spectroscopy (XPS) within about 3 weeks following the end of each phase.

Results and Discussion

Performance of Si Treatment

Dose Maintenance

With the exception of the first 4 weeks of operation, silica doses were adjusted accordingly to maintenance doses of 3, 6, and 12 mg/L (all as SiO₂) representing the low, medium, and high doses. The box plots shown in Figure 4-3 illustrate the accuracy of these targets during the project as depicted by the mean, 25th and 75th percentiles, and minimum and maximum measurements. The silica concentrations represent the contribution of the inhibitor alone. These concentrations were determined as the amount of silica measured above the background from the control line PDS 14.

It should be noted that Figure 4-3 does not include data from the first 4 weeks of sample collection. Originally the intended doses for silica were designated as 10, 20, and 40 mg/L,
during which the average doses were 8.4, 21.6, and 43.1 mg/L. However, following the fourth week of operation, the accumulation of a precipitate was found to be impeding the flow for the PDS treated with the high dose. The average pH was 8.7 for the high dose, while the highest alkalinity and hardness occurred during Phase I. Such conditions favored the precipitation of calcium carbonate, and following analysis of an observed reduction in calcium through the system, its presence was confirmed.

With the possible exception of the medium dose, Figure 4-3 suggests that the targeted doses were maintained accurately about their intended doses with consistency. The medium dose was slightly greater than the targeted dose, operating on average at 6.7 mg/L. The medium dose still demonstrates precision in its maintenance, and may be regarded as a treatment level significantly different from the low and high doses.
Response of Lead to Phase and Treatment

Table 4-6 lists some selected descriptive statistics for the release of lead within the system during the study. PDS 10, 11, and 12 correspond to the low, medium, and high doses of the system, respectively. Both PDS 13 and PDS 14 may be regarded as control units for the study, however, PDS 14 represents the water with which silica was added to for treatment. PDS 13 was of a lower pH than PDS 14 by approximately 0.3 pH units throughout operation with other water quality remaining identical (excluding the level of chlorides that was a consequence of HCl addition for lowering the pH).
Analysis for both total and dissolved lead was performed using ICP. The detection limit for the analysis was 1 ppb as Pb. For measurements that were determined to be below the detection limit, lead was recorded as 1 ppb rather than zero. This approach ensured that there would be, at worse, a conservative bias within the data set; allowing for a more confident assessment concerning the performance of treatment with sodium silicate. The detection limit may complicate the development and evaluation of the regressional analysis. For example, consider the effect of treatment levels for medium and high dose. The data suggest no change, and therefore the effect may be statistical less significant. Another complication arises from the possibility of a skewed statistical distribution threatening the validity of normality assumptions invoked by regressional analyses.
Table 4-6  Summary of lead release for Si and control PDSs

<table>
<thead>
<tr>
<th>Phase</th>
<th>PDS</th>
<th>Dissolved Lead (ppb-Pb)</th>
<th>Total Lead (ppb-Pb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>Min</td>
</tr>
<tr>
<td>I</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>3.9</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>4.8</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>3.7</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>5.2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>16.6</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>5.2</td>
<td>1</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>5.0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>2.7</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>1.7</td>
<td>1</td>
</tr>
</tbody>
</table>

From the tabulated results shown in Table 4-6, it would appear that Si treatment was generally effective for mitigating lead release. For the moment, consider only the average value of lead release measurements. For Phases I, II, and III, all of the levels of Si treatment performed better than the controls. It should be noted as a reminder that the higher levels of treatment (higher dose) also corresponded with an increasing alkaline solution. For Phase IV, however, an apparent anomaly presented itself in the data for the low dose (PDS 10). The average for Phase
IV was much greater than the controls, including the low pH, PDS 13. Also, note that the maximum observation was unusually high as well, perhaps suggesting that the average was skewed by an outlying observation. In order to thoroughly evaluate the differences between treatments, the distribution of the data was assessed using box plots shown in Figure 4-4.

The box plots shown in Figure 4-4 depict the mean, minimum and maximum observations, and the 25\textsuperscript{th} and 75\textsuperscript{th} percentiles of each treatment when applicable. Since lead release is regulated as a percentile rather than a mean average, Figure 4-4 may be used to assess the performance relative to the action level (shown as Lead Action Level) as well as the control PDSs. It should be noted that the USEPA Lead and Copper Rule (LCR) states that the 90\textsuperscript{th} percentile of a sample should not exceed 0.015 mg/L as Pb (or 15 ppb as Pb).

Both Phase I and Phase II clearly suggest that the Si treated system operated well within the limits stated by the LCR. Phase I appears to have been the most effective of the phases, however, this may be a result of the early stages of treatment for Phase I. The initial doses of 10/20/40 mg/L as SiO\textsubscript{2} were employed for Weeks 1 through 5. Although the data used for Figure 4-4 did not include the initial weeks, there had not been any investigation into the possible effects of a sudden change in dose. Any relevant contrast within the data would have to assume that the system was essentially restored as though there had been a previous equilibrium with the 3/6/12 dosing system.
For Phase III and Phase IV, the trend between lead release and silica dose remained similar to that of prior phases. However, contrary to the trend, the low dose appears to be worse than if provided no treatment (more appropriately, pH Adjusted). A paired t-test between the low dose and pH adjusted for Phase III indicated that there was no significant statistical evidence to suggest that the collection of observations differed. However, the same procedure applied to Phase IV suggested, with relatively high confidence, that the low dose was greater than the pH adjusted treatment (p-value of 0.01).
Figure 4-4  Total lead release for silica treated and control PDSs

One possible explanation for the anomaly was the stabilization of a complex associated with a silicate-based ligand. However, an extensive review of the literature provided no evidence supporting the presence of such species. Further investigation was conducted to determine if there was some response to a change in operations. There was no indication that any of the main
water quality parameters deviated significantly relative to the other phases (temperature was excluded). Of particular interest was the effluent pH and effluent dose concentration. Note that effluent parameters were evaluated to eliminate the potential variation that may have been associated with any deviation in water quality occurring between the influent and effluent ports. The statistic initially used to assess the control of blend was the variance. There was no indication of a significant difference in variance between phases for silica concentration. Similar analysis of the effluent pH also suggested no significant difference.

An interesting difference between Phase IV and the other phases was found while conducting a qualitative assessment of data independence. Although it appeared that control was not violated through variance disparities, the effluent pH data hinted on a consistent rising trend as the weeks progressed for Phase IV. This difference is graphically displayed while using data from the untreated blend (PDS 14). The resulting plot is shown as Figure 4-5. There was no evidence that Phases I, II, and III were significantly dependent of the duration of the study. This was verified through linear regression techniques that computed the statistical significant of each respective slope. For Phase IV, however, the PDS 14 data suggested that the effluent pH may have been dependent on project duration (p-value < 0.001).
Figure 4-5  Effluent pH of blend (PDS 14) for every week of operation

Observations below detection limit

Listed in Table 4-7 are the number of observations that were recorded below detection limit on the ICP (< 1 ppb). This provides another perspective for evaluating the performance of the Si treatment. For the purpose of statistical modeling, the recording of an observation below detection limit corresponds to a loss of information concerning the response to Si treatment. After all, consistent measurements below the detection limit are strong evidence supporting effectiveness of the treatment.

Total lead release during Phase I was the lowest among all of the phases, and also had the highest relative frequency of observations below detection for Si treatment. All of the samples, with the exception of one from the medium dose (PDS 11), were recorded below detection limit.
Given the same blend without Si treatment (i.e. PDS 14), it was slightly less probable to detect a sample below detection limit (6/9). The disparity between PDS 14 and Si treatment is made clearer for Phases II, III, and IV. Only 4 samples were recorded below detection limit out of 38 total observations (10.5%), while 55 of the 114 samples treated with Si were recorded below detection (48.2%).

The effect of dose becomes more evident when analyzing the information of Table 4-7 from Phase II, III, and IV. As the dose increases (i.e. PDS increases from 10 to 12), the likelihood of obtaining a measurement below detection limit increases, or, at worse, does not change. Dissolved lead is shown in Table 4-7 as well. Note that the trends exhibited by dissolved lead are similar to total lead, indicating a direct proportionality.

<table>
<thead>
<tr>
<th>Phase</th>
<th>PDS 10</th>
<th>PDS 11</th>
<th>PDS 12</th>
<th>PDS 13</th>
<th>PDS 14</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase I</td>
<td>9</td>
<td>8</td>
<td>9</td>
<td>1</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Phase II</td>
<td>2</td>
<td>12</td>
<td>12</td>
<td>2</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>Phase III</td>
<td>1</td>
<td>5</td>
<td>10</td>
<td>0</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>Phase IV</td>
<td>0</td>
<td>4</td>
<td>9</td>
<td>3</td>
<td>2</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 4-7 Number of observations recorded below the Pb detection limit (< 1 ppb)

<table>
<thead>
<tr>
<th>Dissolved Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase I</td>
</tr>
<tr>
<td>Phase II</td>
</tr>
<tr>
<td>Phase III</td>
</tr>
<tr>
<td>Phase IV</td>
</tr>
</tbody>
</table>
Dissolved fraction of lead

The percentage of dissolved lead from total lead was estimated as the average of all of the observations from the study. Statistical comparisons between phases determined that there was little evidence of any differences in the percentage of dissolved lead between all phases.

