

IMPACT OF CORROSION INHIBITOR BLENDED ORTHOPHOSPHATE ON  
WATER QUALITY IN WATER DISTRIBUTION SYSTEMS

by

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## ABSTRACT

The impact of blended orthophosphate (BOP) inhibitor addition on the corrosion of iron, copper, and lead in drinking water distribution systems was studied under changing water quality environment. Release of iron, copper, and lead were monitored at varying inhibitor doses and changing blends of source waters (groundwater, surface water, and desalinated water). Solid corrosion products on pipe surfaces under BOP treatment were evaluated with surface characterization techniques. Performance of the BOP inhibitor was compared to other corrosion control strategies.

Iron scales for iron and galvanized steel coupons incubated in different blended waters in the presence of BOP inhibitor were analyzed by X-ray Photoelectron Spectroscopy (XPS) for surface composition. Identified iron corrosion products were ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and hydrated ferric oxide ( $\text{FeOOH}$ ), in addition to ferric phosphate ( $\text{FePO}_4$ ) on coupons exposed to BOP inhibitor. Variations of water quality did not significantly affect the distribution of solid iron forms on surface films. Thermodynamic modeling indicated siderite ( $\text{FeCO}_3$ ) was the controlling solid phase of iron release. XPS indicated addition of BOP inhibitor produced a solid phosphate film in the iron scale which could inhibit iron release.

Impact of BOP, orthophosphate, and pH adjustment on iron release in a distribution system was examined. Iron release was sensitive to water quality variations (alkalinity and chloride) associated with source and blends of finished water. Finished waters with high alkalinity content (between 149 and 164 mg/L as  $\text{CaCO}_3$ ) consistently mitigated iron release

regardless of inhibitor use. Dissolved iron constituted about 10% of total iron release. Empirical models were developed that related water quality, inhibitor type and dose to iron release. The BOP inhibitor minimized total iron release followed closely by increasing pH (between 7.9 and 8.1), while orthophosphate dose did not affect iron release. Temperature (ranged from 21.2 to 25.3) had limited influence on iron release with BOP treatment.

Monitoring copper release showed that dissolved copper was the dominant form in the effluent, at about 88%. BOP inhibitor doses of 0.5 to 2.0 mg/L proved beneficial in controlling copper concentrations to an average of below 0.5 mg/L. Control of copper release improved with increasing BOP dose, despite changes in alkalinity. Elevation of pH by 0.3 unit beyond pHs (between 7.9 and 8.1) resulted in noticeable decrease in copper concentrations of about 30%, but was more sensitive to higher alkalinity (146 to 151 mg/L as CaCO<sub>3</sub>) than BOP treatment. Developed empirical models confirmed the importance of BOP inhibitor dose, pH increase, and alkalinity content on copper release. Statistical comparison of the corrosion control strategies proved the advantage of BOP inhibitor, at all doses, over pH elevation in controlling copper release.

The BOP inhibitor mitigated lead release below action level, and consistently outperformed pH elevation, in all water quality conditions. XPS analysis identified lead dioxide (PbO<sub>2</sub>), lead oxide (PbO), cerussite (PbCO<sub>3</sub>), and hydrocerussite (Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>) as the corrosion products in the scale of lead/tin coupons exposed to BOP inhibitor. XPS and Scanning Electron Microscopy (SEM) analysis suggested cerussite or hydrocerussite is the controlling solid phase of lead release. Thermodynamic models for cerussite and hydrocerussite grossly over predicted actual concentrations. Solubility and equilibrium relationships suggested the

possibility of a lead orthophosphate solid that would describe the effectiveness of BOP inhibitor, although no lead-phosphate solid was detected by surface analysis. BOP inhibitor appeared to have mitigated lead release by forming a surface film between lead scale and the bulk water.

Dedicated to

My father who has believed in me all my life, supported me, and made me the man I am.

My mother who brought me to this world

My wife who stood by my side through thick and thin

My son who is the joy of my life

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## ABBREVIATIONS

Abbreviation	Meaning
ANOVA	Analysis of Variance
AWWA	American Water Works Association
AwwaRF	American Water Works Association Research Foundation
BOP	Blended Ortho-polyphosphate
DIC	Dissolved Inorganic Carbon
EDS	Energy Dispersive X-ray Spectroscopy
EN	Electrochemical Noise
EPA	Environmental Protection Agency
GW	Ground Water
HRT	Hydraulic Retention Time
ICP	Ion coupled plasma
OP	Orthophosphate
P	Phosphorous
PDS	Pilot Distribution Systems
PVC	Polyvinylchloride
R <sup>2</sup>	Coefficient of determination



Abbreviation	Meaning
RO	Reverse Osmosis (desalinated) water
SEM	Scanning Electron Microscopy
SW	Surface Water
TBW	Tampa Bay Water
TP	Total phosphorous
UCF	University of Central Florida
WQ	Water Quality
XPS	X-ray Photoelectron Spectroscopy

## 1 INTRODUCTION

This document is a PhD dissertation entitled “Impact of Corrosion Inhibitor Blended Orthophosphate on Water Quality in Water Distribution Systems”. This dissertation is submitted in partial fulfillment of the requirements for the degree of Doctor in Philosophy in Environmental Engineering in the Department of Civil and Environmental Engineering in the College of Engineering and Computer Sciences at the University of Central Florida (UCF).

The Department of Civil and Environmental Engineering is conducting a study to evaluate the ability of corrosion inhibitors to control water quality in distribution systems in changing water quality environment. Blended orthophosphate is one of the inhibitors examined in this study. The study simulates local water distribution system by using a varying blend of three finished water sources and feeding the blend into a pilot distribution system that is composed of different pipe materials. Blended orthophosphate (BOP) is dosed with the blended water into a section of the distribution system at various concentrations. This document is the result of the research effort in studying the impact of BOP on water quality in the dosed pilot distribution systems.

The document comprises of eight chapters. The first chapter gives an introduction about this dissertation and research objectives. Chapter 2 reviews the previous research work carried out in the areas of the dissertation. Chapter 3 discusses the materials and methodology including field facilities at the Tampa Bay Water site. The next four chapters comprise of results and

discussions. Chapter 4 includes a study on surface characterization of iron corrosion products. Chapter 5 is a study on controlling iron release with phosphate inhibitors versus pH control. Chapter 6 addresses control of copper release with BOP inhibitor and pH adjustments. And Chapter 7 examines the impact of BOP on lead release and corrosion scales. The last chapter provides recommendations and conclusions based on the data analysis and thus highlight major points obtained from this research effort for water utilities using blended ortho-phosphate inhibitors and potential future research efforts.

## 1.1 Problem Statement

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. This region, like most of Florida, has historically utilized groundwater for its drinking water supply; however, adverse environmental impacts have mandated that alternatives (non-groundwater sources such as desalinated seawater and treated surface water) be used for future supply.

In order to meet drinking water demands, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use and provide for growth in the region. To seek understanding of the issues involved when multiple-source waters are blended, TBW and UCF conducted research regarding the effect of variable finished water quality on distribution system water quality since 2000. The work had demonstrated that control of the scale or film in the existing distribution systems is a primary factor for maintaining acceptable distribution system water quality.

One feasible method of significantly reducing adverse water quality impacts from the disruption of distribution system scale or film is to replace the controlling scale or film with a film that will not be disrupted when exposed to the expected changing water quality. This is possible with surface active agents such as corrosion inhibitors. Corrosion inhibitors offer an opportunity for scale control because they bond directly with the elemental metal or scale on the pipe surface, forming a barrier between the interior pipe surface and the bulk water and this film will only be dependent on the corrosion inhibitor that is added to finished water.

Blended ortho-polyphosphate (BOP) has been used for years to control metal corrosion and release in distribution systems that may impact the water quality or violate established action levels. Although BOP has been useful in controlling metal release in many instances, full understanding of the mechanism of inhibition by BOP is still lacking, largely due to the proprietary nature of BOP commercial products used by utilities, and the vagueness in distinguishing between the roles of both the orthophosphate and the polyphosphate in the blend.

## 1.2 Research Objectives

The primary goal of the dissertation is to determine or gain insight into the mechanism of blended orthophosphate (BOP) corrosion inhibition in drinking water municipal and home distribution systems. The objectives are:

- Determining the impact of BOP on iron corrosion and release through water quality monitoring and determinations of surface characterization,
- Determining the impact of BOP on lead and copper release in water distribution system under varying water quality.

- Determining inhibition mechanism of BOP.
- Developing models for predicting appropriate inhibitor dose to control metal release with respect to changing water quality.

## 2 LITERATURE REVIEW

### 2.1 Chemical Structure

Blended orthophosphate (BOP) is a mixture of orthophosphates and polyphosphates. Polyphosphate in water industry refers to condensed inorganic phosphate ranging from a simple diphosphate to a long-chain linear polyphosphate. These linear polyphosphates are characterized by a chain-like anion structure, in which an oxygen atom is common to two neighboring ( $\text{PO}_4^{2-}$ ) tetrahedrons as shown in Figure 2-1 (Kalendova 2003). Only linear polyphosphates are used in water industry.

Polyphosphates are formed by dehydration of orthophosphates (Boffardi 1993). Phosphoric acid reacts with a base, such as sodium hydroxide or sodium bicarbonate, to form a slurry. Heat is then applied to dehydrate the slurry and form the  $-\text{P-O-P}-$  linkage, which is the backbone of polyphosphates. The number of P-O-P links determines the type of polyphosphate. If the polymeric-n group equals zero, then orthophosphate exists. When n is 1, pyrophosphate is present, and so on. Commercial polyphosphates used in water industry typically have n values of 12 to 14 (Boffardi 1993).

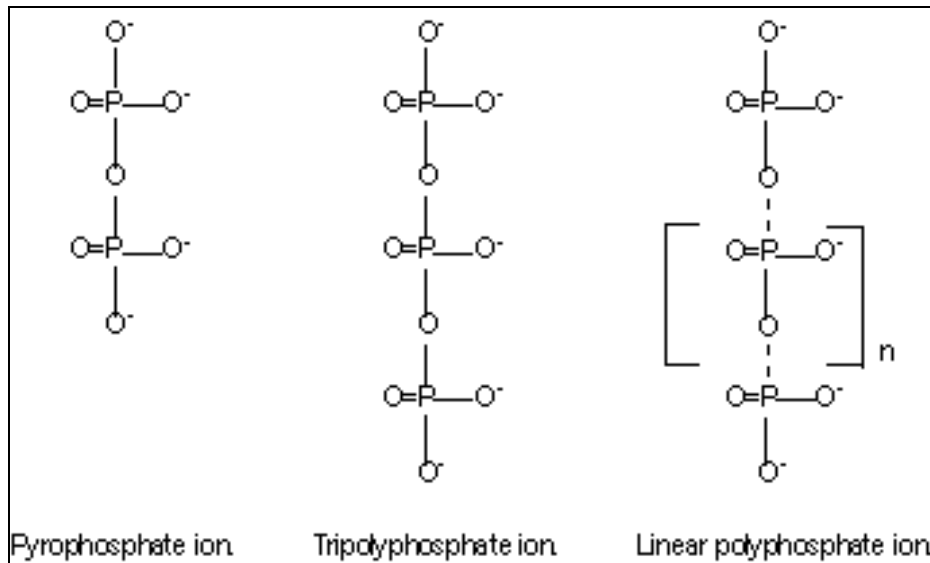


Figure 2-1 Polyphosphate ions(Kalendova 2003).

## 2.2 Polyphosphate Reversion

Blended orthophosphates (BOP) are a mixture of orthophosphates and polyphosphates. The ratio of ortho-to-poly in BOP is not always constant due to reversion. Reversion refers to the transformation of polyphosphate to orthophosphate by hydrolysis over time. Reversion depends on factors such as pH, temperature, detention time, and poly-to-ortho ratio. In addition reversion rate is quicker in diluted stock than in pure product (Powell and Yousef 1994).

Zinder, et. al (1984) studied the hydrolysis of sodium tripolyphosphate to orthophosphate to determine rate law of reversion and concluded that a two-step process takes place where sodium tripolyphosphate hydrolyzes to pyrophosphate, which then decomposes into orthophosphate. They also determined that half-life of tripolyphosphate ranged from few hours to 270 days depending on temperature and pH. Conditions of higher pH and lower temperatures had lower reversion rate.

The rate of reversion of sodium metaphosphate ( $\text{Na}_{15}\text{O}(\text{PO}_4)_{13}$ ) to orthophosphate was studied at different pH values (7-9) and calcium concentrations (<0.4-120 mg/L Ca). The pipe-rig experiment by Holm and Edwards (2003) showed a substantial increase in reversion rate with increasing calcium concentrations. The reversion rate was proportional to calcium concentrations, while pH change has much lesser effect than calcium. The change in rate ranged from 20% to 95% in just 21 days, where higher rates correlated directly with pipe age. In a report by Edwards and McNeill (2001) on phosphate inhibitors, they stated that reversion rate of polyphosphate increased with lower pH and higher Ca concentrations; the rate increased 10 times at calcium concentration of 120 mg Ca/L compared to the absence of Ca. Also stagnation conditions seem to result in much higher reversion rates. Hydrolysis of polyphosphate can be catalyzed by acidic conditions, and that follows an approximately zero order reaction rate regardless of concentrations (de Jager and Heyns 1998).

### 2.3 Utilities Survey on Use of Phosphate Inhibitors

Many utilities across the US use phosphate-based inhibitors to control lead and copper release. Surveyed utilities reported inhibitor doses ranged from 0.2 to 3 mg/L as  $\text{PO}_4$  (McNeill and Edwards 2002).

Full-scale demonstration test programs to control copper corrosion were conducted for three Florida utilities (Duranceau 1997). One utility found that orthophosphoric acid was an effective method to maintain copper concentrations below the action level of 1.3 mg/L. For another utility, pH adjustment to a target of 8.0 provided less variability in copper levels at consumer taps than inhibitor additions. In the third utility, copper and lead corrosion rates were



effectively reduced by pH/alkalinity adjustments and by additions of phosphate-based inhibitors (blended orthophosphate, zinc orthophosphate, and phosphoric acid). However, those inhibitors seemed less effective against pitting corrosion than pH/alkalinity adjustments.

Between 1994 and 2001, a shift from BOP to orthophosphate was observed. Utilities cited increase in soluble metal concentrations and reversion of polyphosphates to orthophosphate as reasons for the shift. The survey also showed that some utilities dose inhibitor “as product” and are unaware of exact concentrations as  $\text{PO}_4$  of inhibitor. According to 1994 survey, many small utilities used phosphate inhibitors based on just one or two known information sources while larger utilities cited a few more sources (McNeill and Edwards 2002).

Dodrill and Edwards (1995) conducted a survey of about 360 utilities to examine their strategies in controlling lead and copper release, in response to the “Lead and Copper Rule” of 1991. They observed that without phosphate inhibitors, higher alkalinity resulted in lower lead release. At low alkalinity, using inhibitors lowered lead release compared to no inhibitors. The survey revealed that for utilities with the low alkalinity and  $\text{pH} < 7.4$ , benefits were found from using orthophosphate but not polyphosphate. Moreover, polyphosphate increased lead release at higher alkalinity. For copper, the survey showed that at high pH, copper release is reduced with and without inhibitors. At  $\text{pH} < 7.8$ , copper release was high at high alkalinity, but inhibitor use mitigated that release well. However, at  $\text{pH} > 7.8$ , inhibitors had variable and adverse effects on copper corrosion by-product release, according to surveyed utilities (Dodrill and Edwards 1995). Generally, polyphosphate use is less understood than orthophosphate due to the proprietary nature of products and the lack of chemical information, in addition to their reversion nature and their possible synergetic effect with orthophosphate.