Percentages were obtained only from observations in which both the total and dissolved lead concentrations were defined (i.e. greater than the detection limit). Table 4-8 suggests that dissolved lead represents approximately half of the total concentration. It was not possible to verify this claim for the medium and high Si dose (PDS 11 and PDS 12). There were no observations in which both the dissolved and total lead concentrations were above detection limit for PDS 12. While only 5 observations satisfied the criteria for PDS 11, likely allowing only extreme, and thereby possibly misrepresentative, observations to provide an estimate of the dissolved fraction.

Table 4-8  Average percentage of dissolved lead

<table>
<thead>
<tr>
<th>PDS</th>
<th>Obs.</th>
<th>Percent Dis.</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>26</td>
<td>47</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>75</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>13</td>
<td>38</td>
<td>47</td>
<td>14</td>
</tr>
<tr>
<td>14</td>
<td>32</td>
<td>46</td>
<td>16</td>
</tr>
</tbody>
</table>

Investigation of Scale Formation

Any attempt of understanding possible mechanistic models for metal release would require some knowledge of the interface between solution and metal source. Upon reaching a state of equilibrium, this interface would ideally represent a region of uniform scale deposits formed

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from by-products of the corrosion process. If accurately identified and understood, equilibrium relationships could possibly be used to describe the metal release of a defined system.

Surface Characterization

XPS was used to identify the chemical composition of scales that formed on lead/tin coupons incubated within the pilot distribution system. For each phase of operation, one 50/50 lead/tin coupon was exposed to medium dose Si during operation for Phases I, II, III, and IV. Note that further mentioning of lead/tin coupons will be referred to as lead coupons. These coupons were then scanned following each phase to limit any possibility of contamination of the original scale. Scans for PDS 13 and PDS 14 were also completed following each phase. A lead coupon was analyzed for each phase providing a total of 8 lead coupons that were not exposed to inhibitor.

A survey scan was produced for the lead coupons using XPS. From those initial scans, high resolution scans for the elements lead, carbon, oxygen, calcium, silica, and zinc were generated. The high resolution scans were then deconvoluted to identify the chemical composition corresponding to the respective element. Published binding energies for the compounds analyzed were obtained from the NIST database. The method for detecting lead corrosion products was consistent with the work of Tang, who used XPS to identify lead surface scales that had been incubated within the very same pilot distribution system (Tang, 2003).

Deconvolution of the lead scans suggested the presence of Pb₃(OH)₂(CO₃)₂ (hydrocerussite), PbCO₃ (cerussite), PbO, and PbO₂. The distribution of the lead corrosion products for the
coupons exposed to Si and the control lines are shown in Figure 4-6. The distributions would not suggest any significant difference between the distribution of lead corrosion products between Si treatment and the controls. During the study, the percentage of PbO₂ was the least, implying that lead was in the +2 oxidation state at the scale surface. Hydrocerussite was the predominant solid for both Si treatment and the controls. The predominance of hydrocerussite agrees well with observations of lead coupons from TBWI (Taylor et. al, 2005). Based on the work of Tang (2003), it was determined that hydrocerussite was the probable controlling solid phase within the pilot distribution system.

Figure 4-6  Distribution of lead compounds for all phases
Given the similarities between the lead corrosion products of the lead coupons exposed to Si and untreated blend, it would seem that addition of the inhibitor did not change the composition of the scale. This seems to contradict the results discussed earlier regarding the effectiveness of Si on reducing lead release. It may be that the scale composition was not influenced by the silica concentration, and the response of lead release to treatment with Si can be accounted for by the pH increase. Given the non-uniform properties of corrosion scales, it is plausible that given only 4 observations, the silica-based scale was simply not detected. Referring to similar work within the TBW II study, it should be noted that the high resolution scans for Pb 4f7 exhibited significant symmetry between lead coupons for phosphate-related treatments and control PDSs (Guan, 2007). Simply stated, the same contradiction was prevalent for treatments other than Si. Despite this finding, it was determined for the phosphate-relate treatments that lead release was likely to be controlled by hydropyromorphite (Pb₅(PO₄)₃OH) as suggested from the literature (Schock, 1989). Although the compound was not specifically identified, its presence was suspect following deconvolution of phosphorus scans for the phosphate treated lead coupons.

The data obtained from scans of other detectable elements is shown in Table 4-9. High resolution scan for carbon were generated for use as a standard. The high resolution scan of carbon was shifted to an energy position of 284.6 eV. All other scans were shifted according to the difference of the carbon adjustment. Carbon was detected for all samples except that of Phase II for both the Si treatment and controls (3 lead coupons in total). Apparently the carbon scan represents an aberration for Phase II. The shift applied to the high resolution scans of Phase
II were estimated based on prior experience with the other lead coupon analyses and with what little information could be obtained from the high resolution scan of carbon.

Oxygen was detected on all of the samples shown in Table 4-9. Deconvolution of oxygen verified the presence of oxide and carbonate scales. Analysis of the calcium scan suggested that the element was dominant in the form of calcium carbonate during Phase III and Phase IV for Si treatment. Calcium carbonate was also detected on lead coupons exposed to PDS 13 (during Phase III and Phase IV) and PDS 14 (during Phase IV) blends. The frequency of calcium carbonate detection between Si treatment and controls does not necessarily suggest that Si favored deposition of calcium carbonate. Although the treatment rendered a higher LSI, there were simply too few samples to propose a beneficial effect of calcium carbonate deposition with Si treatment. It should be noted that calcium was detected, to a lesser degree, as an oxide and a silicate during Phase IV for Si.

Silica was not detected during Phase I and Phase II in the survey scan for Si coupons. Given the importance of identifying silica in the scale, a high resolution scan was generated for Phase II. The high resolution scan was still indistinguishable from the background noise of the scan. Phase III and Phase IV coupons treated with Si revealed a significant presence of silica on the surface scale. Deconvolution suggested that the silica was present as an amorphous solid phase. During Phase III, a fraction of the detected silica was found to be associated with calcium as CaSiO$_3$. This finding was verified through deconvolution of calcium and oxygen.
Table 4-9  Frequency of elements detected by XPS scans

<table>
<thead>
<tr>
<th>Element Surveyed</th>
<th>No. of Positive Detections for the Element</th>
<th>Si (4 total)</th>
<th>pH (controls) (8 total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>4</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>4</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>4</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

From the information regarding the controls in Table 4-9, it may appear that incorporation of silica into the corrosion scale may be accomplished without the application of Si inhibitor. In fact, silica was detected on lead coupons exposed to phosphate-related treatments as well during the comprehensive study. However, a quantitative comparison of the silica high resolution scans was performed that suggested that the lead coupons exposed to Si developed a denser silica-based scale. The study demonstrates that silica can exist within the scale regardless of Si addition, provided there is a natural source. However, addition of Si may have maintained a more predominant silica scale when compared to the controls of the analysis.

Thermodynamic Implications

Corrosion of lead often results in the formation of a passivating scale that may govern the release of soluble lead species into the bulk. Prior surface characterization analysis of the lead coupons identified PbO, Pb(OH)$_2$, PbCO$_3$, and Pb$_3$(CO$_3$)$_2$(OH)$_2$ scales within the pilot distribution system. These solids were thereby considered in the development of an equilibrium model. The
soluble species considered during the development of this model were Pb$^{2+}$, Pb(OH)$^+$, Pb(OH)$_2^0$, Pb(OH)$_3^-$, Pb(OH)$_4^{2-}$, PbHCO$_3^+$, PbCO$_3^0$, and Pb(CO$_3$)$_2^{2-}$. Although the selection of complexes was not limited to the choices previously stated, incorporation of any other complexes sited by the literature proved to be redundant (e.g. PbSO$_4^0$).

The model represents a pe-pH diagram shown as Figure 4-7 varied across a range of alkalinities. It should be noted that the alkalinity shown in the diagram is intended to establish a $C_T$ specifically at a pH of 8.0, thus the alkalinity and pH axes are independent. The diagram was developed while assuming a constant total soluble species concentration ($Pb_T$) of $10^{-6}$ M. This concentration corresponds to a concentration of 207 ppb as Pb. Although this may seem high when compared to the data previously shown, this concentration is more appropriate for a system that has reached equilibrium with the entire bulk (Pinto, 1997). Since the source of lead within the copper loops accounted for a small fraction of the total copper loop surface area, the process was diffusion limited.
pe-pH Diagram for Lead at varying Alkalinitities
\((Pb_T = 10^{-6} \, M)\)

Figure 4-7  pe-pH equilibrium diagram for lead species

The shaded cube shown in Figure 4-7 represents the region of the diagram that would be typical of the study. The pH spans from 7.5 to 8.5, while the pe spans from 9.0 to 12.5 (determined from the 5th and 95th percentiles of the ORP measurements during the study). The region
suggests hydrocerussite was predominant during the study. This result is consistent with the XPS analysis for both the controls and Si treatment with respect to the deconvolution of the lead high resolution scans.

The thermodynamic modeling development considered the Pb(II) silicate solids referenced in the computer program LEADSOL which was used for USEPA research (Schock, 1989). The reactions of these solids are written as follows:

\[
PbSiO_3(s) + H_2O + 2H^+ = Pb^{2+} + Si(OH)_4 \quad \text{Equation 4-1}
\]

\[
Pb_2SiO_4(s) + 4H^+ = 2Pb^{2+} + Si(OH)_4 \quad \text{Equation 4-2}
\]

As implied from Figure 4-7, there was no thermodynamic evidence to suggest that any of these two solids persisted during the study. This analysis was further extended beyond project conditions spanning a pH of 4 to that of 12, and still found no indication of PbSiO_3(s) or Pb_2SiO_4(s). Possibilities with respect to scale formation include the following (1) the equilibrium constants used for PbSiO_3(s) and PbSiO_4(s) are inaccurate for the conditions applied, (2) a Pb(II) silicate exists, however, there is no data pertaining to it found in the literature, and (3) the effect of silicate is inconsistent with Pb(II) silicate scale formation. The literature provides inconsistent conclusions that fail to resolve the limitations of thermodynamically predicting a Pb(II) silicate solid. Schock and Wagner could not identify any solids on a pipe treated with silicate, however, hydrocerussite was found on the control loop for that same experiment (Schock and Wagner 1985). Generally silicate is found to have little to no effect on the release of lead for a constant pH, implying the effect may be attributed to the pH increase.
Unfortunately, no surface analyses were conducted during these studies to offer any insight into these findings (Sheiham and Jackson 1981, MacQuarrie 1997).

Lead release as governed by hydrocerussite was plotted as a log C-pH diagram with varying $C_T$ (alkalinity used as surrogate) and compared to the data from the study. The model was adjusted to approximate the conditions rendered by the diffusion properties of lead release in the system. The following expression was used to describe the lead concentration distance $x$ from the lead coupon in the copper loops.

$$C_x = C_S \left(1 - \text{erf} \left(\frac{x}{\sqrt{4D_{eff}t}}\right)\right)$$

Equation 4-3

Where $C_x$ is the concentration at distance $x$ and time $t$, and $C_S$ is $Pb_T$ at equilibrium. Since the lead coupon is placed approximately 1 foot (0.3 meters) from the sample port, and a typical 1 L sample represents approximately 5 meters of drawn sample, the lead collected within a sample represents lead that has diffused both toward the sample port and entry point of the copper tubing. Given a 1 L sample, the concentration of that sample was estimated using the previous relationship as follows.

$$dM = C_x dV = AC_x dx = AC_S (1 - \text{erf} (x')) dx \text{ or } AC_S f(x') dx$$

Thus,

$$M = AC_{\frac{S}{L}} \left(\int_{0}^{0.3 \text{ m}} f(x') + \int_{0}^{4.7 \text{ m}} f(x')\right) \Rightarrow C_{\text{sample}} = \frac{M}{AL} = \frac{C_S}{L} \left(\int_{0}^{0.3 \text{ m}} f(x') + \int_{0}^{4.7 \text{ m}} f(x')\right)$$
Where $L$ is the length from which the sample is drawn (5 meters). Since $\int_{0}^{0.3m} f(x')$ and $\int_{0}^{4.7m} f(x')$ are essentially identical after 6 hour of incubation,

$$C_{sample} = \frac{2\int_{0}^{0.3m} f(x')}{L} C_S$$

A numerical approximately of this relationship suggests that with a 1 L sample, and after a stagnation time of 6 hours, $C_{sample} = 0.002 C_S$. This relationship was used to adjust the predicted equilibrium concentrations from the hydrocerussite model to the expected concentrations under the conditions previously discussed. The resulting lead release models are shown in Figure 4-8. The model represents the summation of the lead species assumed during the description of the pe-pH diagram previously discussed. Data from the study are shown in Figure 4-8 as well. Two sets of data are compared against the lead release models. One set of data, shown as the up-side down triangles, represent dissolved lead measurements from lead coupon samples following a stagnation period of approximately 1 year. The other set of data represents the average dissolved lead data collected from the pilot distribution system for each phase. Data recorded below detection limit was designated as 1 ppb.
The data points labeled as stored Pb/Sn coupon samples represent measurements taken after Phase III. These lead coupons were stored within an air-tight plastic container that was almost completely filled with water drawn from the PDS of each respective lead coupon treatment. Given the long stagnation time and small volume of the container (100 mL), it was clear that these measurements would more accurately reflect the equilibrium concentration. Only the pH
of the samples was able to be measured because of the small amount of sample available. These measurements suggested that the pH difference between the samples was no longer significant after the 1 year storage. The pH was approximately 8.3 for all samples. In order to display the lead release from the stored coupons on Figure 4-8, the alkalinity was assumed to be the average alkalinity of Phase III for each treatment with a pH of 8.3.

The hydrocerussite model shown as Figure 4-8 predicted much higher lead release than was observed during the study. Since this model represents a system in equilibrium, these results were expected from a system that was not expected to have reached equilibrium. Adjustment of the same model dramatically underestimated lead release in the system. Unfortunately, the model offers a vague distinction between the Si treatment and controls for the data concerned with the pilot operation. Since the hydrocerussite model appears to describe the control just as well as the data representing the Si treatment, there still remains the possibility that hydrocerussite may maintain its role as the controlling solid phase following Si treatment.

Perhaps the most intriguing observation from Figure 4-8 is the relationship for data of the equilibrated samples. The insignificant difference in pH between the samples implies that the effect of silica can be isolated. Prior to these measurements, all other analyses were forced to tolerate the confounding relationship between silica dose and pH. As can be seen from the stored coupons, lead release responded differently from the typical trends observed during the study. For instance, the high dose appears to provide no benefit to controlling lead, whereas the low dose was the most effective treatment. Notice also that the difference in lead release
between the treatments was not as significant as that observed during the study. Observations from the study suggest that lead release was consistently decreased by approximately an order of magnitude for the high dose. Although there seems to be insufficient evidence to disprove the notion that hydrocerussite controls lead release for Si treatment, there is equally insufficient evidence to promote this same notion. Most of the data collected was limited to samples taken from the pilot distribution system. This data was adequate in evaluating practical performance following Si treatment, but did not permit the water quality control necessary to fully explain the effect of silica dose. While the equilibrated set of data corrected for any uncertainties related to the difference in pH and diffusion limitation, there were only 4 samples providing no replication.

Empirical modeling of lead release

**Water Quality Available for Regressional Analysis**

All variables that were considered for regressive analysis are shown in Table 4-10. The quantities shown in Table 4-10 represent the average of the blended source water for a given phase. The water quality associated with the blended source water was likely to be better described using the data from the pH adjusted PDS.
Table 4-10  Average water quality parameters for blend source water by phase

<table>
<thead>
<tr>
<th>Water Quality Parameters</th>
<th>Phase I</th>
<th>Phase II</th>
<th>Phase III</th>
<th>Phase IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (mg/L as SiO₂)</td>
<td>11</td>
<td>5</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>164</td>
<td>106</td>
<td>151</td>
<td>125</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>7.9</td>
<td>8.1</td>
<td>7.9</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>43</td>
<td>65</td>
<td>65</td>
<td>58</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>62</td>
<td>102</td>
<td>67</td>
<td>76</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>77</td>
<td>72</td>
<td>78</td>
<td>58</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>7</td>
<td>36</td>
<td>41</td>
<td>32</td>
</tr>
<tr>
<td>UV-254 (cm⁻¹)</td>
<td>0.073</td>
<td>0.076</td>
<td>0.079</td>
<td>0.065</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>8.8</td>
<td>7.6</td>
<td>7.7</td>
<td>8.9</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.2</td>
<td>26.5</td>
<td>25.6</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Model Evaluation

The release of total lead may be described by Equation 4-4. A series of stepwise methods was used to identify variables that were significant to at least $\alpha = 0.05$. All of the water quality parameters shown in Table 4-10 were investigated on a stepwise basis. A power model was used so that the temperature could be modeled as an exponent of some constant. Note the $Dose$ term from Equation 4-4 include the addition of 1. This provides somewhat of a numerical convenience for the power model when dealing with $Dose$ values of zero. This was necessary for incorporating the control data into the regressional analysis. The overall ANOVA for the model was significant, as were all of the estimated constants (p-values < 0.008). The $R^2$ value was 0.60 for the data set of Si and controls.
\[
Total \ Pb = 1.15^{(T-25)} \left( Dose_{SiO_2} + 1 \right)^{0.45} (pH)^{-6.72} (Alk)^{1.90} (Cl)^{1.63} \]