## 2.4 Corrosion and Iron Release

Metal corrosion in general requires four components (Snoeyink and Jenkins 1980):

- An anode: site of metal oxidation and dissolution
- A cathode: site of reduction
- An electrolyte solution: in which the oxidized metal ion dissolves, and allows transport of ions between anode and cathode to maintain electroneutrality
- A conducting path for electrons between anode and cathode.

Iron corrosion is the formation of ferrous ions from iron metals



Electron acceptors such as oxygen, chlorine, or hydrogen ions, complete the above reaction. At near neutral pH, oxygen reduction is the predominant cathodic reaction



Since corrosion is an electrochemical process, real-time electrochemical measurements may allow for better optimization of corrosion control strategies. Duranceau and colleagues (Duranceau et al. 2004) used electrochemical noise (EN) as an on-line corrosion monitoring technique with probes containing copper, lead, and steel electrodes at different utilities. They found that EN can provide good indications of changes in the rate of corrosion. However, it was not possible to accurately predict corrosion rate from EN measurements (Duranceau et al. 2004).

Iron release is the transport of iron from the metal surface of the corrosion scales to the bulk water in either particulate or soluble form. The release of iron in water distribution system can be the result of metal corrosion, dissolution of corrosion scale components, or hydraulic scouring action of flowing water (Sarin et al. 2001). Ferrous ions produced by the corrosion

reaction either dissolve in the water or deposit as scale on the corroded metal surface. Iron corrosion products may also dissolve and contribute to the amount of iron release. The released iron into the bulk water as ferrous ion Fe(II) may also be oxidized into Fe(III), which forms particles because of its low solubility and contributes to color and turbidity in water (Sarin et al. 2004).

The composition and structure of iron scales in pipes can vary between water distribution systems based on several factors including water quality parameters (i.e. pH and alkalinity), water flow patterns and seasonal temperature fluctuations. However, scales from different systems can have similarities in compositions; compounds often found in iron corrosion scales include goethite ( $\alpha$ -FeOOH), lepidocrocite ( $\gamma$ -FeOOH), magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), ferrous oxide (FeO), siderite ( $\text{FeCO}_3$ ), ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ), and ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) (Sarin et al. 2004).

The top layer of the iron corrosion scale at the scale-water interface is in contact with flowing water and is greatly influenced by water quality and hydraulic conditions. This layer may contain iron oxides in addition to precipitants of silicates, phosphates and carbonates. The top layer is loosely held and portions of it can be transported to the bulk water by hydraulic and turbulent flows causing turbid and colored water (Sarin et al. 2004).

Sarin et. al. (2001) studied iron scales from two different water distribution systems, and identified corrosion scales in old iron pipes as porous deposits of iron oxides with a “shell-like” dense layer near the scale water interface in all analyzed scales. Differences in porosity and corrosion products identified on scales from the two study sites are noted. These two sites received waters with different qualities (i.e. alkalinity, hardness, sulfate and dissolved oxygen).

Analysis of the chemical compositions of aged iron pipe surfaces by Lin et. al. (2001) showed that the predominant materials are from iron corrosion processes and not from particles precipitating from the bulk water. The surface analysis also found that the dominant iron species was Fe(III) (over 90%) mostly in the form of goethite ( $\alpha$ -FeOOH) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The authors proposed the following mechanism for the formation of corrosion material: Metallic Fe is oxidized to Fe(II) by dissolved oxygen and released into the water, then further oxidized into Fe(III) forming solid  $\text{Fe}(\text{OH})_3$ , which gradually dehydrates and forms other Fe(III) oxides (FeOOH).

Tang et. al. (Tang et al. 2006b) investigated iron corrosion products on unlined cast iron and galvanized steel pipe coupons. FeOOH,  $\text{Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$  were identified as major corrosion products, also  $\text{FeCO}_3$  was found on unlined cast iron coupons. X-ray Photoelectron Spectroscopy (XPS) analysis did not reveal significant presence of  $\text{FeCO}_3$  on unlined cast iron because  $\text{FeCO}_3$  would transform into  $\text{Fe}_2\text{O}_3$  upon removal from incubation and exposure to air (Heuer and Stubbins 1999). Iron release data showed a positive correlation with  $\text{Fe}_2\text{O}_3$  content on the scale, however, predicted solubility of  $\text{Fe}_2\text{O}_3$  was much less than measured iron release concentrations. Siderite ( $\text{FeCO}_3$ ) was assumed the solid controlling iron release, and its developed thermodynamic model resulted in good prediction of total iron release relative to other identified iron corrosion products.

Characterization of  $\text{FeCO}_3$  film by Heuer & Stubbins (1999) showed that it is not chemically stable. XPS analysis after exposure to air for only 4 hours showed a significant amount of  $\text{Fe}_2\text{O}_3$  is present on the surface. This suggests that  $\text{FeCO}_3$  oxidizes readily when exposed to air (oxygen) as proposed by the following reactions:



#### 2.4.1 Effect of Water Quality

Several water quality parameters influence iron release in water systems (Sarin: 2004):

- *Dissolved Oxygen*

The influence of dissolved oxygen on iron release depends on the characteristics of the iron scale present. If scale is highly porous, dissolved oxygen would readily react with metal iron causing the release of ferrous ions Fe(II) into solution. However, if the scale is more dense, oxygen is consumed both in the corrosion reaction of the iron metal and in the oxidation of the ferrous iron Fe(II) into Fe(III) that may then precipitate, making the scale denser and less permeable to Fe(II) diffusion. Based on this analogy, higher dissolved oxygen concentrations supplied by flowing water may decrease iron release in old established scales compared to stagnant conditions.

- *pH*

Increase in pH should decrease iron release, considering that iron release in water is mostly controlled by solubility of ferrous phases such as siderite and ferrous hydroxide. Also increase in pH increase the rate of formation of ferric (hydr)oxides, which are less likely to dissolve than ferrous solids.

- *Alkalinity*

Higher alkalinity decreases iron release. A decrease in alkalinity may promote the dissolution of a carbonate-containing iron such as FeCO<sub>3</sub>, which leads to increase in iron

release. Also high alkalinity water may minimize local pH variations because of its higher buffer capacity, which promotes a denser scale structure and that decreases iron release. Shi and Taylor (2007) reported that surface water treated with ferric sulfate coagulation had low alkalinity and high sulfates, which caused high iron release. In addition, the low alkalinity and high chloride levels in desalinated water also increased iron release.

- *Phosphates*

It is believed that iron phosphate precipitants form discontinuous protective film within the top layer of iron oxide film, thereby reducing porosity and limiting ferrous ions diffusion. Continuous application of phosphate insures the formation of this phosphate-based protective film. Advantages of phosphate-based inhibitors can be realized when aiming to simultaneously control lead, copper, and iron release. Imran et al. (2006) found that optimizing source water blends to identify acceptable water quality for simultaneous control of lead, copper and iron can be illusive. They found that ideal water quality for copper and lead control, such as alkalinity levels based on blend ratios, can be counter productive for iron control (i.e. low alkalinity).

Zhang and Edwards (2007) found that for new iron surfaces, the type of disinfectant can influence iron release. Less iron was released when using chlorine compared to chloramine. However, higher nitrate concentrations resulted in faster chlorine decay and more iron was released (Zhang and Edwards 2007).

In a summary of past literature, McNeill & Edwards (2001) demonstrated the complexity of understanding iron corrosion and the often contradictory results of previous research efforts. The authors identified the main problems of iron pipes corrosion as 1) pipe mass loss through oxidation, 2) scale accumulation of corrosion products that could increase head loss, and 3) release of soluble or particulate iron corrosion by-products to the water.

## 2.5 Inhibition of Iron Release by Phosphate Inhibitors

The inhibition capabilities of orthophosphate and polyphosphates on iron corrosion by-product release have been studied under various conditions of water qualities and hydraulic flows. Generally, polyphosphate use is less understood than orthophosphate due to the proprietary nature of products and the lack of chemical information, in addition to their reversion nature and their possible synergetic effect with orthophosphate.

The role of polyphosphate as an inhibitor was cited in numerous studies (McNeill and Edwards 2001), many of which concluded that polyphosphate could prevent iron corrosion. However, different theories were presented for this polyphosphate role. Some researchers believed that polyphosphate formed a protective film by adsorbing to the iron surface (Hatch and Rice 1945), while others stressed the importance of calcium in polyphosphate effectiveness in forming a protective layer (Huang 1980; Kamrath et al. 1993; Rangel et al. 1992). In other studies, researchers tied polyphosphate efficiency to flow conditions and stagnation periods (Larson 1957; McNeill and Edwards 2000; Rompre et al. 1999).

Use and applicability of polyphosphates in the water industry have been realized for many years (Larson 1957). Red water, or rusty water, is generally attributed to ferric hydroxide.

Ferric hydroxide forms from the reaction of insoluble (ferric) iron with water after the oxidation of soluble (ferrous) iron to the insoluble ferric in water. It has been shown in the past that polyphosphate is able to reduce red water when dosed at about 2-4 ppm per 1 ppm of iron (Larson 1957). Effectiveness of polyphosphate in corrosion control of municipal water is progressively greater at increasing flow velocities (2-5 fps). At slow velocities (around 0.5 fps) or in stagnant water, the ability of polyphosphate to control iron corrosion is greatly diminished (Larson 1957). Therefore, the advantage of polyphosphate might not be fully realized because turbulent flow velocities are not continually maintained in all parts of a typical distribution system.

Klueh et. al. (1988) investigated effectiveness of sequestering iron in groundwater by polyphosphate addition. Effectiveness was measured by percentage (%) iron filterability, where a high percentage meant less iron precipitation into particles that causes color and turbidity. Polyphosphate addition proved beneficial in sequestering iron, compared to no polyphosphate addition, but the presence of calcium adversely limited iron sequestration by polyphosphate (Klueh and Robinson 1988). Higher turbidity was recorded at high polyphosphate doses, which was attributed to exceeding the solubility of calcium phosphate. Wilhelmy et. al.(1985) studied complexation of iron (III) with phosphoric acid and the results showed the formation of two complexes,  $\text{FeH}_2\text{PO}_4^{2+}$  and  $\text{Fe}(\text{H}_2\text{PO}_4)_2^+$ . Harwood et. al. (1995) reported no significant difference in sequestration capacities of iron ions among four different commercial polyphosphate products. However, polyphosphates sequestration capacity for  $\text{Fe}^{2+}$  is only about 14% of the capacity for sequestering  $\text{Fe}^{3+}$ . The estimated sequestration capacity of  $\text{Fe}^{3+}$  by polyphosphates is about 2.16 mg Fe/mg P (Harwood et al. 1995).



Lytle and Snoeyink (2002) used a bench-scale experiment to evaluate and compare effect of orthophosphate and polyphosphate on properties of iron particles and suspension. Turbidity and apparent color, as measures of iron, were examined at various pH values and iron concentrations. Orthophosphate reduced turbidity by an average of 1 NTU over a wide pH range, and apparent color values decreased with increasing orthophosphate concentrations between 1 and 3 mg/L. Authors suggest that orthophosphate altered properties of Fe colloids by adsorbing to the particles surfaces. This adsorption has two effects:

- Increasing zeta potential, so particles are more stable.
- Limiting size of colloids by inhibiting formation of crystalline Fe.

The authors found that polyphosphate caused dramatic reduction in turbidity more than orthophosphate. Apparent color was reduced, but percent reduction was less than that of turbidity. Operating mechanism of polyphosphate is different from orthophosphate. Lytle and Snoeyink suggest that a polyphosphate-Fe complex is formed, which limits formation of Fe nuclei and particle size. Polyphosphate reduced particle size more dramatically than orthophosphate (Lytle and Snoeyink 2002), which may lead to better color control.

McNeill and Edwards (2002) investigated phosphate inhibitors in iron pipes in stagnant conditions. They used new pipes for stagnation periods up to 72 hours. Five different water qualities (variable pH and alkalinity) were used, and dosed with either orthophosphate, polyphosphate or none. Examination of iron release measurements showed that both orthophosphate and polyphosphate either increased or had no effect on iron concentrations. The only tested conditions that showed reduced iron release was at high alkalinity (300 mg/L as  $\text{CaCO}_3$ ) and pH of 7.2. This observation of phosphate inhibitors influence in stagnant pipes is

opposite to common experiences in flowing water conditions, in which polyphosphate addition reduced iron release in non-stagnant conditions (Cohen et al. 1999; Larson 1957). On average, other pH and alkalinity conditions showed an increase in iron release during stagnation when polyphosphate is used, compared to pipes with no inhibitor (McNeill and Edwards 2002).

McNeill & Edwards (2000) attempted to correlate total iron release to the amount of phosphate consumed, but no relationship was found. In general, phosphate consumption increased with pipe age and longer stagnation times. For pipes that received polyphosphate, a sharp increase in iron release was observed when dosing was stopped. This may be explained by iron scale release into the water. Inspection of the pipe showed less scale buildup than on pipes still receiving polyphosphate.

According to Boffardi (1995), blended phosphate has a synergistic effect; where the polyphosphate controls calcium carbonate scale, orthophosphate protects against copper and lead corrosion. Boffardi (1995) found that polyphosphate can prevent the formation of calcium carbonate scales in pipes, with as little concentration as 0.7 mg/L  $\text{PO}_4$ . In addition, polyphosphate concentration at approximately 1 to 2 mg/L achieved iron and manganese stabilization, and prevented red or black water. Overdosing polyphosphates can cause old loose deposits, especially iron oxide deposits, to dislodge from pipe surface and disperse, increasing red water problems (Boffardi 1993).

Sarin et. al. (2003) investigated iron release from corroded unlined cast-iron pipe under changing pH and alkalinity conditions, as well as orthophosphate addition. Using old unlined cast-iron pipe segments from an actual distribution system, they found that raising the pH to 9.5 resulted in a noticeable decrease in iron release over a period of few months (from >1.5 mg/L to

<0.3 mg/L). Variations of alkalinity at constant pH levels indicated that a lower alkalinity value often corresponded to a higher iron release and visa versa. Dosing orthophosphate at 2-3 mg/L PO<sub>4</sub> to iron pipe system at a pH range of 7.4-7.8 resulted in reduced iron levels below 0.2 mg/L. It is believed that orthophosphate provided additional benefits to pH and alkalinity controls.

In another study by Rompre et. al. (1999), a blend of ortho-polyphosphates at 1 mg PO<sub>4</sub>/L was tested on pilot-scale and full-scale water distribution system. Iron release was reduced with the application of the BOP under flowing water conditions. However, at reduced flow or stagnant conditions, iron release increased despite the BOP application. Also maintenance of phosphate dose was required to curtail iron release, because when the dose was dropped below 1.0 mg PO<sub>4</sub>/L, iron concentrations increased in effluent measurements. Hydraulic capacity of the tested pipes seemed to benefit from the application of phosphate. After 5 months of phosphate application at 1.0 mg PO<sub>4</sub>/L the hydraulic capacity increased by 55% compared to the capacity measured before application of phosphate inhibitor (Rompre et al. 1999).

Volk et. al. (2000) studied the impact of corrosion control strategies (pH adjustment or phosphate addition) on iron pipes by monitoring corrosion rates. They found that corrosion rates were strongly dependent on seasonal variations and water temperature, even with the addition of phosphate inhibitor. Slight increases in phosphate dose (from 0.9mg PO<sub>4</sub>/L to between 1.5 and 2.0 mg PO<sub>4</sub>/L) were necessary to maintain low corrosion rates, especially during warm periods.