Equation 4-4

where

Total \ Pb = total lead, ppb

\( Dose_{SiO_2} = \) silica concentration above background, mg/L-SiO_2

\( pH = -\log[H^+] \)

\( Alk = \) alkalinity, mg/L as CaCO_3

\( Cl = \) chloride, mg/L

\( T = \) temperature, °C

Equation 4-4 agrees with the observed relationship between silica dose and total lead release. This relationship is inferred from the negative exponent for the silica variable. The magnitude of this exponent does not account for the full effect of silica dose on lead release. Instead it is the combined effect of silica dose and pH that best define the effects of Si treatment within the system. Since the pH of the Si lines was significantly dependent (i.e. confounded) on silica dose, the isolated effect of silica dose remains unclear. Reversing this idea, the isolated effect of pH associated with the Si lines is unclear as well. However, from the concepts of regressional analysis, the individual effect of pH that is shown in Equation 4-4 has a more valid estimate. This was because the two control lines were maintained to have a differing pH. Thus the difference in lead release observed between PDS13 and PDS14 may be essentially regarded as a pH effect.

Equation 4-4 also identifies chloride, alkalinity, and temperature as the other significant water quality parameters affecting lead release. All of which the model implies are not beneficial.
within the range of this study. It should be apparent from the actual data shown in Figure 4-4 that the variation in lead release between phases was more salient for the control lines rather than for Si. Thus, the model should not be expected to accurately reflect the magnitude of water quality effects for Si. The model may be more appropriately understood as a compromise between data sets for the control (silica dose of zero) and the Si data.

Phase I and Phase III of the study were intended to have the same blend composition. The only water quality parameter that was expected to differ between Phase I and Phase III was temperature. Thus the increase in lead release observed during operation of Phase III should represent the isolated effect of temperature. However, there was an unfortunate difference in chloride between Phase I and Phase III due to seasonal variations of the surface water. During Phase III, chlorides were greater than during Phase I. Had the opposite been true, then the effect of temperature would have been more clear. Instead, because both temperature and chlorides impart an undesirable effect, the increase in lead release during Phase III represents a combination of effects that may not be analyzed separately.

It should be noted that the significance of chloride may be a result of the consistent chloride difference between the controls. As previously explained, the pH of the blend for PDS13 was lowered through addition of HCl. As a consequence, the chloride concentration was significantly higher for PDS13 than PDS14. Thus, the main effect of chloride should be suspect. Although the literature supports the presence of Pb(II) chloride complexes that would increase $Pb_T$, equilibrium data support that these complexes would be insignificant in drinking water.
However, the effect of temperature could be explained as 1) an increase in the diffusivity ($D_{\text{eff}}$) of lead species, 2) decrease in water viscosity that would benefit the diffusion rate of lead species, and 3) change in governing equilibrium relationship (may not be beneficial).

The role of alkalinity may be associated with complex formation and scale formation if the controlling solid phase is lead carbonate-based. Regardless of the solid phase, Pb$^{2+}$ governed by the solid has the potential to strongly coordinate with HCO$_3^-$ and CO$_3^{2-}$. Equilibrium modeling for the diagram in Figure 4-8 demonstrates that, within the depicted range, Pb(II) carbonate-based complexes account for greater than 90% of $Pb_T$. Thus, the dominant effect of $C_T$ would likely be an increase in lead release, regardless of the solid phase present.

The overall performance of Equation 4-4 can be seen from the assessment of Figure 4-9. The diagram shown in Figure 4-9 represents a comparison of average prediction and average measurements of lead release from the study. The upper limit whiskers represent the estimated 90th percentile from the predicted and measured lead release data, while the lower limit whiskers represent the minimum lead release value from the predicted and measured data. The model predicts the mitigating trends seen as the dose is increased as indicated by the negative exponent on the dose term. The trend is apparent from Figure 4-9.
Figure 4-9 Total lead release summary for Si treated samples by phase

The model fails to account for the violations observed for the low dose during Phase III and Phase IV. It was discussed earlier this data seemed anomalous, especially given the fact that the low dose performed worse than the blend despite consistently having a higher pH. For the medium and high doses the predicted data seems to have been overestimated due to the water quality effects established in the model. Since data was generally collected biweekly for the Si lines, while controls were collected weekly, there was a bias within the data set that favored the water quality terms corresponding to the control lines. However, the inaccuracies of the model provide a relatively conservative estimate of a response to the medium and high dose.
Conclusions

Total lead release data collected during this study indicated that lead release can be effectively controlled with proper dosing of sodium silicate. A list of specific findings from the study are as follows:

- Data from this study suggested that reduction of lead release continued as the dose increased. In some cases, this trend could not be verified for the medium and high doses because there were too few observations that were above the ICP detection limit for Pb.

- Treatment with sodium silicate was generally more effective than no treatment with respect to mitigation of lead release. This relationship between Si addition and no treatment (more appropriately PDS14) was challenged by observations from the low dose PDS for Phase III and Phase IV. During these phases, it appeared as though the low dose encouraged lead release when compared to the untreated blend. This was puzzling considering that the effluent pH for the low dose was significantly greater than that of PDS14. T-tests suggested that there was no evidence of a significant difference in lead release for Phase III, however, the t-test was conclusive for Phase IV. A precise explanation for this event could not be deduced, however, it was mentioned that the blend pH had significantly increased throughout the duration of Phase IV.

- Lead release for a water with water quality similar to some phase of this study can be controlled using Si to levels within the regulatory action level for total lead.

- XPS surface characterization indicated that the deconvolution scans of lead for Si treated and control lead coupons were similar. Regardless of treatment with Si, the predominant
corrosion products were no different from the lead coupons that were untreated (PDS13 and PDS14). These corrosion products were identified as PbO, PbO₂, PbCO₃ (cerussite), and Pb₃(OH)₂(CO₃)₂ (hydrocerussite), with hydrocerussite apparently existing as the predominate lead corrosion solid phase.

- XPS found evidence of silicate scale formation. Silicon had been detected on both Si treated and control lead coupons (and also on phosphate-based inhibitor treated lead coupons during a related study). However, silicon had a slightly greater likelihood was being detected on lead coupons treated with Si. Also, deconvolution scans suggested that Si treatment may encourage a denser scale. Silicon was found almost exclusively as an amorphous solid, with some indication that calcium silicate may be prevalent.

- Thermodynamic modeling suggested that the Pb(II) silicates (Pb₂SiO₃ and PbSiO₄) were not favorable during the study. Instead, the modeling effort corroborated the results from XPS.

- A solubility model was developed assuming hydrocerussite as the controlling solid phase. Both the equilibrium and a diffusion limiting condition were considered. Actual data averaged from the study was then compared against the models. Neither model was accurate for predictive purposes, but did correctly represent the observed relationship between lead release and, both, pH and alkalinity. Based on the lead release data from the pilot study alone, there remains little evidence to conclude that hydrocerussite governs lead release within a system treated with silica.

- The hydrocerussite solubility model was extended to evaluate lead release data that had been obtained from lead coupon samples that had been equilibrated with the surrounding solution. The pH of these samples was essentially the same, thus the confounding effect between silica
dose and pH was no longer a complication. The hydrocerussite model was accurate to within the same order of magnitude of dissolved lead release for the stored samples. Also, the trends observed during the pilot study (e.g. higher silica dose, then a reduction in lead release) were not present. Provided that this was an accurate representation of lead release in the system, this observation would seem to suggest that hydrocerussite acted as the controlling solid phase. Thus implying that the benefit effect of Si was largely due to its contribution to increasing pH. This, however, would be a rather bold conclusion for an analysis that relied on only 4 samples, and had no replicates to follow. Thus, the author is hesitant to simply suggest that silica treatment would be no different from pH adjustment without further investigation into this area. The surface composition of the lead coupons suggests that silica may coordinate on the surface of a corroded lead surface. From there, a stabilized film may promote further diffusion limitations for dissolved lead migrating towards the bulk solution. Thus lead could still lower lead levels for a given stagnation time by a mechanism other than an increase of pH. It should be noted that an increase in pH, for all practical conditions in drinking water, would benefit control of lead release regardless of hydrocerussite or a Pb(II) silicate-based controlling solid phase.

- Empirical modeling of the data set suggested that temperature, alkalinity, chlorides, and pH had an effect on the release of lead during the study, along with the dose of silica. With implications that temperature, alkalinity, and chlorides encouraged lead release, and silica and increasing pH decreased lead release. The empirical model should be regarded simply as a tool for predicting lead release within a system of water quality similar to the study.
Implications of the empirical are not necessarily directly causal, and should not be used to propose a mechanism.
References


CHAPTER 5
COMPARISON OF SAMPLE MEANS AND VARIANCES OF COPPER RELEASE FOLLOWING VARIOUS CORROSION CONTROL STRATEGIES

Abstract

Federal regulations require that utilities operate within an action level of 1.3 mg/L for copper. The action level represents a 90th percentile, suggesting that 10 percent of the samples should not exceed 1.3 mg/L-Cu. Regression models were developed using data obtained during a field study involving a pre-existing drinking water distribution pilot system. However, formulation of these models was only sufficient for describing the expected value (mean) for copper release. Thus, in order to properly assess the model in accordance with federal regulations, the mean function (regression model) must be altered to define the 90th percentile. The validity of representing the copper data as a normal distribution was statistically analyzed and found that the variation in copper data for a given treatment could be described by a normal distribution. The assessment for normality under the project conditions was ideal. The immutability of the experimental system allowed for replication within which variations could be confidently attributed to random fluctuations. This quality is not attainable for utilities sampling consumers. Variations recorded from this method of sampling provide an estimate of the variance that includes several possible sources of variation (e.g. differences in household plumbing, time of day, etc.). Since an analysis of the normality and variance of the copper data was necessary to determine a relationship between the regression models and the 90th percentile, the assumptions associated with an ANOVA were essentially verified during the analysis. Thus, an ANOVA was used to directly compare the effects of the inhibitors and their doses. The findings suggest that
the phosphate-based inhibitors were consistently more effective than sodium silicate when comparing the same treatment levels (i.e. doses). Among the phosphate-based inhibitors, the effectiveness of each respective treatment level was inconsistent (i.e. there was no clear indication that any one phosphate-based inhibitor was more effective than the other). As the doses increased for each inhibitor, the contrasts generally suggested that there was a corresponding tendency for copper release to decrease.

Introduction

The regulation of copper in accordance with the USEPA Lead and Copper Rule (LCR) has provided an incentive for utilities to review various corrosion control strategies. While many researchers have documented the effect of these control strategies, very few of the studies serve as a comprehensive assessment of multiple control strategies for copper. Studies have generally considered either a phosphate or silicate based inhibitor.

Edwards et al (2002) studied the mitigating effects of polyphosphate (also known as blended orthophosphate) and orthophosphate on copper release. During the study, copper release was typically lower when treated with orthophosphate as opposed to polyphosphate. Zinc orthophosphate and orthophosphate were analyzed as corrosion inhibitors for copper by Schneider et al (2007). The study indicated that there was no appreciable difference between the effect of zinc orthophosphate and orthophosphate on copper release. MacQuarrie et al (1997) analyzed both zinc orthophosphate and sodium silicate, suggesting that sodium silicate was more effective than zinc orthophosphate with regards to controlling copper release. Schock et al
(2005) monitored a distribution system after a utility switched from polyphosphate to sodium silicate corrosion inhibitors. The change in treatment occurred because the utility was unable to meet the LCR action level. Copper release fell below the 1.3 mg/L copper action level following treatment with sodium silicate.

These studies represent only a small sample of studies concerned with corrosion inhibitors and copper release. Unfortunately these studies are insufficient to make an overall comparison of the effects of the various inhibitors. In other words, if accuracy is of interest, these studies should not be directly compared. For instance, if a comparison of zinc orthophosphate and polyphosphate was of interest, then a comparison between Edwards et al (2002) and Schneider et al (2007) would not be advised despite that the two studies shared a common link (orthophosphate). Comparisons across different studies are complicated by factors other than inhibitor type and dose that affect copper release (such as alkalinity, pH, NOM, and temperature). For this reason a comparison of inhibitors should be conducted in a manner that limits possible sources of variability between experimental units. In effect, the experiment will provide confidence that any variability in copper release will be associated with the treatment.

To the author’s knowledge at this time of this writing, only one study had been published that was as comprehensive as the study reported herein. Pinto et al (1997) researched the effects of pH adjustment, blended orthophosphate, zinc orthophosphate, orthophosphate, and sodium silicate for a common water. The study suggested that all of the corrosion control strategies
reduced copper release; however, there was no formal statistical analysis to compare the performance of the treatments with each other.

This paper provides a comprehensive evaluation of the effect of blended orthophosphate (BOP), orthophosphate (OP), zinc orthophosphate (ZOP), and sodium silicate (Si). Since the study was conducted over four different phases, each representing a different water quality, statistical inferences were carried out in the form of a two-way ANOVA. Both treatment (inhibitor type and corresponding dose) and phase were designated as main effects in the ANOVA model. In the process of verifying the normality assumption for the ANOVA, a relationship was developed that described the 90th percentile of the regression models for copper release that were developed as part of the overall study.

For approximately one year, weekly samples were collected during a pilot study that was intended to evaluate the performance of several treatments for controlling copper release. The study utilized a pilot distribution system that had been previously constructed and managed during Taylor et al (2005). The follow-up study included corrosion control strategies using corrosion inhibitors that are commonly accepted by utilities. The study consisted of treatments with BOP, OP, ZOP, and Si throughout the duration of the study.
Methods

Pilot Plant Components

Pilot Distribution System

This project used existing facilities from a previous study examining the effects of varying water quality on metal release without the use of corrosion inhibitors (Taylor et al, 2005). Blended source water was pumped into 14 different pilot distribution systems (PDS) comprised of varying materials and labeled lines 1 to 14. Both the source water and inhibitor were fed into an upright, influent standpipe. Lines 1 to 14 were known as hybrid lines. A description of these lines is shown in Table 5-1.

<table>
<thead>
<tr>
<th>Order of Entry</th>
<th>Pipe Material</th>
<th>Length (feet)</th>
<th>Nom. Diameter (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>PVC</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>Lined Cast Iron</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>Unlined Cast Iron</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>Galvanized Steel</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

The PDSs were designed to operator at a two-day hydraulic residence time (HRT). Such operating conditions were designed to simulate characteristics of the Tampa Bay Water (TBW) Member Government’s distribution systems.

Copper Loops

Upon flowing to the upright, effluent standpipes, a portion of effluent water from each PDS line was pumped into a system of copper loops. These copper loops were housed within a non-air...
conditioned shed. Each copper loop was 30 feet in length and 5/8 inch in diameter, thus was able to hold approximately 1.8 L of water. To simulate the hydraulic conditions of common household water usage by consumers, the corrosion loops were flushed with approximately two gallons of water every morning. Samples were collected six hours after flushing the copper pipes. Total copper was measured using an inductively-coupled plasma (SM 3120B ICP Method).

Experimental Operation

Phase Description
Blends were prepared from various proportions of conventionally treated groundwater (GW), enhanced coagulation-sedimentation-filtration surface water (SW), and desalinated water by reverse osmosis (RO). While the GW and RO were obtained from the project site, SW was obtained from the TBW regional surface water treatment plant. The water quality of each source water was intended to remain unchanged throughout operation. However, some minor variations of surface water were understandably unavoidable with seasonal changes.

The project duration required four phases of operation. Each phase generally took three months of data collection to complete. The phases represented a difference in blend, and thus a difference in water quality, that was obtained from predetermined ratios of source water. The corresponding ratios of GW, SW, and RO for each phase are shown in Table 5-2, while the average water quality for the blends are shown in Table 5-3. Although the ratios for Phase I and
Phase III are identical, water quality was somewhat dissimilar as a consequence of seasonal variations with source waters (namely SW).

<table>
<thead>
<tr>
<th>Table 5-2 Blend composition for each phase of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>I</td>
</tr>
<tr>
<td>II</td>
</tr>
<tr>
<td>IV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5-3 Average water quality for the blended source water by phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Quality Parameters</td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>Silica (mg/L as SiO₂)</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
</tr>
<tr>
<td>UV-254 (cm⁻¹)</td>
</tr>
<tr>
<td>DO (mg/L)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
</tbody>
</table>

PDS Treatments

As previously discussed, there were a total of 14 different PDSs simply labeled PDS 1 through PDS 14. Each PDS was unique with respect to the treatment. Each treatment was applied during every phase of operation. For discussion purposes, the treatment refers to the type of corrosion inhibitor applied during the study. The study called for 4 different corrosion inhibitors; blended
ortho-phosphates (BOP), ortho-phosphates (OP), zinc ortho-phosphates (ZOP), and sodium silicate (Si). Each corrosion inhibitor was applied to 3 different PDSs at different levels (doses). A summary of the PDSs, and their associated treatments is shown in Table 5-4.