The Southern California Water Company conducted a study of polyphosphate's role in iron corrosion products formation and chlorine residual levels on an actual distribution system that consisted of mostly unlined and lined cast iron pipes (Cohen et al. 1999). Results showed that polyphosphate addition can soften and remove existing corrosion layers on pipe surface,

resulting in a smoother pipe surface and increased hydraulic capacity with regular flushing. Polyphosphate addition also resulted in fewer consumers complaints of red water incidents at tap.

### 2.5.1 Mechanism of Iron Release Inhibition

Effectiveness of polyphosphate depends on several factors, mainly the presence of divalent cations, dissolved oxygen, and hydraulic conditions (flowing vs. stagnant). Various interpretations of polyphosphate inhibiting mechanisms include adsorption of polyphosphate or a polyphosphate complex on metal surface; or deposition of protective phosphate coating on the local cathodic area by migration of phosphate complexes (as cations or positively charged colloidal particles) (Koudelka et al. 1982).

Polyphosphates have been used to sequester metals in solution and prevent precipitation. i.e. keeping iron in solution to prevent stains, and holding calcium in solution to prevent excessive  $\text{CaCO}_3$  buildup (Cantor et al. 2000). This characteristic of polyphosphate can lead to elevated concentrations of pipe metals in solution. When a blended orthophosphate (BOP) is used, or when some of the polyphosphate reverts to orthophosphate, there is a decrease in metal sequestering in solution and a decrease in metal leaching from pipe wall (Cantor et al. 2000). This suggests that orthophosphate is dominant in controlling corrosion on pipe surface, and that effectiveness of polyphosphate depends on the degree of reversion.

Moriarty (1990) examined surface corrosion in cooling water systems when a BOP inhibitor is used. Electron spectroscopy and argon-ion sputtering were used to determine thickness and composition of a steel tube surface. Electron spectroscopy was used to determine

film thickness, film composition, and the structure of interface between film and steel surface. Sputtering is the removal of the top layers of the film in order to determine composition. Moriarty (1990) found two types of protective film formed on the pipe surface:

- An inner thin monolayer film formed on the pipe surface from adsorption of an inhibitor film.
- An outer thicker layer composed of a weakly soluble compound, generally porous, that serves as a physical barrier to diffusion and electron transfer.

According to Moriarty (1990), the inner pipe surface is covered with iron oxide, which helps adhesion of phosphate film and reduces iron dissolution. This is called anodic inhibition caused by orthophosphate. Polyphosphate are cathodic inhibitors because they form positively charged colloidal particles with Ca, Mg, and Fe that migrate to the cathode and form a protective film. The formed film acts as a barrier to oxygen diffusion, resulting in a decreased cathodic reaction rate.

Polyphosphate films are generally composed by complexation with calcium (i.e. hydroxyapatite,  $\text{Ca}(\text{PO}_4)_3\text{OH}$ ) and they are believed to form the outer thick layer (Moriarty 1990).



\* (Snoeyink and Jenkins 1980)

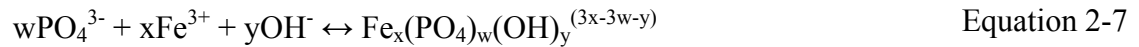
According to Boffardi (1993), Polyphosphates require a minimum concentration of calcium ions to form protective film on steel. Calcium-to-polyphosphate ratio is more critical than polyphosphate concentration, at least 1-to-5 weight ratio of calcium to phosphate.

Polyphosphates can prevent crystal growth of calcium carbonate scale in water pipes. It is worth noting that polyphosphate cannot prevent, nor remove, deposits of magnesium hydroxide (Larson 1957).

According to Lin and Singer (2005), phosphate-based corrosion inhibitors prevent the deposition of calcium carbonate scale on pipe walls in distribution systems by sequestering calcium and inhibiting calcium carbonate (calcite) precipitation. Several polyphosphates were tested and found to inhibit calcite crystal growth by adsorbing to the calcite surface. This inhibitory capability of polyphosphates is about two orders of magnitude greater than that of orthophosphate. It is believed that when polyphosphate is present, saturation indices, such as the Langleir Saturation Index, are not valid unless modified to account for polyphosphate sequestration abilities and its inhibition of precipitation (American Water Works Association. and Letterman 1999).

Koudelka et. al. (1982) studied the impact of polyphosphate on corrosion of pure iron pipe. They found through surface analysis by XPS that the film responsible for the anodic control of iron corrosion appears to be an oxide film with substantial presence of ferric phosphate ( $\text{FePO}_4$ ). They suggested the mechanism behind the creation of this protective film is the formation of soluble iron-polyphosphate complex ions, which go through hydrolysis (reversion) leading to precipitation of ferrous or ferric orthophosphate.

Tesfai et. al. (2006) states that an oxidant in the water (disinfectant) will oxidize most ferrous ions into ferric ions. Ferric ions then react with alkalinity and/or phosphate to form insoluble precipitates, as generalized by the equation:



When a higher level of phosphate was dosed (3.2 mg/L), it formed flocs with metal ions resulting in white cloudy turbid appearance in distribution system (Tesfai et al. 2006).

Ler and Stanforth (2003) investigated surface precipitation of phosphate on goethite. They confirmed a precipitation model that involves the dissolution of the goethite crystal to release iron and subsequent adsorption of the iron on surface-bound phosphate. This leads to the formation of iron phosphate compounds.

In studying the nucleation and growth of phosphate on metal oxide thin films, Nooney et al. (1998) found that in controlled laboratory conditions, uptake of phosphate by hematite surface showed a two-step process: initial rapid phosphate chemisorption onto the surface, followed by non-uniform phosphate precipitation.

A series of batch and continuous-flow laboratory corrosion tests, using commercial polyphosphates as corrosion inhibitors, showed that reducing corrosion rate of cast iron specimens required high dose of polyphosphate (greater than 20 mg/L) (Huang 1980). Further reduction of corrosion rate was further reduced when increasing alkalinity, pH, and calcium concentrations, as well as reducing dissolved oxygen. Huang (1980) proposed a mechanism for iron corrosion inhibition where polyphosphates react with cations in water such as ferrous and calcium ions, forming charged colloidal particles. These particles are subsequently deposited on the cathodic area as a protective coating that decreases the corrosion rate of cast iron.

## 2.6 Lead and Copper Corrosion

The EPA's "Lead and Copper Rule" established regulatory action levels for Pb and Cu at concentrations of 15 ppb and 1.3 ppm, respectively (USEPA 1991). Since then, research efforts have examined the impact of using phosphate-based corrosion inhibitors on meeting those target levels.

### 2.6.1 Copper Corrosion

Copper tubing in water systems may suffer from three forms of corrosion: 1) general; 2) impingement; and 3) pitting corrosion (James M. Montgomery Consulting Engineers. 1985). General corrosive attack is rare and occurs at low rates, while impingement and pitting attacks are rapid and severe.

- *General Corrosion*

General corrosion occurs at a low rate and is characterized by gradual buildup of corrosion products. General corrosion of copper is mostly associated with soft, acid water, and is mainly influenced by pH, hardness, temperature, age of pipe, and oxygen content in the water. Waters with pH lower than 6.5 and softness less than 60 mg/L as CaCO<sub>3</sub> are aggressive to copper, and general attacks are more prevalent in hot water systems (James M. Montgomery Consulting Engineers. 1985).

- *Impingement Corrosion*

Impingement attack results from excessive water flow velocities (more than 4 fps), where these high velocities disrupt the formation of protective films, which promotes more electrochemical attacks. Other factors that aggravate impingement corrosion are



soft water, high temperature, and low pH (James M. Montgomery Consulting Engineers. 1985). Impingement attack is characterized by a rough surface with U-shaped pits.

- *Pitting Corrosion*

Pitting corrosion of copper tubing commonly occurs in cold water piping. Pitting attacks are more prevalent in new pipe installations before a protective coating is established on the pipe's surfaces (James M. Montgomery Consulting Engineers. 1985). Lytle and Schock (2008) found that pitting corrosion of copper was favored in low dissolved inorganic carbon (DIC) (5 to 25 mg/L C) and in high pH water (pH 9). They found no pitting corrosion at pH below 7, and chloride was essential for pit propagation. However, pitting corrosion was prevented by increasing DIC to 50 mg/L C or adding orthophosphate at 3 mg/L PO<sub>4</sub> at pH of 9 (Lytle and Schock 2008)

Surface analysis of copper scale exposed to varying blends of source waters (ground, surface, and saline) showed that top layer contains Cu<sub>2</sub>O, CuO, and Cu(OH)<sub>2</sub> corrosion products (Xiao et al. 2007). Predicted copper release by thermodynamic model of Cu(OH)<sub>2</sub> was in reasonable agreement with actual data, with a slight underestimation of total copper release. This is not surprising since particulate copper contributes to total release, but is not accounted for in the model (Xiao et al. 2007). Both predicted and actual copper release data increased with increasing alkalinity in the water blend, and decreased with increasing pH values. This suggests that preventing copper release can be maximized by maintaining high pH and low alkalinity as possible within operational and quality constraints.

## 2.6.2 Lead Corrosion

Lead pipes were first used in plumbing because the material is ductile and can be bent to desired shapes easily. However, later health concerns about lead poisoning from corrosion by-products in drinking water reduced the use of lead in water piping. Also, public health problems such as retardation and hypertension further emphasized the need to control lead release into drinking water at the tap (James M. Montgomery Consulting Engineers. 1985). Lead release can be attributed not only to lead solders in household plumbing systems, but also to brass fixtures in all-plastic plumbing (Kimbrough 2007).

The form of lead in water depends strongly on pH, under typical water conditions. At lower pH, the dissolved plumbic ion ( $\text{Pb}^{2+}$ ) is the most stable form, while at neutral pH, lead carbonate (cerussite  $\text{PbCO}_3$ ) is more favored (James M. Montgomery Consulting Engineers. 1985). At higher pH values, hydrocerussite  $\text{Pb}_2(\text{OH})_2(\text{CO}_3)_2$  or the hydroxide  $\text{Pb}(\text{OH})_2$  are the dominant forms of lead. As pH decreases below pH 8, the solubility of lead increases dramatically for a fixed alkalinity.

Surface characterization of lead coupons in distribution system receiving variable source water blends indicated that  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ,  $\text{PbCO}_3$ , and  $\text{PbO}$  were the major lead corrosion products (Tang et al. 2006a).  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  content on coupons (area percentage) obtained by XPS analysis was linearly correlated with lead release, suggesting that  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  may be the solid phase controlling lead release (Tang et al. 2006b; Taylor et al. 2005). An equilibrium model of hydrocerussite ( $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ) was developed to predict soluble lead concentrations, the model indicated that pH and alkalinity have a major role in predicted lead release.

## 2.7 Inhibition of Lead & Copper Release by Phosphate inhibitors

McNeill and Edwards (2004) examined lead and copper in stagnant pipes and found that for copper pipes, orthophosphate reduced soluble copper concentrations but had little effect on particulate copper, while dosing with polyphosphate resulted in high levels of particulate copper, probably due to formation of copper-phosphate solid. For lead pipes, a significant fraction of corrosion by-product release was particulate. Both orthophosphate and polyphosphates reduced lead particulate species, although polyphosphate increased soluble lead concentrations.

A study by Vesecky et. al. (1997) included comparisons of film formation on copper and lead coupons at two separate sites using different poly-orthophosphate blends. Authors used SEM images and XPS scanning to describe and identify chemical composition of coupons surfaces, and they found that copper and lead coupons exposed to orthophosphate developed an oxide layer. When exposed to blended orthophosphate inhibitor, both Pb and Cu coupons formed two distinct surface layers; bottom layer composed of small particles (salt-like morphology) while the top layer showed three-dimensional growth.

Schock and Fox (2001) found that Increasing orthophosphate residual to 3 mg/L as  $\text{PO}_4$  resulted in a successful decrease of copper level in aged plumbing systems to below the action level of 1.3 mg/L (90th percentile copper level were reduced to 1.04 mg/L). Simultaneously, this orthophosphate residual also maintained lead levels below 0.005 mg/L for the 90th percentile.

In a report by Edwards et. al. (2001), experiments demonstrated the ability of polyphosphate to complex lead and copper in solution, which likely enhances dissolution of lead and copper in pipes during stagnation periods. However, lead complexation was less strong in

the presence of 40 mg Ca/L. Lead complexation by polyphosphate also increases the rate of dissolution from lead scale compounds such as  $\text{PbCO}_3$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ .

Compared to conditions when inhibitors were absent, orthophosphate resulted in reduced lead concentrations, while hexametaphosphate (polyphosphate) resulted in an increase in the soluble lead release (Edwards et al. 2001). Copper release was noticeably reduced equally by orthophosphate and polyphosphate dosing. Yet in every experiment, polyphosphate resulted in higher soluble copper concentrations after stagnation compared to orthophosphate, which is attributed to the complexation of copper by polyphosphate (Edwards et al. 2001).

#### 2.7.1 Copper Release Inhibition

When inhibitors are not considered, copper release can be controlled best by raising pH (Edwards et al. 2002). It was demonstrated that bicarbonates adversely affected copper release, and that a slight pH increase (in 7.0-8.0 range) showed significant reduction in copper release.  $\text{CO}_2$  stripping was the recommended method for raising the pH without raising alkalinity.

(Edwards et al. 2002; 2001) compared the benefits of orthophosphate vs. polyphosphate in controlling copper corrosion by-product release in aged copper pipes, at variable pH and alkalinity values. Polyphosphate seems to perform less favorably than orthophosphate at comparable concentrations of 1 mg/L as P. The authors believed that orthophosphate reduced copper solubility by forming a cupric phosphate scale. While in the absence of any phosphate inhibitors, an insoluble malachite scale ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) formed over a period of years. Polyphosphate, however, increased copper release in comparison to orthophosphate because it complexed copper, increasing soluble copper release.

Dartmann and others (2004) used copper loops to study the effect of orthophosphate inhibitor on drinking water while varying pH. Without orthophosphate, high pH water showed a decrease in copper concentration. When orthophosphate is dosed, copper concentrations decreased further in the higher pH water, while the same dose increased copper concentration in lower pH water. Two suggested mechanisms for influence of orthophosphate on copper corrosion:

- Orthophosphate reduced O<sub>2</sub> consumption by the copper, resulting in less copper being oxidized and going into solution.
- Conversely, the addition of orthophosphate hindered copper precipitation and the formation of a surface layer.

For the lower pH water and without orthophosphate, copper pipes showed formation of a surface layer that consisted of malachite (Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>). When orthophosphate was dosed, a copper oxide layer (cuprite, Cu<sub>2</sub>O) was formed on the surface, but no malachite was found (Dartmann et al. 2004). The cuprite layer is instable and resulted in higher copper concentrations. Authors believe that orthophosphate can decrease or increase copper concentration depending on which mechanisms is more dominant, which could be influenced by pH.

Souissi and Triki (2007) tested two inorganic phosphates, Na<sub>2</sub>PO<sub>4</sub> and Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>, for controlling copper corrosion in aqueous media. Pure copper coupons were exposed to corrosive experimental conditions and mass loss was measured. Both phosphate inhibitors reduced copper mass loss compared to no inhibitor addition in the given corrosive conditions (between 25% and 56%), and the less efficient protection was observed for polyphosphate (Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>).

Solubility models are used to predict maximum soluble concentration of a metal in water, given a controlling solid phase. Controlling solid phase for copper is believed to be  $[\text{Cu}(\text{OH})_2]$  or  $[\text{Cu}_3(\text{PO}_4)]$  in the presence of phosphate inhibitors, while for lead it could be cerussite  $[\text{Pb}(\text{CO}_3)]$ , hydrocerussite  $[\text{Pb}_3(\text{CO}_3)_2\text{OH}]$ , and hydroxypyromorphite  $[\text{Pb}_5(\text{PO}_4)_3\text{OH}]$  (Edwards et al. 1999). Edwards et al. (1999) argue that solubility modeling is not accurate at predicting copper and lead by-product release due to several factors such as the accuracy of constants in the model, misunderstanding of scale types, or influence of other mechanisms like colloid detachment from the surface. The authors used data collected from many utilities to verify solubility models for copper and lead. However, they chose to disregard utilities employing phosphate-based inhibitors because of the added complexity (Edwards et al. 1999).