Referring to Table 5-4, note that the list of treatments includes pHBlend-0.3 and Blend. The Blend “treatment” refers to the original blended source water used for PDSs 1-14. The pHBlend-0.3 represents a separate blend obtained after lowering the pH of the blended source water (the same water used for PDS 14) by 0.3 pH units in order to attain a pH of pHs. Levels refer to the doses of each inhibitor. For BOP, OP, and ZOP, the doses were 0.5, 1.0, and 2.0 mg/L-P for the low, medium, and high levels, respectively. For Si, the doses were 3, 6, and 12 mg/L as SiO₂ for the low, medium, and high levels, respectively. The inhibitor doses represent the amount added, and do not incorporate any phosphate or silica originally present in the blended source water.
Treatments refer to the combination of treatment/level as shown in Table 5-4 (e.g. PDS 2 represents a treatment in the context of a statistical analysis, while BOP may be referred to as a treatment during a general discussion of inhibitors).

Statistical Analysis

Outlier Analysis

Residuals from a given sample were evaluated to assess the likelihood of a possible outlier. A sample consisted of a particular inhibitor dose during a phase of operation. These residuals were standardized using the standard deviation of an observation’s corresponding sample.

Standardized residuals were calculated as follows.

\[
z_{ijt} = \frac{y_{ijt} - \bar{y}_{ij}}{s_{ij}} \quad \text{Equation 5-1}
\]

Where \(z_{ijt}\) represents the standardized residual, \(y_{ijt}\) is the copper concentration for the observation in question, \(\bar{y}_{ij}\) is the mean average of the corresponding sample, and \(s_{ij}\) is the standard deviation of the corresponding sample. If the sample was derived from a normal distribution, then approximately 99.7% of the standardized residuals for a sample lie between -3 and +3. If a standardized residual was found to be outside of this interval, then the corresponding observation was deemed an outlier.
Kolmogorov-Smirnov Test

The Kolmogorov-Smirnov test is known as a goodness-of-fit test that assesses the normality of a sample. The test compares a hypothesized cumulative distribution with the observed cumulative distribution. The cumulative distribution function is denoted as $F_o(x)$, and represents the probability that a value of the random variable $X$ is less than or equal to $x$ (i.e. $F_o(x) = Pr(X \leq x)$). The cumulative distribution function observed from the data set is denoted as $S(x)$, and represents the proportion of sample observations less than or equal to $x$. The function is calculated as follows.

\[
S(x) = \frac{\text{number of sample observations less than or equal to } x}{n} \quad \text{Equation 5-2}
\]

The test statistic ($D$) for the Kolmogorov-Smirnov Test is derived from $S(x)$ and $F_o(x)$ as follows.

\[
D = \sup_x |S(x) - F_o(x)| \quad \text{Equation 5-3}
\]

Where sup represents the supremum, over all $x$. The supremum essentially represents the maximum $D$ from the sample set. Graphically, $D$ represents the greatest vertical distance between $S(x)$ and $F_o(x)$. If the value of $D$ is found to be significantly unlikely given the number of observations in the sample, then it will be concluded that a normal distribution does not adequately describe the sample. The hypothesis for the Kolmogorov-Smirnov test may be described as follows.

$H_0$: The sample population is normally distributed

$H_a$: The sample population is not normally distributed
Bartlett’s Test

Bartlett’s test evaluates the equality of variance amongst \( r \) populations. The test assumes that all of the populations are normally distributed, and that random errors are independent. Bartlett’s test is somewhat flexible, when compared to other statistical tests for homogeneity of variance, in that the test is effective for samples of unequal sizes. The test utilizes the mean square error (MSE) and geometric mean square error (GMSE) to formulate a test statistic. The \( MSE \) and \( GMSE \) are calculated as follows.

\[
MSE = \frac{1}{n_T - r} \sum (n_j - 1)s_j^2 \quad \text{Equation 5-4}
\]

\[
GMSE = \left[ (s_1^2)^{n_1-1} (s_2^2)^{n_2-1} \cdots (s_r^2)^{n_r-1} \right]^{\frac{1}{n_T - r}} \quad \text{Equation 5-5}
\]

It can be shown that the following relationship exists between \( MSE \) and \( GMSE \).

\[
GMSE \leq MSE \quad \text{Equation 5-6}
\]

Both the \( MSE \) and \( GMSE \) are equal if all sample variances are equal. Thus, the ratio of \( MSE \) to \( GMSE \) would be close to unity if the sample variances are similar. However, if the sample variances are dissimilar, then the ratio would be greater than 1. The Bartlett test transforms this ratio as follows.

\[
\log_{10}(MSE/GMSE) = \log_{10} MSE - \log_{10} GMSE \quad \text{Equation 5-7}
\]

From this quantity, the test statistic for Bartlett’s test \( (B) \) can be written as:

\[
B = \frac{2.302585}{C} \left[ (n_T - r) \log_{10} MSE - \sum_{j=1}^{r} (n_j - 1) \log_{10} s_j^2 \right] \quad \text{Equation 5-8}
\]

Where \( C \) would be calculated as:

\[
C = 1 + \frac{1}{3(r-1)} \left[ \sum_{j=1}^{r} \frac{n_j}{n_T - 1} - \frac{1}{n_T - r} \right] \quad \text{Equation 5-9}
\]
The hypothesis statement for Bartlett’s test is shown below.

\[ H_0: \sigma_1^2 = \sigma_2^2 = \cdots = \sigma_r^2 \]

\[ H_A: \text{at least one of the } \sigma_j^2 \text{ are dissimilar} \]

Note that the test statistic approximately follows a \( \chi^2 \) distribution with \((r - 1)\) degrees of freedom. The test statistic shown in the results of this paper represents the value of \( B \) as shown in Equation 5-8.

**Independence Analysis**

A time-series analysis was conducted to assess any trend with respect to the residuals of the data set. Since samples were collected regularly on a weekly basis, the order of sample collection would have been proportional to the time of collection. The coefficient of determination \((R^2)\) was used to quantify any possible correlation between the residuals and the corresponding week of collection. If a least square estimate for the coefficients of the model, \( \hat{y}_i = \eta x_i + \eta_o \), are found (where \( \hat{y}_i \) represents the expected residual at the \( i^{th} \) observation, and \( x_i \) is the week of the \( i^{th} \) observation); then \( R^2 \) may be determined as:

\[
R^2 = 1 - \frac{SSE}{SS_{yy}} = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2} \tag{Equation 5-10}
\]

Although this does not represent a statistical test, if the residuals are independent of time, then the \( R^2 \) would be expected to be consistently low. Thus, the assessment of independence was not objective, but rather demonstrated a practice of good judgement.


**ANOVA Model**

A two-way fixed effects model with an interaction term was used during the analysis of variance. The model includes two main effects representing the treatment (PDS number) and phase of operation. The interaction term, if shown to be significant, would suggest that effects associated with a change in phase would not apply equally to each treatment. If the interaction term were determined to be significant, then an interpretation of the main effects would be limited to simply identifying, significantly, a source of variation. In other words, there would be little predictive value to contrast main effects. The model may be written as Equation 5-11.

\[
Y_{ijt} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \epsilon_{ijt} 
\]

Equation 5-11 suggests that an observation, \( Y_{ijt} \), is controlled by main effects \( \alpha_i \) and \( \beta_j \), the interaction of these main effects, \( (\alpha\beta)_{ij} \), and the random error associated with the population, \( \epsilon_{ijt} \). As previously mentioned, the main effects in the model are described by the treatment and phase of this study. Proper inference of the ANOVA require that the error terms, \( \epsilon_{ijt} \), are independent and normally distributed. Equality of variance amongst the samples (represented by combinations of treatment and phase) is also ideal for interpretation of the ANOVA.

Once the model was verified, Tukey’s method for all pairwise comparisons was used to evaluate the contrasts of the main effects. Contrasts simply represent the difference between specified populations. For instance, suppose the contrast between two different treatments is of interest. The contrast simply represents the difference between each sample’s mean averages. Tukey’s
method of pairwise comparisons would be implemented to determine the significance of this
difference. The statistical analyzes were conducted using the statistical software program, SAS®.

Results and Discussion

Analysis of Outliers
Using the criteria discussed in the methods section for detecting outliers, there were no such
observations recorded. However, a few observations were noted as suspected outliers ($z_{ij} > 2$).
Until further evidence has been gathered (i.e., some method other than standardized residual
analysis), these observations remained in the data set for the initial assessment of the assumption
of normality.

Assessment of Normality

Goodness-of-Fit Test
Table 5-5 summarizes the results from the Kolmogorov-Smirnov goodness-of-fit test. The
treatment describes the inhibitor or blend, and the level describes the corresponding doses.
Levels 1, 2, and 3 refer to doses of low, medium, and high, respectively (a level of zero implies
that doses did not apply). Of the 56 sample sets, 10 were found to provide sufficient evidence to
suggest that these samples were not normally distributed. A Type I error of 0.05 was applied
during the analysis (i.e. $\alpha = 0.05$).
Table 5-5  Kolmogorov-Smirnov test of complete data set (p-value)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Level</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Phase 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOP</td>
<td>1</td>
<td>&lt; 0.01</td>
<td>0.03</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>OP</td>
<td>1</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.02</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.03</td>
<td>&lt; 0.01</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>ZOP</td>
<td>1</td>
<td>&gt; 0.15</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>0.05</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>&gt; 0.15</td>
<td>&lt; 0.01</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>pHs</td>
<td>0</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>pHs+0.3</td>
<td>0</td>
<td>&gt; 0.15</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
</tbody>
</table>

Correction of Data

The Kolmogorov-Smirnov test for the complete data set suggested that nearly 18% of the samples did not follow a normal distribution. Although the decision was somewhat arbitrary, there seemed to be little evidence to suggest that the null hypothesis could be accepted in general. For this reason, the aforementioned suspect outliers were reviewed. Those samples that were found to not follow a normal distribution are shown in Table 5-5 shown as the italicized, bold numbers. The highest suspected outliers in these samples (assuming at least one existed) were removed. The Kolmogorov-Smirnov test was performed once again to evaluate the effect of the suspect outliers on the normality of the sample. The results to this test are shown in Table 5-6.
Table 5-6  Kolmogorov-Smirnov test for corrected data (p-value)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Level</th>
<th>Phase 1</th>
<th>Phase II</th>
<th>Phase III</th>
<th>Phase IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOP</td>
<td>1</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>OP</td>
<td>1</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>0.10</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.01</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>ZOP</td>
<td>1</td>
<td>&gt; 0.15</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>0.05</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>pHs</td>
<td>0</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>pHs+0.3</td>
<td>0</td>
<td>&gt; 0.15</td>
<td>0.04</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
</tbody>
</table>

Removal of suspected outliers lowered the occurrence of rejecting the null hypothesis from 10 to 4 samples. This represents approximately 7% of the samples; a significant improvement from the summary of Table 5-5. It should be noted that the removal of suspected outliers did not always reverse the original results of the Kolmogorov-Smirnov test. During such cases the suspected outliers were put back into the sample set. Most of the suspected outliers were drawn from samples that had been collected during 5/30/2006. It was clear that most of the copper concentrations of these observations were much less than the sample mean. In fact, the suspected outliers identified had negative standardized residuals. Observations such as these were likely a result of not allowing an adequate stagnation time before samples were drawn from the copper loops.
Equality of Variance

The equality of variance was of interest during this study because: 1) variance equality of samples is preferred with use of the $F$ distribution during ANOVA or multiple comparisons; although it has been suggested that the $F$ distribution is robust under conditions of unequal variance (Neter, 1974), and 2) development of regression models for the prediction of copper release only account for the mean; however, for regulatory purposes, the 90th percentile of an event is of concern.

Bartlett’s Test

Bartlett’s test was used to test whether the variances of the sample sets were statistically unequal. The results from the test, shown in Table 5-7, suggest that there is sufficient evidence to claim that there the variances among the 56 samples are not equal.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>$\chi^2$</th>
<th>Pr. &gt; $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>55</td>
<td>642</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>

Variance/Mean Relationship

The Bartlett test determined that the variances were statistically unequal. A relationship associated with the variance was investigated to possibly validate the use of a particular transformation. Common behavior of the variance noted in statistics texts is for the variance to
display some proportionality to the sample mean (Dean, 1999). This relationship between the variance and sample mean is described mathematically as Equation 5-12.

$$\sigma_{ij}^2 = k(\mu + \tau_{ij})^q$$  \hspace{1cm} \text{Equation 5-12}

Where $\sigma_{ij}^2$ represents the variance of the population, $k$ and $q$ are constants, and $\mu + \tau_{ij}$ represents the mean response for the corresponding treatment. Figure 5-1 suggests that there may be some validity to this relationship. It is apparent that the standard deviation (square root of the sample variance) has a tendency to increase as the mean response of the system increases.

![Figure 5-1](image_url)  

Figure 5-1  Relationship between standard deviation and sample mean
Data Transformation

The coefficients from the relationship shown in Equation 5-12 were estimated following appropriate rearrangements and substitutions of the function. Unbiased estimates for the variance and mean response of Equation 5-12 are shown below.

\[
\hat{\sigma}^2_{ij} = s^2_{ij} \quad \text{Equation 5-13}
\]

\[
\hat{\mu} + \hat{\tau}_{ij} = \bar{y}_{ij} \quad \text{Equation 5-14}
\]

Where \( s^2_{ij} \) and \( \bar{y}_{ij} \) are the sample variance and sample mean average of each sample, respectively. These estimates were then substituted into Equation 5-12 to produce Equation 5-15.

\[
s^2_{ij} = k(\bar{y}_{ij})^q \Rightarrow \ln(s^2_{ij}) = q \ln(\bar{y}_{ij}) + \ln(k) \quad \text{Equation 5-15}
\]

Equation 5-15 now resembles a simple linear model with an intercept. A least squares regression estimated the coefficients of \( q \) and \( \ln(k) \) to be 2 and -3.3, respectively. The plot representing the regression of this data, along with the linear model, is shown in Figure 5-2. The linear model was found to be statistically significant (p-value < 0.001) with an \( R^2 \) of 0.49. The resulting linear model, along with the estimated coefficients, is shown as Equation 5-16.

\[
\ln(s^2_{ij}) = 2\ln(\bar{y}_{ij}) - 3.3 \quad \text{Equation 5-16}
\]

It has been suggested that for data that exhibits a variance/mean relationship such as that shown in Equation 5-12, with an estimate of \( q \) approximately equal to 2, that a valid transformation for data is the natural logarithm function shown as Equation 5-17 (Dean, 1999).

\[
h(y_{ijt}) = \ln(y_{ijt}) \quad \text{Equation 5-17}
\]
The estimates of the coefficients from Equation 5-15 can be used to derive a relationship between the 90th percentile of a mean function, \(E(y \mid x)\), representing copper release as a function of variable(s), \(x\). Since it has already been established that the data may very well follow a normal distribution, a z-score is incorporated to provide a connection between the standard deviation, mean function, and 90th percentile. The derivation of the generalized z-score is shown below as Equation 5-18.

\[
z_i = \frac{y_i - E(y \mid x)}{\text{std}(y \mid E(y \mid x))} = \frac{y_i - E(y \mid x)}{k^{1/2}(E(y \mid x))^{3/2}}
\]

Equation 5-18
If \( y_i \) is defined as the 90th percentile (\( y_{90\%} \)) of \( E(y \mid x) \), then Equation 5-18 may be written, and rearranged, as Equation 5-19 to describe the 90th percentile. The \( z \)-score for a normal distribution at the 90th percentile (i.e. \( z_{90\%} \)) is 1.28.

\[
z_{90\%} = \frac{y_{90\%} - E(y \mid x)}{k^{1/2}(E(y \mid x))^{1/2}} \quad \Rightarrow \quad y_{90\%} = z_{90\%} \sqrt{k(E(y \mid x))^{1/2}} + E(y \mid x)
\]

Equation 5-19

Stabilization of Variance

Following the transformation of the data, the equal variance assumption was assessed for the newly transformed data using Barlett’s test. The results of the test are shown in Table 5-8. The test suggests that the variances are still not equal; however, a reduction in the chi-square test statistic suggests that the transformation had an effect towards stabilizing the variance. It has been previously mentioned that the \( F \) test has been shown to be robust when sample sizes are equal (Rogan, 1977). For this reason it has been recommended that when using ANOVA, or contrast methods, to maintain balance amongst the sample sizes. Although not all of the sample sizes are equal for the data, all sample sizes are relatively similar; hence the data is balanced (sample size range between 11 and 14, with \( 3/4 \) of the sample sizes being either 12 or 13).

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>( \chi^2 )</th>
<th>Pr. &gt; ( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>55</td>
<td>261</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>

Normality Assumption of Transformed Data

The Kolmogorov-Smirnov test was conducted for the transformed data to verify that the transformation did not affect the normality assumption. The results of the test are shown in
Table 5-9. Note that the frequency of rejecting the null hypothesis, a total of four occasions, is the same as before the transformation.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Level</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>Phase 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOP</td>
<td>1</td>
<td>0.10</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>OP</td>
<td>1</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.04</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>ZOP</td>
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<td>&gt; 0.15</td>
<td>0.03</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>0.05</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.02</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>pHs</td>
<td>0</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>pHs+0.3</td>
<td>0</td>
<td>&gt; 0.15</td>
<td>0.10</td>
<td>&gt; 0.15</td>
<td>&gt; 0.15</td>
</tr>
</tbody>
</table>

Independence of Data

Evaluation of $R^2$

Independence of the error term, $\varepsilon_{ijt}$, in Equation 5-11 was decided based upon an assessment of $R^2$ values obtained from the samples. Independence of the error term (i.e. the residuals of a sample) suggests that any information of one observation does not provide any information concerning another observation. Given that a system must be given time to stabilize under new water quality conditions (e.g. phase changes), the time required to stabilize may effect the variation in the mean response (Wysock, 1995). Time was not considered a source of variation during the study; it was assumed that the system was stabilized at the beginning of each phase.
Strong correlations between copper release and time (represented by week of collection) would be expected if the error term was not independent. The relative frequencies of the $R^2$ results are shown in Figure 5-3. The histogram suggests that a majority of $R^2$ values were less than 0.4, with the larger concentration of $R^2$ calculations being less than 0.10. There is little evidence to suspect that there was a strong time-series correlation for copper release within the data set. It will be assumed for further analysis that the error term in Equation 5-11 exhibits independence.