### 2.7.2 Lead Release Inhibition

Schock, M. (1989) evaluated some factors that effect lead control in utilities, mainly water quality and inhibitor use. He indicated that pH adjustment has strong influence on lead solubility. However, the magnitude of pH effect is dependant on the dissolved inorganic carbon (DIC) concentration in the water. The use of orthophosphate can form insoluble solids with lead, such as hydroxypyromorphite  $(\text{Pb}_5(\text{PO}_4)_3\text{OH})$  or  $\text{Pb}_3(\text{PO}_4)_2$ . Higher DIC concentrations can affect orthophosphate film formation and the optimum pH at which the film forms due to the interconnected roles of phosphate solubility and carbonate complexation (Schock 1989).

Polyphosphates are used as sequestering agents because of their ability to complex with most metals. Calcium complexation reduces calcium carbonate scale deposition. Polyphosphates use has reduced staining in consumers' water by complexing  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$

(Holm and Schock 1991). Holm and Schock (1991) studied the effects of polyphosphate products on lead solubility in plumbing systems. They tested three different BOP products in household plumbing. Test conditions were pH of 8.0, 40 mg/L Ca, and approximately 1 mg/L total P. Results showed elevated soluble lead concentrations compared to no inhibitors use at a wide range of alkalinity values. Authors believe that Pb complexation by polyphosphates would reduce free Pb in water, which promotes the dissolution of hydrocerussite [ $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ], the most common Pb mineral in plumbing systems. That is why elevated Pb concentrations are found when polyphosphates are used.

However, Boffardi et al. (1991) expressed disagreement to Holm and Schock (1991) findings and experimental procedure. Boffardi claims that test conditions were not representative of most potable water systems. He stated that pH and ionic strength used by Holm and Schock were higher than normal (pH=8 and I=0.1M) and that resulted in unfavorable performance by polyphosphate. Holm and Schock disputed Boffardi's criticism and showed that a change in ionic strength from 0.001M to 0.1M increased lead solubility by less than 2%, which is very small (Holm and Schock 1991). They also showed that even though complexation by polyphosphate at pH=7 was less than at pH=8, it was still significant. Further determination of pH effect needed more information about the proprietary polyphosphate product, which were not available from the manufacturers.

Edwards & McNeill (2002) compared lead release from pure lead pipes under various water conditions (variable alkalinity and pH) when exposed to orthophosphate or hexametaphosphate (polyphosphate) treatments. They found that in stagnant conditions (between 8 to 72 hours), polyphosphate increased both soluble and total lead release under most

water quality conditions. Conversely, orthophosphate dosing typically reduced soluble lead release by about 70%.

Testing of lead pipe corrosion in laboratory setup by Boffardi and Sherbondy (1991) showed that orthophosphate ions are more effective in controlling lead release at near neutral pH than polyphosphate. An XPS analysis of lead coupons indicated that orthophosphate inhibited lead release by reacting directly with the lead surface, whereas polyphosphates reacted with divalent ions in the water (i.e. calcium ions) and developed a protective barrier on the lead surface (Boffardi and Sherbondy 1991).

Atassi et al. (2004) tested the impact of phosphate-based corrosion inhibitors on lead levels through a pipe loop setup by varying doses and considering seasonal temperature variations. They found that orthophosphate was more effective (at 1 mg/L) than polyphosphate, but equally effective as blended ortho-polyphosphate in controlling lead levels. Higher temperatures resulted in moderate increases in lead levels, while short term variations in phosphate feed showed no impact on lead levels. All pipe loops had a visible white powdery deposit that increased with higher orthophosphate dose.

Hozalski et. al. (2005) studied the benefit of inhibitors in controlling lead release from lead pipe. They used orthophosphate, polyphosphate, BOP, and stannous chloride ( $\text{SnCl}_2$ ). All inhibitors performed better than no-action alternative (control) at reducing lead release with various degrees. The ranking of inhibitors based on total lead concentrations, from lowest to highest, in the tested pipe loops was as follows: orthophosphate <  $\text{SnCl}_2$  < BOP < polyphosphate < control (Hozalski et al. 2005). The authors also observed that phosphate-based inhibitors resulted in increased bio-growth compared to the stannous chloride and control pipes.



## 2.8 Advantages of Ortho/Poly-phosphate Blends

The properties of the ortho-phosphates and the poly-phosphates are enhanced when blends of the two are used. Because ortho-phosphates are very reactive in solution and form insoluble salts with calcium, iron and lead, it may be difficult in some circumstances to keep a sufficient concentration of ortho-phosphate in the treated water to maintain its effectiveness. To compensate for this, the ortho-phosphate dose must be increased, which augments operational costs, and creates areas of excessive deposition in the system while other areas downstream are under-treated. Poly-phosphates on the other hand are unlikely to be precipitated until they undergo reversion. Therefore, blended phosphate products can offer better protection than either ortho or poly-phosphate can alone.

## 2.9 References

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### 3 MATERIAL AND METHODS

#### 3.1 Pilot Plant Design

A research facility was constructed for investigation of distribution system water quality at the Cypress Creek Water Treatment Facility near Tampa Bay, Fla. Photos of the facility are shown in Figure 3-1, Figure 3-2, and Figure 3-3. The facility contains 14 identical pilot distribution systems (PDS) that receive the same blended water at the same flow rate. The PDSs are operated to maintain a two-day hydraulic residence time. Each PDS is a hybrid line of five pipe segments as shown in Table 3-1; a polyvinylchloride (PVC) pipe segment, followed by a lined cast iron pipe, then an unlined cast iron pipe, and finally a two consecutive galvanized steel pipe segments.

Table 3-1 Characteristics of each PDS

Length	Diameter	Material
20 feet (6.1 m)	6-inch (0.15 m)	PVC
20 feet (6.1 m)	6-inch (0.15 m)	Lined Cast Iron
12 feet (3.7 m)	6-inch (0.15 m)	Unlined Cast Iron
40 feet (12.2 m)	2-inch (0.05 m)	Galvanized Steel





Figure 3-1 Water Production Area and Laboratory Trailer



Figure 3-2 Influent Standpipes, Inhibitor Tanks and Pipes System



Figure 3-3 Effluent Standpipes, Coupon Cradles and Corrosion Loops

The PDSs were constructed of aged pipes that were obtained from existing utility distribution systems to represent the pipe materials used in the TBW Member Government's

distribution systems. Sampling ports are provided between pipe segments. Each PDS is connected to 4-inch clear stand pipe at each end (head works and tail works) for hydraulic stability and to keep the system under pressure.

Every three PDSs are dosed with one inhibitor at varying concentrations; so PDS 1, 2 and 3 were fed with the BOP inhibitor at low, medium and high dose respectively. The target low dose was 0.5 mg/L as total P, 1.0 mg/l as total P for the medium dose and 2.0 mg/L as total P for the high dose. PDSs 13 and 14 do not receive any inhibitor dose and are used as control. PDS 13 receives blended water at pH equal to  $pH_s$ , while PDS 14 receives blended water at pH of approximately  $pH_s+0.3$ .

Effluent from each PDS feeds a copper loop that mimics in-house plumbing system that includes copper pipe material and plumbing fixtures with varying lead content. The copper loop system experiences stagnant condition with daily flushing event. Lead coupons are inserted in the copper loops to monitor lead corrosion. In addition, a pipe cradle per PDS is provided as housing for coupons made of the same pipe material as PDSs. The cradle receives same blended water and inhibitor dose as its corresponding PDS.

PDSs receive blended water and inhibitors for 12-month duration divided into four consecutive phases (each phase is approximately three months). Inhibitor doses to PDSs are kept constant for the 12-month duration, however, blended water is varied every phase. Once every two weeks, the PDSs are flushed to reduce biofilm accumulation by simulating a velocity encountered in a full-scale distribution system. The flow rate during the flush cycle is selected to achieve a velocity of approximately 1.0 ft/sec. The duration of the flush cycle is regulated to

pass a volume equal to three pipe volumes. The cradles are also flushed at the same time the PDSs are flushed.

### 3.2 Source & Blend Water Characteristics

Three different process waters are used in this study, surface water (SW), groundwater (GW), and desalinated -reverser osmosis- water (RO). GW and RO waters are generated onsite, while SW is hauled from a public water plant. These process waters are stabilized and dosed with chloramines residual before blending, which is done on a weekly basis. Blending ratio is changed every phase to achieve variability in water quality, as shown in Table 3-2 below. Phase I and Phase III have the same blends (WQ1) in order to study the seasonal effects-winter and summer respectively. The finished process water quality and blended water quality are presented in Table 3-3.

Table 3-2 Water Blend Ratios

Phase	Blend	% GW	% SW	% RO
I (Feb – May 2006)	WQ1	62	27	11
II (May - Aug 2006)	WQ2	27	62	11
III (Aug – Nov 2006)	WQ1	62	27	11
IV (Nov 2006 – Feb 2007)	WQ3	40	40	20

Table 3-3 Water Quality of Source and Blended Waters

Parameter	Units	GW	RO	SW	WQ1	WQ2	WQ3
pH		7.8	7.8	7.8	7.9	7.9	8.0
TDS	mg/L	355	285	433	365	388	414
HCO <sub>3</sub>	mg/L as CaCO <sub>3</sub>	211	70	81	163	109	154
Ca	mg/L as CaCO <sub>3</sub>	214	63	227	202	185	206
Mg	mg/L as CaCO <sub>3</sub>	28	6	33	29	28	23
Turbidity	NTU	0.25	0.07	0.26	0.3	0.19	0.21
Cl	mg/L	36	93	51	47	59	95
SO <sub>4</sub>	mg/L	29	2	191	72	112	74
DO	mg/L	7.3	8.2	8.7	8.7	8	8
NH <sub>2</sub> Cl	mg/L Cl <sub>2</sub>	5	5	5	5	6	6

### 3.3 Inhibitor

The selected BOP product for this project is called (SK-7641) by Stiles-Kem/Met-Pro corporation. Table 3-4 presents some of the product's characteristics provided by the manufacturer.

Table 3-4 Properties of the Inhibitor Product

Property	Value
Manufacturer	Stiles-Kem/Met-Pro
Product Name	SK-7641 Sodium Polyphosphate
CAS#	68915-31-1
Percent Polyphosphate	60%
Percent Orthophosphate	40%
Bulk Density	11.5 lbs/gal
Specific Gravity	1.38
pH of 1% solution	6.3-6.6
Solubility in Water	60g/100g water

The manufacturer claims that the blend in SK-7641 contains 60% polyphosphate and 40% orthophosphate. However, monitoring of BOP dose administered during the project indicated a ratio in the range of 60-80% of orthophosphate to polyphosphate. SK-7541 BOP

inhibitor was investigated in 1994 by Pinnellas County, Fla and UCF (Powell and Yousef 1994). The total phosphorous was estimated to be 39% ortho-phosphate and 61% poly-phosphate.

Periodic determination of the actual ortho/poly ratio was necessary to administer the correct dose of the product in the field. The target concentrations of inhibitor are in terms of total phosphate, but the field equipment can only measure orthophosphate, not total phosphate. Therefore, the predetermined ratio of ortho/poly was used to achieve the desired dose of total phosphate by measurement of orthophosphate concentrations.

The inhibitor stock is prepared twice a week. Each batch is approximately 40 gal in volume and at a concentration of 21.6 mg total-P/L. The inhibitor is fed from the common stock tank to each PDSs through a dedicated pump. In order to achieve the desired inhibitor concentrations in each PDS, adjustments to the pumps are made based on inhibitor concentration measurements in PDSs feeds. The pumps were acid cleaned when necessary to remove any phosphate deposition that could alter the flow rate.

### 3.4 Sampling and Analysis

Weekly and biweekly samples are collected from influent, effluent, and corrosion loops sampling ports for each PDS. Analysis of water quality parameters is done onsite and back at UCF. Parameters analyzed on site include pH, dissolved oxygen, temperature, alkalinity, orthophosphate, turbidity, chlorine, color, oxidation-reduction potential, and nitrite. The remaining analysis for parameters such as metals (dissolved & total) and total phosphate is done back at UCF labs using Ion-coupled plasma (ICP) Spectrophotometer. Analytical procedures utilized during this research effort confirm to those stated in the Standard Methods (American

Public Health Association. et al. 1998). A list of analyzed parameters and methods of analysis is presented in Table 3-5.

Table 3-5 PDS Water Quality Parameters

Parameter	Method of analysis	Units
Ammonia	Ammonia probe	mg NH <sub>3</sub> -N /L
pH	pH probe	
Alkalinity	Titration	mg/L as CaCO <sub>3</sub>
Calcium	Titration / ICP	mg/L
Magnesium	Titration / ICP	mg/L
UV- 254	Spectrophotometer	cm <sup>-1</sup>
Dissolved Oxygen	Probe	mg/L
Temperature	Probe	°C
Silica	Spectrophotometer /ICP	mg/L
Total chlorine	Spectrophotometer	mg/L
Free chlorine	Spectrophotometer	mg/L
Turbidity	Spectrophotometer	NTU
Apparent color	Spectrophotometer	CPU
Conductivity	Probe	μS/cm
Ortho-phosphate	Spectrophotometer	mg/L
Total phosphate	ICP	mg/L
Sodium	Spectrophotometer	mg/L
Chloride	Titration / ICP	mg/L
Sulfate	Spectrophotometer / ICP	mg/L
Copper	ICP	mg/L
Zinc	ICP	mg/L
Lead	ICP	mg/L
Iron	Spectrophotometer / ICP	mg/L

Quality assurance and quality control of both the laboratory and field determinations of water quality parameters was established by duplicating analyses of at least 10% of the samples. Where appropriate standards were available, 10% of the samples were spiked with known concentrations of the parameter being analyzed and the recovery measured. Blind duplicates and spikes were also used to determine the accuracy of measurements. Dynamic control charts were used to monitor any control violations.

### 3.5 Pipe Coupons and Surface Characterization

Coupons are used for surface characterization experiment. The coupons are made from pipe materials of the distribution system and placed into cradles at end of each PDS or in a trailer which received PDS effluent and was also used for an Electrochemical Noise (EN) investigation. Each cradle is exposed to the same blending water and inhibitor dose received by its corresponding PDS. Coupons are kept in cradles for a full phase, then removed for analysis and replaced with new coupons.

The Number and types of pipe coupons for each cradle, per phase, are:

- 3 coupons of cast iron
- 3 coupons of galvanized steel
- 3 copper coupons
- 3 lead coupons

For PDSs 1-3, a total of 36 coupons (12 X 3 PDSs) are prepared, installed, collected, and analyzed for each phase. It should be noted that the other inert materials including lined cast iron and PVC are not included in order to save labor and time.

Pipe surface characterizations were conducted at the Material Characterization Facility (MCF) at the Advanced Materials Processing and Analysis Center (AMPAC) of the University of Central Florida. To protect the corrosion layers formed in the pilot PDS, the coupon samples were stored in clean plastic boxes containing the same water in which the coupons had been incubated. These boxes were covered with plastic wrap (polyethylene film) to avoid reactions with the atmosphere after the coupon samples were harvested and then the coupons were transported back to UCF.

The techniques employed for surface characterization analysis were X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The XPS spectra patterns identify chemical components of the top surface of the corrosion layer. SEM visually magnifies the physical structure of the scale surface for identification of the corrosion products. EDS identifies the elemental composition of the corrosion layer.

### 3.5.1 XPS

Coupons were inserted into the PDSs at the beginning of each phase of pilot plant operation, and then retrieved at the end of the phase. The XPS scanning consists of a two-step process: an initial “survey” scan followed by a “high resolution” scan. The survey scan, conducted over a broad range of energy levels, is useful for confirming the presence or absence of elements on the surface of the coupon. In contrast, a high resolution scan, conducted over a narrow range of energy levels is useful for establishing the chemical states present for a given element.



The elements are indicated on the survey scan by pronounced peaks above the background of the survey, and these peaks are then selected individually for a second “high resolution” scan for each element. Additionally, elements of interest, such as those associated with inhibitors, coupon material, or water quality, were analyzed with high resolution scans. Possible compounds associated with a given element were determined through deconvolution of the high resolution scan.

### 3.5.2 SEM/EDS

SEM is capable of producing high magnification images of solid materials with a high depth of field. In SEM, the sample is scanned with an electron beam produced by a tungsten gun. When the electron beam reaches the sample surface, electrons and electromagnetic radiation are emitted and can be used to produce images. The secondary electrons emitted from the atoms because of the incident electron beam bombardment occupy the sample top surface and produce readily interpretable image of the surface. The corrosion layer can be differentiated by analyzing the difference of physical structure. Under certain circumstances, the crystalline structure could be observed clearly resulting in the identification of chemical components, thus verifying indirectly the results of other detection techniques as an auxiliary approach. The corrosion layer formed in water solution may not exhibit the legible crystalline structures, but amorphous state within short-term incubation. In this case, SEM can still provide information to determine if the corrosion is homogeneous or pitting. The physical morphology can also clarify whether the corrosion layer formed is compact or porous and help make the correct decision about protecting strategy.

The interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray along with other continuous spectrum. The emitted X-ray has an energy characteristic of the parent element. EDS can provide rapid qualitative or quantitative analysis of elemental composition with a sampling depth of 1-2 microns. X-rays may also be used to form maps or line profiles showing the elemental distribution in a sample surface.

### 3.6 References

American Public Health Association., Eaton, A. D., Clesceri, L. S., Greenberg, A. E., Franson, M. A. H., American Water Works Association., and Water Environment Federation. (1998). *Standard methods for the examination of water and wastewater*, American Public Health Association, Washington, DC.

## 4 CHARACTERISTICS OF IRON CORROSION SCALES IN THE PRESENCE OF BLENDED ORTHOPHOSPHATE INHIBITOR UNDER CHANGING WATER QUALITY ENVIRONMENT

### 4.1 Abstract

Iron scales for iron and galvanized steel coupons incubated in different blended waters in the presence of a blended orthophosphate (BOP) inhibitor were analyzed by X-ray Photoelectron Spectroscopy (XPS) for surface composition. Identified iron corrosion products were ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and hydrated ferric oxide ( $\text{FeOOH}$ ), in addition to ferric phosphate ( $\text{FePO}_4$ ) on coupons exposed to BOP inhibitor. Variations of water quality did not significantly affect the distribution of solid iron forms on surface films. Thermodynamic modeling indicated siderite ( $\text{FeCO}_3$ ) was the controlling solid phase of iron release. XPS indicated addition of BOP inhibitor produces a solid phosphate film in the iron scale which could inhibit iron release.

## 4.2 Introduction and Literature Review

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida, a region that historically has utilized groundwater for its drinking water supply. In order to meet drinking water demands, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use. To seek understanding of the issues involved when multiple-source waters are blended, TBW and University of Central Florida (UCF) conducted research regarding the effect of variable finished water quality on distribution system water quality since 2000. The work had demonstrated that the metal scale or film in the distribution system affects distribution system water quality.

Utilization of corrosion inhibitors at constant dose could provide a stable film and reduce the disruptive impact of varying water quality produced from utilization of alternate sources on distribution system scale, controlling scale or film. This paper examines the impact of blended ortho-polyphosphate inhibitor on iron corrosion scale in water distribution system, and how it relates to iron release in changing water quality environment.

Blended ortho-polyphosphate (BOP) has been used to control metal corrosion and release in distribution systems that may impact the water quality. Although BOP has been useful in controlling metal release in many instances, full understanding of the mechanism of inhibition by BOP is lacking.

Numerous studies have been conducted to investigate iron corrosion products with or without impact of phosphate-based inhibitors to explain iron release mechanisms. In the absence

of corrosion inhibitors, the release of iron in water distribution system can be the result of metal corrosion, dissolution of corrosion scale components, or hydraulic scouring action of flowing water (Sarin et al. 2001). The composition and structure of iron scales in pipes can vary between water distribution systems based on several factors including water quality and flow patterns. Yet, scales from various systems share similar corrosion products that include goethite ( $\alpha$ -FeOOH), magnetite ( $\text{Fe}_3\text{O}_4$ ), ferrous oxide (FeO), siderite ( $\text{FeCO}_3$ ), ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ), and ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) (Sarin et al. 2004).

Tang et. al. (2006b) investigated iron corrosion products on unlined cast iron and galvanized steel pipe coupons, as part of previous research effort conducted on the same pilot distribution system used for this current study (Taylor et al. 2005). FeOOH,  $\text{Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$  were identified as major corrosion products. Iron release data showed a positive correlation with  $\text{Fe}_2\text{O}_3$  content on the scale, however, predicted solubility of  $\text{Fe}_2\text{O}_3$  was much less than measured iron release concentrations. Since  $\text{Fe}_2\text{O}_3$  can result from the oxidation of siderite ( $\text{FeCO}_3$ ) when exposed to air (Heuer and Stubbins 1999),  $\text{FeCO}_3$  was assumed the solid controlling iron release, and its developed thermodynamic model resulted in good prediction of total iron release (Tang et al. 2006b).

Since BOP is a blend of orthophosphate and polyphosphate, examining the role of polyphosphate on iron corrosion may help understand the mechanism of iron scale formation under BOP inhibitor.

The role of polyphosphate as an inhibitor was cited in numerous studies (McNeill and Edwards 2001), many of which concluded that polyphosphate could prevent iron corrosion. However, different theories were presented for this polyphosphate role. Some researchers

believed that polyphosphate formed a protective film by adsorbing to the iron surface (Hatch and Rice 1945), while others stressed the importance of calcium in polyphosphate effectiveness in forming a protective layer (Huang 1980; Kamrath et al. 1993; Rangel et al. 1992). In other studies, researchers tied polyphosphate efficiency to flow conditions and stagnation periods (Larson 1957; McNeill and Edwards 2000; Rompre et al. 1999).

Moriarty (1990) examined surface corrosion of water pipes under a BOP inhibitor treatment, and found two types of protective film formed on the pipe surface:

- An inner thin monolayer film formed on the pipe surface from adsorption of orthophosphate to iron oxides present on inner pipe surface.
- An outer thicker layer composed of a weakly soluble compound, generally porous, that serves as a physical barrier to diffusion and electron transfer. This layer is attributed to Polyphosphates that form positively charged colloidal particles with Ca, Mg, and Fe, which migrate to the cathode and form a protective film.

Polyphosphates can prevent crystal growth and deposition of calcium carbonate scale on pipe walls in distribution systems by sequestering calcium and inhibiting calcium carbonate precipitation (Larson 1957; Lin and Singer 2005). Koudelka et. al. (1982) studied the impact of polyphosphate on corrosion of pure iron pipe, and found through surface analysis by XPS that the film responsible for the anodic control of iron corrosion appears to be an oxide film with substantial presence of ferric phosphate ( $\text{FePO}_4$ ). They suggested the mechanism behind the creation of this protective film is the formation of soluble iron-polyphosphate complex ions, which go through hydrolysis leading to precipitation of ferrous or ferric orthophosphate. Ler and Stanforth (2003) investigated surface precipitation of phosphate on goethite and confirmed the

dissolution of the goethite crystal to release iron and subsequent adsorption of the iron on surface-bound phosphate, which led to the formation of iron phosphate compounds.

In studying the nucleation and growth of phosphate on metal oxide thin films, Nooney et. al. (1998) found that in controlled laboratory conditions, uptake of phosphate by hematite surface showed a two-step process: initial rapid phosphate chemisorption onto the surface, followed by non-uniform phosphate precipitation. Huang (1980) proposed a mechanism for iron corrosion inhibition where polyphosphates react with cations in water such as ferrous and calcium ions, forming charged colloidal particles. These particles were subsequently deposited on the cathodic area as a protective coating that decreased the corrosion rate of cast iron.

### 4.3 Material and Methods

#### 4.3.1 Pilot Plant Design

A research facility was constructed for investigation of distribution system water quality at the Cypress Creek Water Treatment Facility near Tampa Bay, FL. The facility contained 14 identical pilot distribution systems (PDS) that received the same blended water and were made from increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series (Figure 4-1). The PDSs were constructed of aged pipes that were obtained from existing utility distribution systems to represent the pipe materials used locally. Effluent from each PDS feeds a copper loop that mimicked in-house plumbing system, which included copper pipe material and plumbing fixtures with varying lead content. PDSs received blended water and inhibitors for 12-months. The blends were changed quarterly. Inhibitor type and dose to PDSs were constant for the 12-month operational period.



Figure 4-1 Pilot Distribution Systems

The BOP PDSs (1, 2 and 3) received doses 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L as total phosphorous, respectively. The BOP inhibitor was a commercial product that was a blend of 60%-80% orthophosphate and 20%-40% polyphosphate. Two PDSs (13 and 14) received only NaOH for corrosion inhibition and were used as controls. PDS 13 and 14 received blended water at  $\text{pH}_s$  and  $\text{pH}_s+0.3$ .

#### 4.3.2 Source and Blend Waters

Varying blends of three different process waters were used in this study, surface water (SW), groundwater (GW), and desalinated -reverser osmosis- water (RO). The Blends were changed every phase to vary water quality as shown in Table 4-1. Phase I and Phase III have the same blend (WQ1) in order to study the seasonal effects.



Table 4-1 Water Blend Ratios

Phase	Blend	% GW	% SW	% RO
I (Feb – May 2006)	WQ1	62	27	11
II (May - Aug 2006)	WQ2	27	62	11
III (Aug – Nov 2006)	WQ1	62	27	11
IV (Nov 2006 – Feb 2007)	WQ3	40	40	20

#### 4.3.3 Sampling and Analysis

Daily, weekly and biweekly samples were collected from the influent, effluent, and corrosion shed locations and analyzed in the field laboratory and UCF laboratories. Data was collected throughout the year of operation.

#### 4.3.4 Pipe Coupons and Surface Characterization

Surface characterization was conducted using coupons made from the same pipes that were used to construct the PDSs. The galvanized steel coupons for surface characterization study were housed in cradles following every PDS. The iron coupons were housed in another cradle in a trailer which received PDS effluent and was also used for an electrochemical noise (EN) investigation. Coupons in the EN trailer were limited to only 1.0 mg/L as total P, resulting in a single coupon per phase of each material.

Surface characterization was performed on coupons using X-ray Photoelectron Spectroscopy (XPS). Some of the coupons were analyzed as well by scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The XPS spectra patterns identify chemical components of the top surface of the corrosion layer. SEM visually magnifies

the physical structure of the scale surface. EDS identifies the elemental composition of the corrosion layer pictured in the magnified image obtained by SEM.

#### 4.4 Results and Discussion

##### 4.4.1 Scale Characterization by XPS Analysis

Coupons used for XPS analyses were inserted into the pilot distribution systems (PDS) at the beginning of each phase of pilot plant operation, and then retrieved at the end of the phase. The XPS scanning consists of a two-step process, where an initial “survey” scan was performed to identify all possible elements present on the coupon. A survey scan, conducted over a broad range of energy levels, was useful for confirming the presence or absence of elements on the surface. In contrast, a “high resolution” scan, conducted over a narrow range of energy levels was useful for establishing the chemical states present for a given element. High resolution spectra were shifted along the energy axis to conform to a 284.6 eV adventitious carbon (C 1s) standard.

The elements are indicated on the survey by pronounced peaks above the background of the survey, and these peaks are then selected individually for the high resolution scan for each element. Elements of interest, such as those associated with inhibitors, coupon material, or water quality, were analyzed. Possible compounds associated with a given element were determined through deconvolution of the high resolution scans.

#### 4.4.1.1 Elemental Analysis

Both iron and galvanized steel coupons yielded similar survey scans and detected elements as shown in the representative XPS survey scan in Figure 4-2. The identified elements from the coupon surveys, and selected for high resolution scans, include carbon, calcium, iron, oxygen, phosphorous, silicon, and zinc.

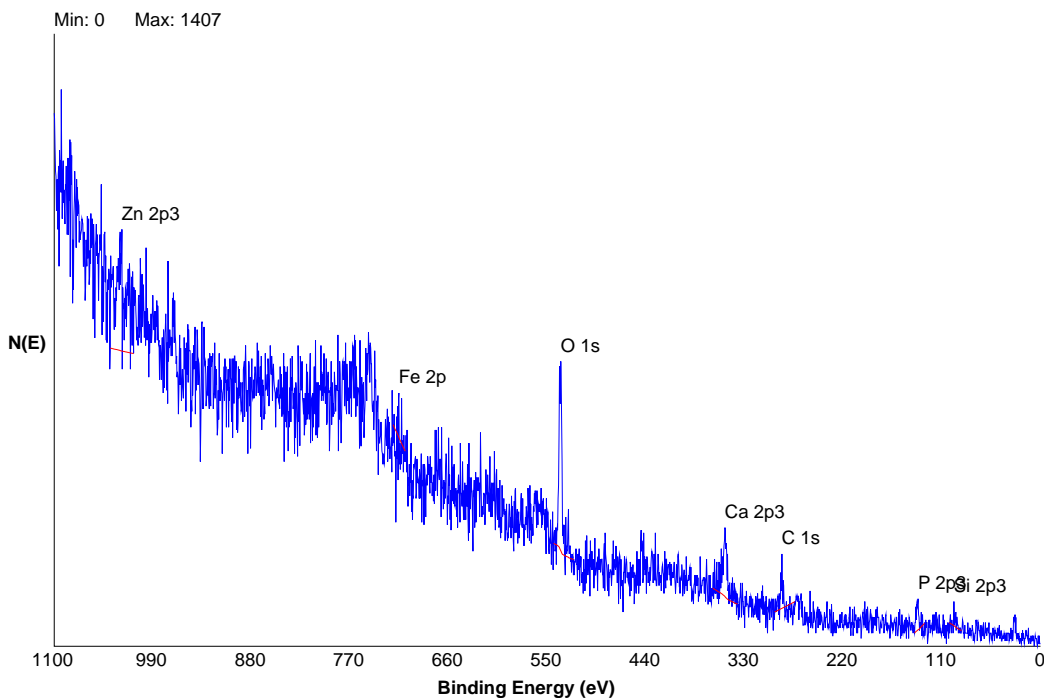


Figure 4-2 Representative XPS Survey Scan of an Iron Coupon.

Table 4-2 shows the occurrence of elements on scanned coupons. The examined coupons include iron and galvanized steel coupons that were exposed to either BOP (at 1.0 mg/L total P) or pH treatment (pH<sub>s</sub> and pH<sub>s</sub>+0.3 conditions). Carbon, iron and oxygen were found in all scale samples, which suggests that iron oxides were continuously distributed throughout the coupon scales. The raw water always contained carbonate alkalinity (carbon), hardness (calcium), oxygen, and silicon. All eight coupons receiving BOP inhibitor showed the presence of all

elements, except silicon on one galvanized steel coupon. The sixteen coupons under pH control treatment showed no presence of phosphorous, which is not surprising since no BOP dose was applied. Phosphorous was found in the scale of all coupons exposed to BOP treatment, suggesting that BOP was successful in forming a solid film on pipes' surfaces.