![Figure 5-3 Histogram representing the coefficient of determination ($R^2$) for all treatment/phases](image)

Figure 5-3  Histogram representing the coefficient of determination ($R^2$) for all treatment/phases

Analysis of Variance
Preliminary Assessment of Effects

A summary of the mean average of the data used for the ANOVA is shown in Table 5-10. These averages represent the copper release data prior to transformation. The averages seem to suggest that the treatments (inhibitors), at the levels tested, were effective at reducing copper release when compared to the original blended source water (shown as Treatment “Blend”). An increase in level (dose) appears to further mitigate copper release for the treatments. Copper release was lower for the medium dose (Level 2) when compared to the low dose (Level 1). Except for BOP during Phase I, the average copper release for the medium dose (Level 2) is higher than the high dose (Level 3).

It appears that the performance of the phosphate-based inhibitors was similar. In contrast, the effect of sodium silicate addition, although effective, did not perform as well as the phosphate-based inhibitors.
Two-Way ANOVA

The ANOVA table for the complete model shown as Equation 5-11 is displayed in Table 5-11. The results suggest that the terms in the complete model are significant to describing the variation in copper release. The main effects were represented by the treatment (consisting of inhibitor type and level) and phase. Note that there were no levels for the Blend and pHBlend-0.3. The interaction term was found to be significant as well. When analyzing the change in copper release across each phase in Table 5-10, the change in copper release is more obvious for the blends. This observation implies that the effect of phase was somehow dependent on the treatment used. Hence, there is an interaction between the two effects. The significance of an
interaction is that it may complicate the interpretation of the main effects. Since some portion of 
the total variation (SST) must be assigned to the interaction term, the perceived variations 
amongst the main effects are likely to contribute to the interaction effect as well.

Table 5-11 ANOVA table for the transformed copper data

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>13</td>
<td>141.9</td>
<td>10.9</td>
<td>210.8</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Phase</td>
<td>3</td>
<td>1.8</td>
<td>0.59</td>
<td>11.4</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Interaction</td>
<td>39</td>
<td>5.6</td>
<td>0.14</td>
<td>2.75</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Error</td>
<td>654</td>
<td>33.9</td>
<td>0.052</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>709</td>
<td>182.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Effect of Treatment

The results from the pairwise comparison for the treatments are shown in Table 5-12. The table 
displays the possible contrasts amongst the treatments and identifies the contrasts as either 
significant or insignificant. Using Tukey’s method for multiple pairwise comparisons assumed 
an overall confidence level of $\alpha = 0.05$ for the analysis. Tukey’s method for pairwise 
comparisons is regarded as a conservative method for confidence interval of pairwise contrasts 
(Dean, 1999). It should be noted that the magnitude of the point estimate for each contrast has 
little meaning since the point estimates of the contrasts represent a difference of means that came 
from a sample set that underwent a natural logarithm transformation. It is not mathematically 
feasible to convert these point estimates back into units of copper concentrations. However, the 
sign of the point estimate suggests the relative position of the contrasts. Simply put, the point 
estimate can be used to determine which entity within the pairwise contrast better controlled 
copper release for those conditions tested.
For BOP, the medium dose and high dose were found to be significantly different from the low dose. However, there was insufficient evidence to suggest that the medium dose was different from the high dose. The point estimate of the contrast suggested that the low dose was less effective than the medium dose and high dose. For OP, the high dose was significantly more effective than both the low and medium doses, with no indication that the low dose was any different from the medium dose. ZOP was the only inhibitor with which Tukey’s method suggested that the doses were significantly different. The relationship between dose and significance for Si was identical to OP.
When comparing the inhibitors with common doses (e.g. if BOP and OP are compared, there respective levels (doses) must be the same) it becomes clear that Si is significantly different from BOP, OP, and ZOP. A review of the contrasts suggests that when matched with a common level (any level), BOP, OP, and ZOP were more effective than Si with copper control. Another interesting observation from Table 5-12 is that the contrast in which Si was not significantly
different occurs at the highest dose (Level 3). This implies that it took the highest dose of sodium silicate during the study (12 mg/L-SiO₂ above background) to perform similarly to the low doses (Level 1) of BOP, OP, and ZOP (0.5 mg/L as P). For the remaining high doses, BOP was found to be significantly different from OP, ZOP, and Si. The contrasts suggest that the high dose of BOP was less effective than the high doses of OP and ZOP.

For the medium doses there are fewer differences between the inhibitors. Copper release in Si was significantly greater than BOP, OP, and ZOP. There was evidence to suggest a difference amongst BOP, OP, and ZOP for the medium dose.

For the low doses only the differences between BOP and OP were found to be insignificant. Both ZOP and Si were significantly different from the other low dose inhibitors. Si was found to be less effective than BOP, OP, and ZOP for low doses. ZOP was found to be less effective than BOP and OP for low doses. The analysis implies that either BOP or OP performed the best for the low doses.

Note that the analysis identified the inhibitor doses as being effective (i.e. the treatment/levels are significantly different from both the Blend and the pHBlend-0.3). Both the Blend and pHBlend-0.3 were determined to be significantly different, with the Blend treatment performing better than pHBlend-0.3 on average.
Effect of Phase

The results from the pairwise comparison for the phases are shown in Table 5-13. The results indicated that Phase I was significantly different from all of the other phases on average. A review of the contrast between Phase I and other phases suggests that Phase I experienced more copper release than either Phase II, III, or IV. This may seem unusual given the trend in copper release for $p$HBlend-0.3 shown in Table 5-10. For pHBlend-0.3, Phase I experienced its lowest levels in copper release, while for the Blend, its highest average copper release occurred during Phase I. The contrasts appear to contradict the behavior of pHBlend-0.3, while at the same time, accurately describe the behavior of the Blend. As discussed earlier, the significance of an interaction term can complicate the interpretation of the main effects. When comparing the results from the contrasts of the treatment effect (e.g. inhibitor) with the actual data from Table 5-10, the analysis (Tukey’s method) seems to agree, in part, with actual observations. However, the phase effect in the model appears to have contributed a significant fraction of its variation ($SSTr$) to the interaction term. Any conclusion based on the information from Table 5-13 should be made with caution.
Table 5-13  Results from Tukey's multiple pairwise comparisons of phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>X</td>
<td></td>
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<tr>
<td>III</td>
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<td>X</td>
<td></td>
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</tr>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Note: The cells that are marked by an X represent contrasts that were not significantly different.

Conclusions

- The null hypothesis for the Kolmogorov-Smirnov goodness-of-fit test was rejected 4 of the 56 samples when applying a Type I error of 0.05. This suggested that 4 of the 56 samples exhibited sufficient evidence that the samples did not follow a normal distribution. It seems reasonable to assume that the samples were drawn from a normal population.

- The Bartlett test for homogeneity of variance suggested that the variances of the samples were not all equal. A relationship between the variance and mean was later evaluated and described in the form of Equation 5-16.

- Based on the normality assumption and the relationship between the variance and mean, the definition of a z-score was manipulated to derive an equation that would describe the 90th percentile of a function, $E(y \mid x)$. Where $E(y \mid x)$ represents the mean function of copper.
release ($y$) as a function of variable(s), $x$. The result is shown as Equation 5-19; where $k = e^{-3.3}$, $q = 2$, and $z_{90\%} = 1.28$.

- A 2-way ANOVA suggested that the main effects of treatment and phase were significant (treatment representing the PDS). However, the interaction term between treatment and phase was found to be significant as well. This complicated the interpretation of the phase effect.

- Tukey’s method of multiple pairwise comparison suggested that a common level of sodium silicate was less effective at reducing copper release than any of the other phosphate-based inhibitors. The only pairwise contrasts associated with sodium silicate and the phosphate-based inhibitors that were insignificant were the contrasts between the low doses of BOP, OP, and ZOP and the high dose of Si.

- Tukey’s method of multiple pairwise comparisons also suggested that the high doses of OP and ZOP exhibited the highest reduction in copper release. The medium dose contrasts were insignificant between BOP, OP, and ZOP. The low doses of BOP and OP performed better than the low dose for ZOP.

- Of the 12 possible contrasts between the levels corresponding to a particular inhibitor only 3 were found to be insignificant. These contrasts are comparisons between $L1-L2$, $L2-L3$, and $L1-L3$ for BOP, OP, ZOP, and Si. When these particular contrasts were found to be significant, the higher level (i.e. higher dose) was always found to correspond with lower copper concentrations.
References