Table 4-2 Number of coupons containing detected elements from XPS scan

Detected element	No. of coupons on which an element was detected			
	Iron coupons		Galvanized steel coupons	
	BOP (4 total)	pH (8 total)	BOP (4 total)	pH (8 total)
Carbon (C)	4	8	4	8
Calcium (Ca)	4	7	4	7
Iron (Fe)	4	8	4	8
Oxygen (O)	4	8	4	8
Phosphorous (P)	4	0	4	0
Silicon (Si)	4	6	3	6
Zinc (Zn)	4	5	4	7

Calcium carbonate is a common form of calcium and carbon found on iron scale, all coupons contained calcium except two coupons under pH control. This suggests that  $\text{CaCO}_3$  was not completely distributed throughout the iron scale. Given the nature of corrosion in distribution systems, it is not unusual to find non-continuous scales. Hence the partial or complete presence of carbon, calcium, iron, oxygen, phosphorous, silicon, and zinc on iron coupons is not surprising. The presence of silicon and zinc in scales of the majority of coupons indicates that the raw water silicon was adequate to form scale on the iron coupons. The coupons were housed downstream of the pipe system and received PDS effluent, which contained metal release from galvanized steel and unlined cast iron pipe, which could contain zinc, iron and calcium solids.

#### 4.4.1.2 Identification of Iron Corrosion Products

Identification of iron scale corrosion products were done by deconvolution of high resolution iron scans ( $\text{Fe}_{2p}$  or  $\text{Fe}_{2p3}$ ). Findings from previous work suggested that major iron corrosion products included hydrated ferric oxide ( $\text{FeOOH}$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ), and magnetite ( $\text{Fe}_3\text{O}_4$ ) (Taylor et al. 2005).

$\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeOOH}$  were detected in all iron and galvanized steel coupons. Coupons exposed to BOP inhibitor treatment showed detectable ferric phosphate solids ( $\text{FePO}_4$ ), in addition to the iron corrosion products  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeOOH}$ . Hence, this suggests that the same oxygen based iron corrosion products form on the surface of iron pipe in the presence of BOP inhibitor. When both iron and galvanized steel coupons were exposed only to pH control treatment, deconvoluted scans of those coupons had no detectable ferric phosphate ( $\text{FePO}_4$ ), suggesting that formation of ( $\text{FePO}_4$ ) is dependent on the application of BOP inhibitor.

Representative curve fits that include detected ( $\text{FePO}_4$ ) on the surface of both iron and galvanized steel coupons are shown in Figure 4-3 and Figure 4-4. Ferric phosphate was detected on all coupons receiving the BOP inhibitor except one iron coupon, suggesting that BOP has an influence on the formation of iron corrosion products. Figure 4-5 and Figure 4-6 show curve fits with identified corrosion products when ferric phosphate is not detected, for both iron and galvanized steel coupons, respectively.

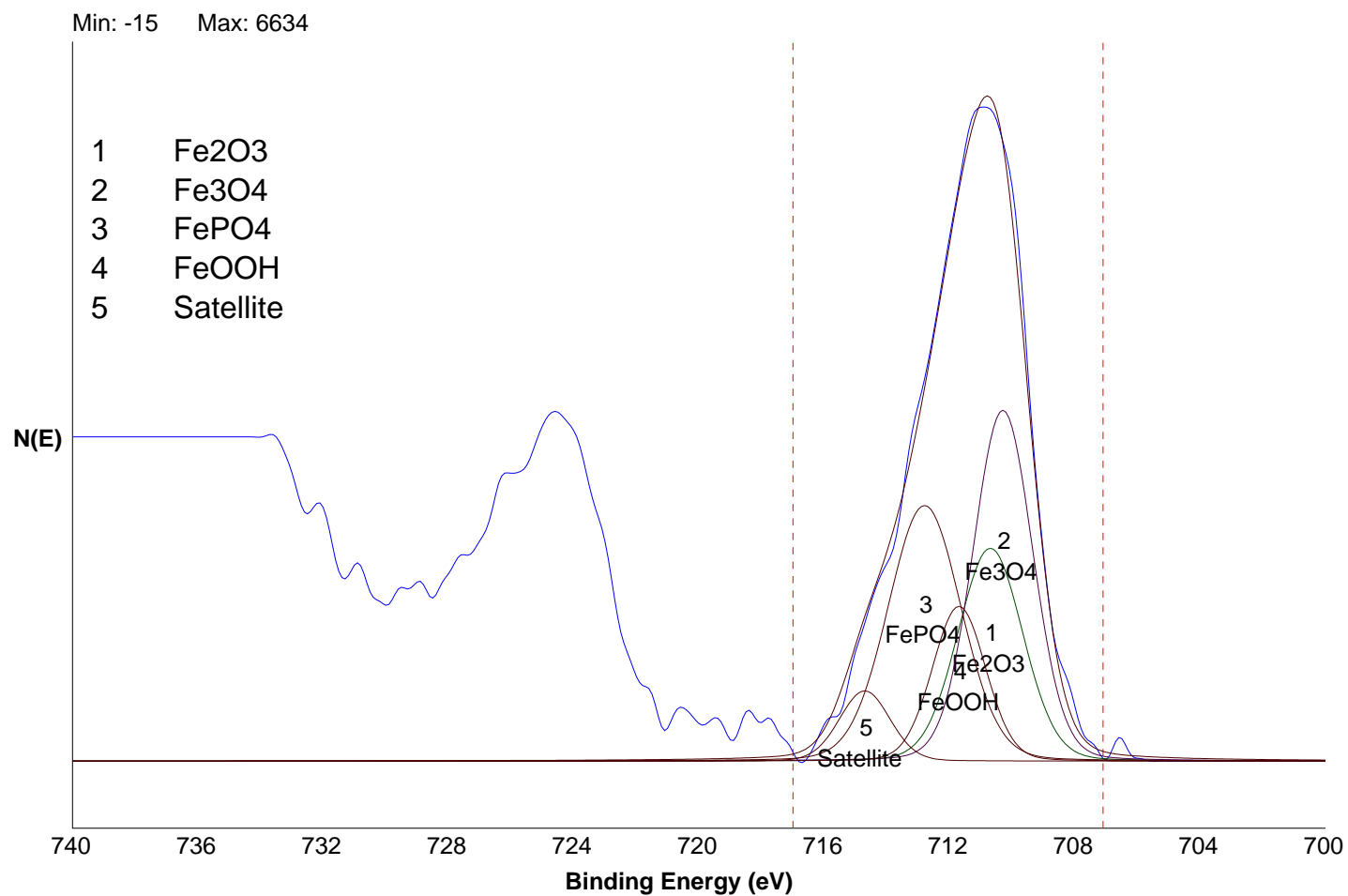


Figure 4-3 High-resolution XPS deconvoluted scans of Fe peak of corrosion products formed during 3-month incubation under BOP treatment on an iron coupon in Phase I

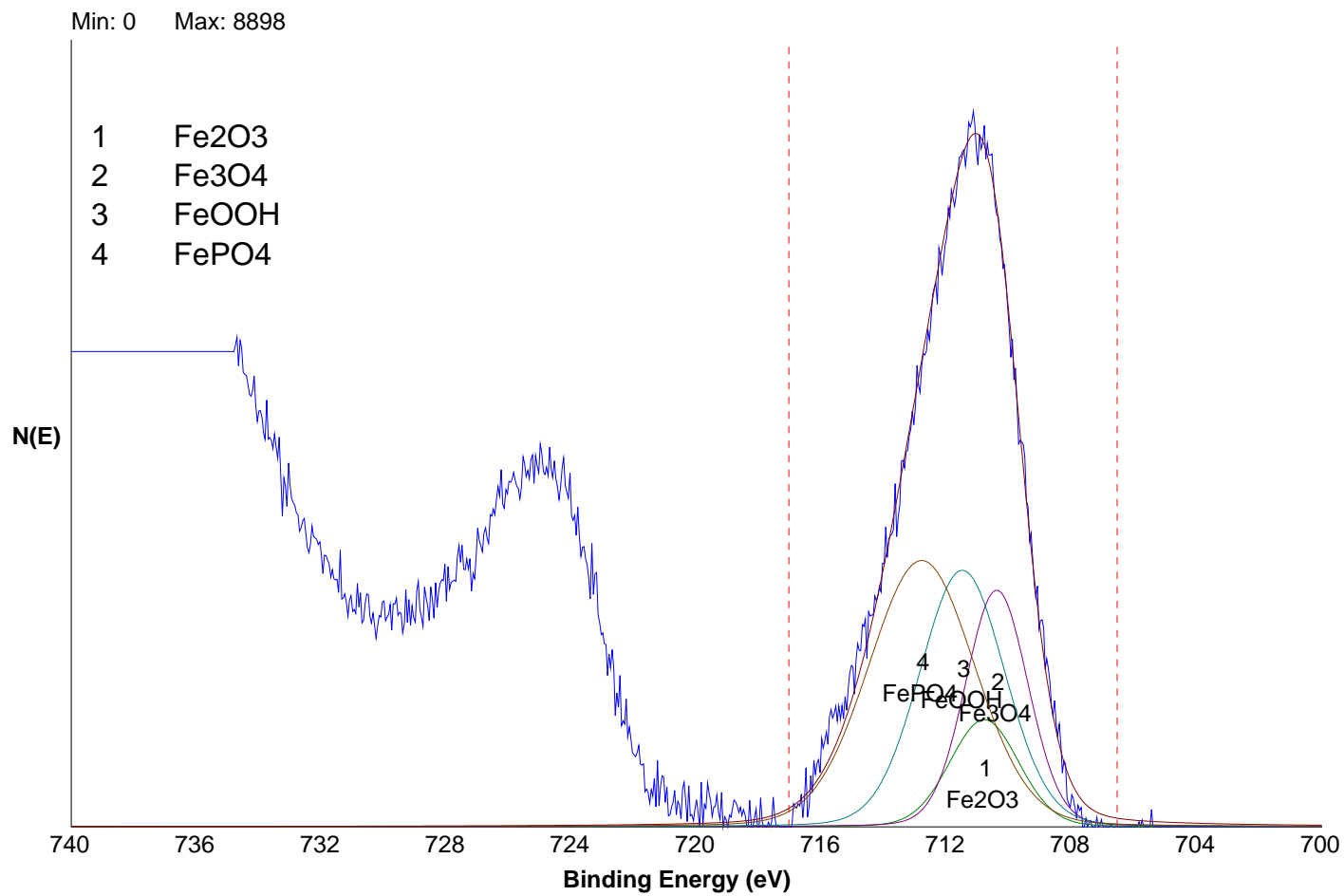


Figure 4-4 High-resolution XPS deconvoluted scans of Fe peak of corrosion products formed during 3-month incubation under BOP treatment on a galvanized steel coupon in Phase III

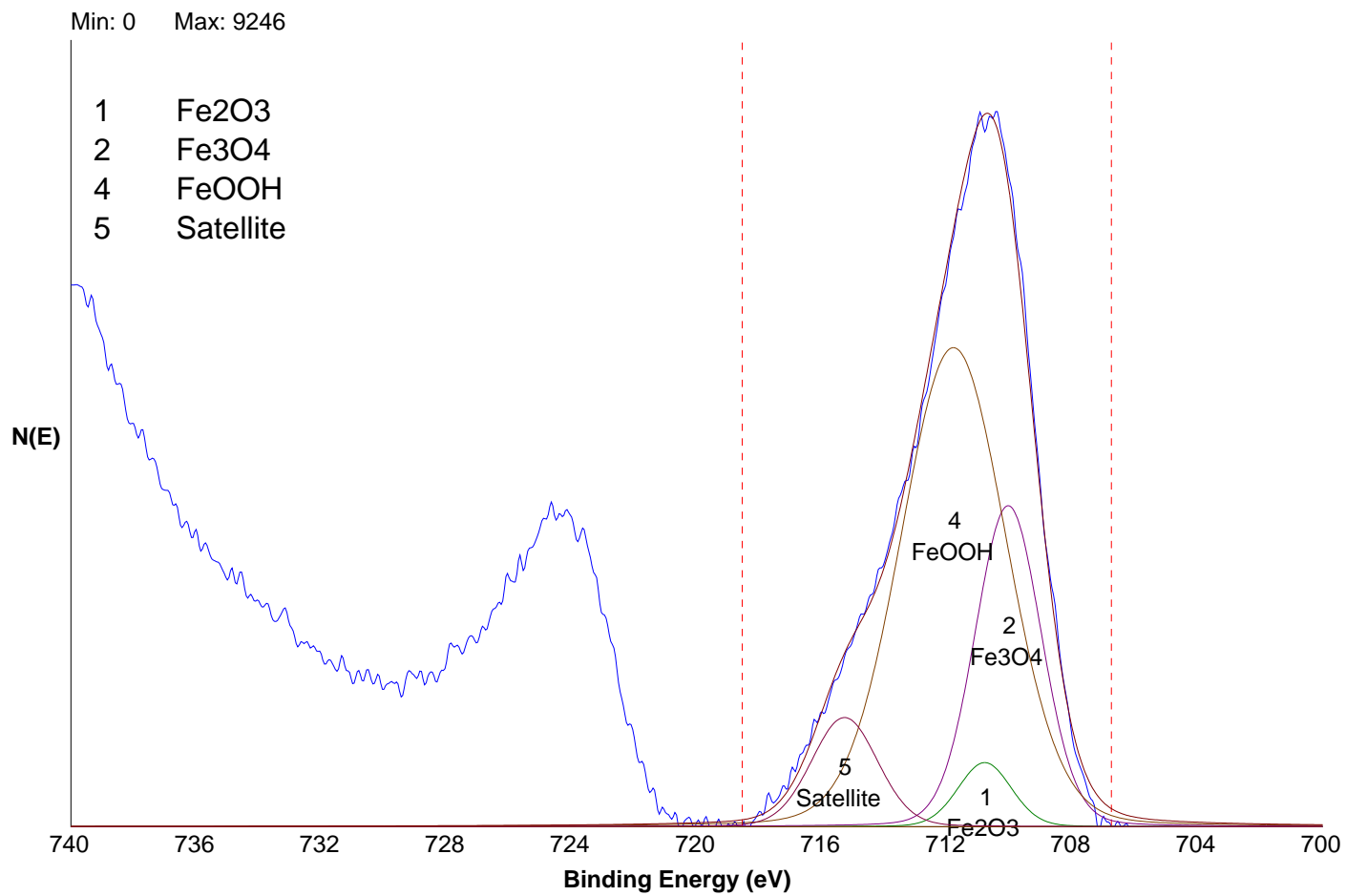


Figure 4-5 High-resolution XPS deconvoluted scans of Fe peak of corrosion products formed during 3-month incubation under pH control on an iron coupon in Phase IV



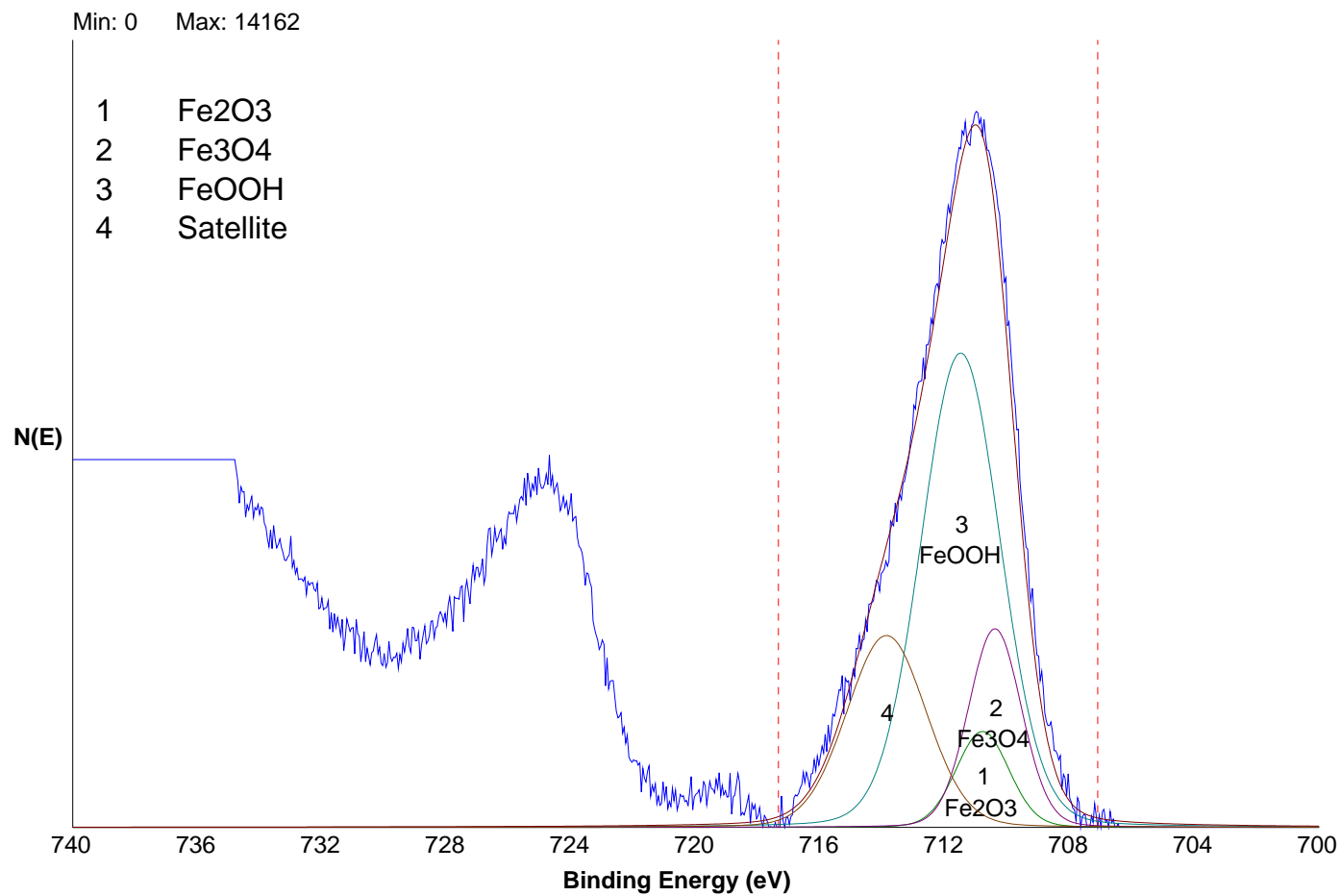


Figure 4-6 High-resolution XPS deconvoluted scans of Fe peak of corrosion products formed during 3-month incubation under pH control on a galvanized steel coupon in Phase III

Relative distribution of identified iron corrosion products in the scale of the iron and galvanized steel coupons are illustrated in Figure 4-7 and Figure 4-8, respectively, using a bar and whiskers format. The bars represent the average while the whiskers represent the minimum and maximum of all four phases. The percentages represent the average relative fraction of each corrosion product in the scale, based on curve fitting results from the XPS scans. In every phase, one coupon of each material (iron and galvanized steel) is exposed to a different treatment. The figures compare results for BOP and pH control treatments. Target dose of the BOP inhibitor applied to all coupons were kept constant between phases at around 1.0 mg P/L.

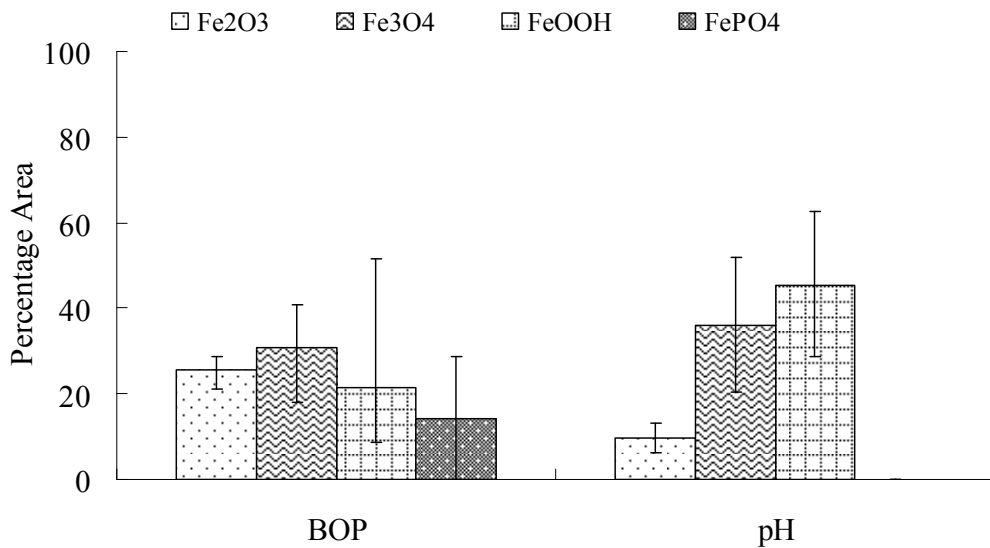


Figure 4-7 Distribution of Identified Iron Compounds on Iron coupons for all Phases

Figure 4-7 and Figure 4-8 show that none of the identified corrosion products is dominant over the others on pipe scales, neither for a given treatment nor a pipe material. However, both hydrated ferric oxide (FeOOH) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) seem to cover more area on the pipe scale in the absence of ferric phosphate (FePO<sub>4</sub>), as shown in both Figure 4-7 and Figure 4-8. This

suggests that  $\text{FePO}_4$  may compete with  $\text{FeOOH}$  and  $\text{Fe}_3\text{O}_4$  in interior scales or form (precipitate) on top of previously existing scale of  $\text{FeOOH}$  and  $\text{Fe}_3\text{O}_4$ .

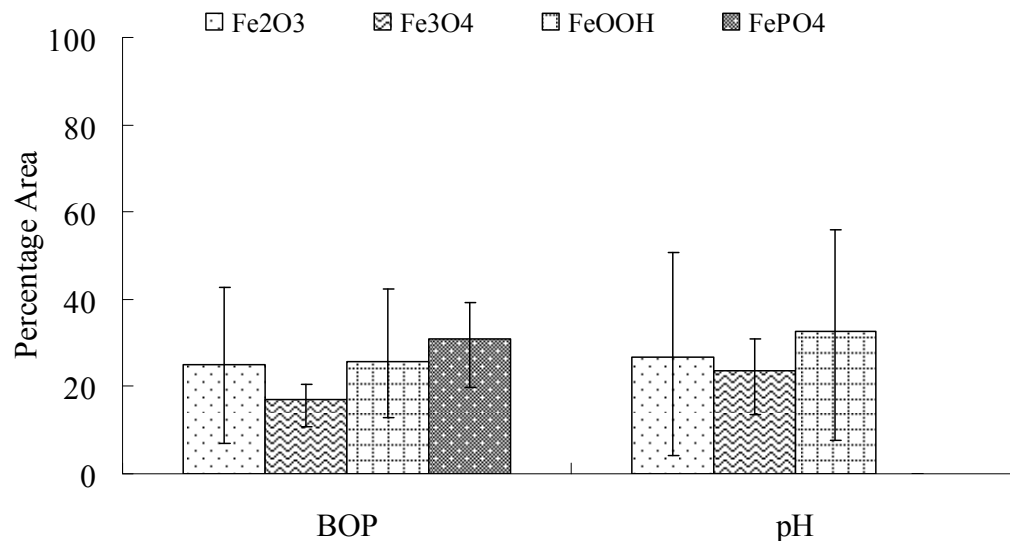


Figure 4-8 Distribution of Identified Iron Compounds on Galvanized Steel Coupons for all Phases

Attempts to correlate percentage composition of identified surface compounds to iron release yielded no evidence of correlation to a given compound. Yet, the strong presence of these iron oxides on all iron and galvanized steel coupons confirms their major impact, collectively, on iron release. The application of BOP inhibitor introduced an additional surface compound, ferric phosphate ( $\text{FePO}_4$ ), which suggests the phosphate inhibitor may produce a solid phosphate film that could inhibit iron release.

#### 4.4.1.3 Effects of Water Quality Variations by Phase

The effect of water quality variations between phases on the composition of the scale ion and galvanized steel coupons was evaluated for the identified iron scale compounds,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeOOH}$ , and  $\text{FePO}_4$ . Figure 4-9 shows variations in iron compounds composition of both

iron and galvanized steel coupons exposed to BOP inhibitor across all phases of operation. Water blend in Phases I and III had higher groundwater (GW) ratios than other phases, while Phase II blend contained more surface water (SW) than the remaining phases. Varying water quality appears independent of the composition of iron scale compounds as shown in Figure 4-9 and Figure 4-10.

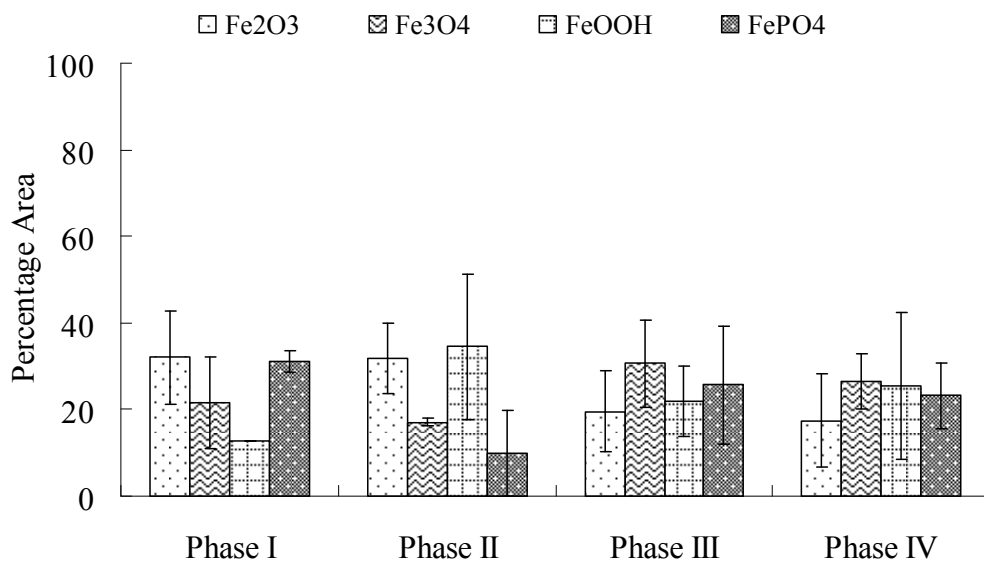


Figure 4-9 Averaged variations of composition of identified iron scale compounds on iron and galvanized steel coupons exposed to BOP inhibitor, separated by Phase.

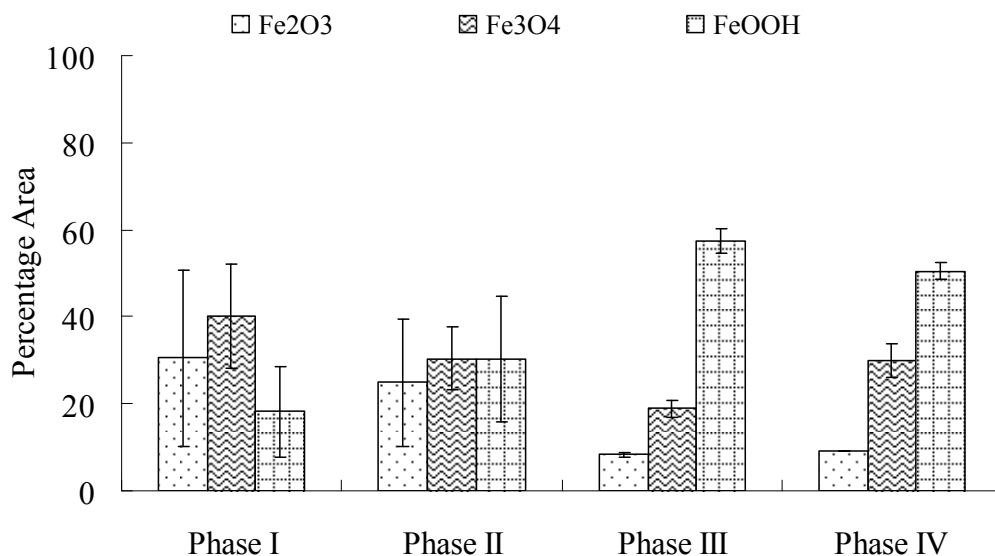


Figure 4-10 Averaged variations of composition of identified iron scale compounds on iron and galvanized steel coupons exposed to pH treatment, separated by Phase.

#### 4.4.2 Surface characterization by SEM/EDS

In addition to employing XPS, iron corrosion surfaces were further characterized by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Representative images obtained from SEM/EDS analysis of coupons incubated in BOP inhibitor are presented in Figure 4-11 and Figure 4-12. Figure 4-11 shows SEM images of iron coupons during Phase II (left image) and Phase III (right image). The image from Phase II was obtained at about twelve times the magnification of the image from Phase III. Even though water quality in Phase II was different from Phase III (lower alkalinity and calcium, higher sulfates and chlorides), scales from both phases shown in Figure 4-11 have structure similarities; most of the iron structures are a mixture of pseudo-hexagonal and sharp edged rod-like structures. This

finding agrees with XPS analysis results, in which phase change had little impact on composition of iron scale.

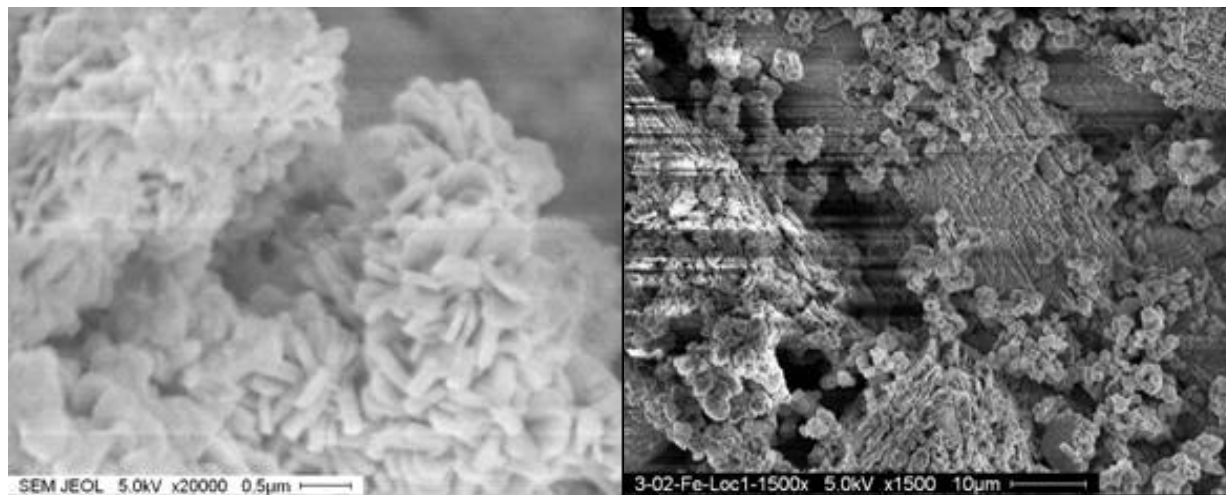


Figure 4-11 SEM images of iron coupon exposed to BOP during Phases II (left) and III (right)

The SEM image in Figure 4-12 is of an iron coupon from Phase IV and shows rounded pebble-like structures throughout the image and was found on other coupons. SEM imaging revealed that corrosion scales were not uniform and varied by location on the iron coupons. The EDS resulting analysis of elemental composition shown in Figure 4-12 was typical of most iron coupons scales exposed to BOP inhibitor. Most scale structures were composed of Fe and O and with small amounts of C, P and Si. Although phosphorus was not the dominant element, phosphorus was detected in the scale of most iron coupons. This result supports previous statements concerning the presence and corrosion inhibition of solid phosphate films.

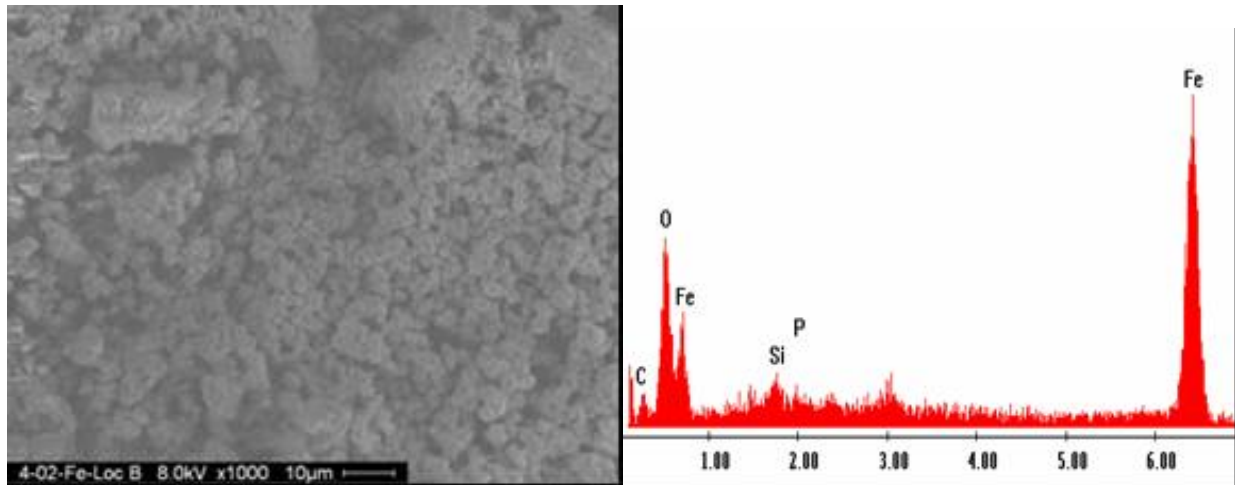


Figure 4-12 SEM image of iron coupon exposed to BOP during Phase IV and a typical EDS analysis results

#### 4.4.3 Thermodynamic Model Development for Iron Release

Iron release from pipe surfaces may be predicted by the solubility of solid phases formed within the corrosion scales using thermodynamic models. Such models are limited to the soluble species, and would be expected to under predict total iron release given significant particulate iron is present. The XPS analysis of iron and galvanized steel coupons  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeOOH}$ , and  $\text{FePO}_4$  were present in the iron scale and were assumed as controlling solid phases for thermodynamic modeling and was similar to the approach used by Tang et al. (2006b) No correlation was found between the composition of any iron scale compound and iron release,

The XPS analysis of iron coupons exposed to BOP inhibitor also revealed the presence of solid ferric phosphate ( $\text{FePO}_4$ ) on the surface. However thermodynamic modeling of iron release assuming ferric phosphate as the controlling solid phase for iron release grossly under predicted iron release. A siderite ( $\text{FeCO}_3$ ) model, as shown in Equation 4-1, was previously proposed for

control of iron release (Taylor et al. 2005) and was found to most accurately predict iron release of all models considered.

$$\begin{aligned}
 Fe &= [Fe^{2+}] + [FeOH^+] + [Fe(OH)_2^0] + [Fe(OH)_3^-] + [FeHCO_3^+] + [FeCO_3^0] \\
 &+ [FeSO_4^0] + [FeCl^+] + [FeH_2PO_4^+] + [FeHPO_4^0]
 \end{aligned}
 \tag{Equation 4-1}$$

$$= \frac{10^{-10.89} \times [H^+]}{[HCO_3^-] \times 10^{-10.3}} \left( \begin{aligned}
 &1 + \frac{10^{-9.5}}{[H^+]} + \frac{10^{-20.6}}{[H^+]^2} + \frac{10^{-32}}{[H^+]^3} + 10^2 [HCO_3^-] + \\
 &10^{4.38} [HCO_3^-] \times \frac{10^{-10.3}}{[H^+]} + 10^{2.25} [SO_4^{-2}] + 10^{0.9} [Cl^-] + \\
 &\frac{[TP]}{\frac{[H^+]}{10^{-2.1}} + 1 + \frac{10^{-7.2}}{[H^+]} + \frac{10^{-19.5}}{[H^+]^2}} + \frac{[TP]}{\frac{[H^+]^2}{10^{-9.3}} + \frac{[H^+]}{10^{-7.2}} + 1 + \frac{10^{-12.3}}{[H^+]}}
 \end{aligned} \right)$$

The siderite model development was based on the assumption that ORP was 0.43V (the average of all phases water quality) and at a temperature of 25°C. Under these conditions, Fe(II) concentrations are much more abundant than Fe(III) concentrations, and therefore, ferric species are ignored in model development.

Calculated iron concentrations from the siderite model in Equation 4-1 that incorporates soluble iron-phosphate complexes are compared to concentrations from the ferric phosphate model and actual iron release data in Table 4-3. Calculated dissolved concentrations by the siderite model slightly over predicted actual release. This suggests that dissolved iron release is not solely dependent on FeCO<sub>3</sub> but rather may depend on FePO<sub>4</sub> or other iron phosphate solids that may form and reduce iron release with BOP inhibitor addition.



Table 4-3 Iron thermodynamic modeling for BOP inhibitor

Phase	Actual Iron Release (mg/L)		Modeled Iron Release (mg/L)	
	Dissolved Fe	Total Fe	FePO <sub>4</sub>	FeCO <sub>3</sub>
I	0.04	0.14	1.0E-05	0.11
II	0.01	0.23	1.2E-05	0.20
III	0.01	0.22	5.9E-07	0.10
IV	0.00	0.24	2.4E-07	0.17

Solubility limits of iron from both considered solids (FePO<sub>4</sub> and FeCO<sub>3</sub>) without complexation are presented in Figure 4-13. The diagram suggests that under equilibrium conditions, FePO<sub>4</sub> was the limiting solid in iron release, which agrees with predicted iron release shown in Table 4-3. This confirms that the presence of a phosphate-based solid contributes to the reduction of iron release. Although inhibitor addition did not change the controlling solid for iron release, it may promote the formation of ferric phosphate solids that reduce the rate of iron release.

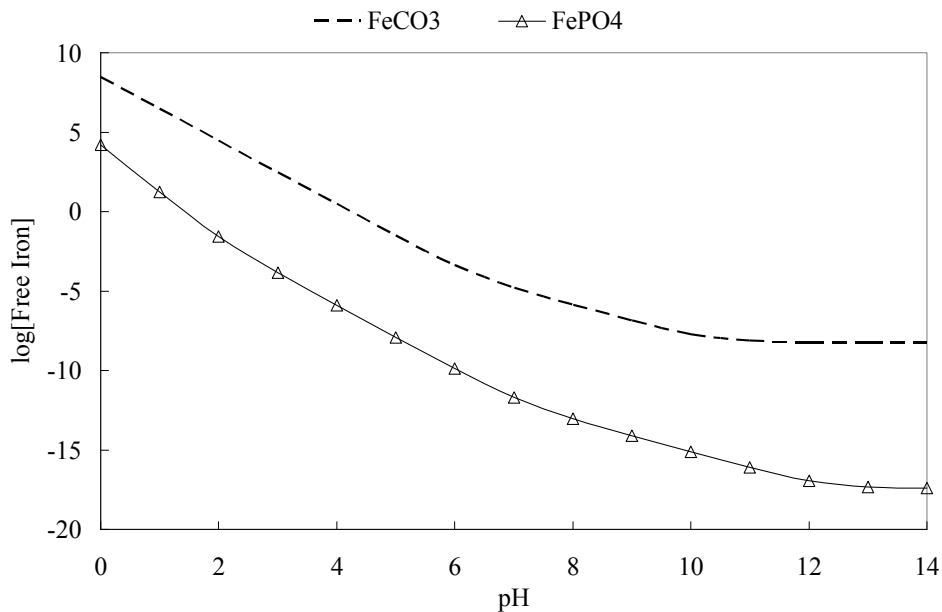


Figure 4-13 Solubility limits of iron for both FePO<sub>4</sub> and FeCO<sub>3</sub>

## 4.5 Conclusion

This study examined the impact of BOP inhibitor on iron corrosion scales in pipe distribution system with changing water quality conditions by varying source water blends. Under these conditions, resulting iron corrosion scales on iron and galvanized steel coupons were analyzed by XPS and SEM to gain insight into the controlling solid phase and mechanism of iron release with BOP inhibition.

Ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), hydrated ferric oxide ( $\text{FeOOH}$ ) and ferric phosphate ( $\text{FePO}_4$ ) were the major corrosion products identified in the surface scale on coupons incubated in BOP inhibitor and were found to be uniformly distributed throughout the coupon scales. There was no evidence of correlation between  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeOOH}$  surface compounds and iron release, however iron oxides were consistently the greatest solid form of iron in the films and must be involved in the iron release from iron and galvanized steel pipe. Deposition of  $\text{FePO}_4$  was attributed to inhibitor addition as no phosphate scale was detected in the pH inhibited coupons. This suggested BOP inhibitor may produce a solid phosphate film which could be a barrier to iron release from pipe materials and consequently inhibit iron release. Variation of phase water quality did not significantly affect the distribution of solid iron forms in the films. This suggests that BOP inhibitor hindered the impact of variations in water quality that otherwise might adversely affect iron release.

Thermodynamic models for identified corrosion compounds were developed to predict iron release. Although ferric phosphate ( $\text{FePO}_4$ ) solid was present under BOP treatment,  $\text{FePO}_4$  model grossly under-predicted iron concentrations and was ruled out as the controlling solid phase of iron release. A siderite ( $\text{FeCO}_3$ ) thermodynamic model that incorporates possible iron-

phosphate complexes showed good agreement with actual data, with slight over prediction of actual iron release. This suggests that dissolved iron release is not solely dependent on  $\text{FeCO}_3$  but rather may depend on  $\text{FePO}_4$  or other iron phosphate solids that may form and reduce iron release with BOP inhibitor addition.

#### 4.6 Acknowledgements

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## 5 CONTROLLING IRON RELEASE WITH PHOSPHATE INHIBITORS VERSUS pH ADJUSTMENT IN DISTRIBUTION SYSTEM

### 5.1 Abstract

Impact of phosphate-based inhibitors and pH adjustment on iron release in a distribution system was examined. Iron release was sensitive to water quality variations (alkalinity and chloride) associated with source and blends of finished water. Finished waters with high alkalinity content (between 149 and 164 mg/L as CaCO<sub>3</sub>) consistently mitigated iron release regardless of inhibitor use. Dissolved iron constituted about 10% of total iron release. Empirical models were developed that related water quality, inhibitor type and dose to iron release. Blended orthophosphate (BOP) minimized total iron release followed closely by increasing pH (between 7.9 and 8.1), while orthophosphate (OP) dose did not improve iron release control. Temperature (ranged from 21.2 to 25.3) had limited influence on iron release with BOP treatment.

## 5.2 Introduction and Background

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. In order to meet drinking water demands, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use. To seek understanding of the issues involved when multiple-source waters are blended, TBW and University of Central Florida (UCF) conducted research regarding the effect of variable finished water quality on distribution system water quality. The capacities of corrosion inhibitors to control these effects, including metal release, were investigated. This paper examines the impact of blended ortho-polyphosphate (BOP) inhibitor on iron release in water distribution system, and compares it to the performance of orthophosphate (OP) and pH adjustments in a changing water quality environment. These corrosion control strategies were evaluated based on an empirical model developed to predict iron concentrations for varying inhibitor dose and water quality conditions.

Iron release is the transport of iron from the metal surface of corrosion scales to the bulk water in either particulate or soluble form. The release of iron in water distribution system can be the result of metal corrosion, dissolution of corrosion scale components, or hydraulic scouring action of flowing water (Sarin et al. 2001). Ferrous ions produced by the corrosion of metal iron either dissolve in the water or form scales on the metal surface, which can also dissolve and release iron. The released ferrous ions Fe(II) may be oxidized into ferric ions Fe(III), which form particles because of their low solubility and contribute to turbidity and color (red water) (Sarin et al. 2004).

The role of polyphosphate as an inhibitor was cited by in numerous studies, many of which concluded that polyphosphate could prevent corrosion (McNeill and Edwards 2001). However, different theories were presented for the polyphosphate role. Some researchers believe that polyphosphate formed a protective film by adsorbing to the iron surface, while others stressed the importance of calcium to polyphosphate effectiveness in forming a protective layer. In other studies, polyphosphate efficiency was related to flow conditions and stagnation periods.

It has been shown in the past that polyphosphate is able to reduce red water when dosed at about 2-4 ppm per 1 ppm of iron (Larson 1957). Effectiveness of polyphosphate in corrosion control of municipal water is progressively greater at increasing flow velocities (2-5 fps). At slow velocities (around 0.5 fps) or in stagnant water, the ability of polyphosphate to control iron corrosion is greatly diminished (Larson 1957). Therefore, the advantage of polyphosphate might not be fully realized because turbulent flow velocities are not continually maintained in all parts of a typical distribution system.

Klueh and Robinson (1988) investigated effectiveness of sequestering iron in groundwater by polyphosphate addition, where effectiveness was measured by percentage (%) iron filterability. Polyphosphate addition proved beneficial in sequestering iron, compared to no polyphosphate addition, but the presence of calcium adversely limited iron sequestration by polyphosphate (Klueh and Robinson 1988). Higher turbidity was recorded at high polyphosphate doses, which was attributed to exceeding the solubility of calcium phosphate. Wilhelmly et al. (1985) studied complexation of Fe(III) with phosphoric acid and showed the formation of two complexes,  $\text{FeH}_2\text{PO}_4^{2+}$  and  $\text{Fe}(\text{H}_2\text{PO}_4)_2^+$ . Harwood et. al. (1995) reported no



significant difference in sequestration capacities of iron ions among four different commercial polyphosphate products.

Lytle and Snoeyink (2002) evaluated effects of orthophosphate and polyphosphate on turbidity and apparent color, as measures of iron, at various pH values and iron concentrations. Orthophosphate reduced turbidity by an average of 1 NTU over a wide pH range, and apparent color values decreased with increasing orthophosphate concentrations between 1 and 3 mg/L. Orthophosphate altered properties of Fe colloids by adsorbing to the particles surfaces. The authors found that polyphosphate caused dramatic reduction in turbidity more than orthophosphate (Lytle and Snoeyink 2002).

Operating mechanism of polyphosphate is different from orthophosphate. Lytle and Snoeyink (2002) suggest that a polyphosphate-Fe complex is formed, which limits formation of Fe nuclei and particle size. Polyphosphate reduced particle size more dramatically than orthophosphate, which may lead to better color control.

McNeill and Edwards (2000) investigated phosphate inhibitors (orthophosphate and polyphosphate) in iron pipes in stagnant conditions, and at different water qualities (variable pH and alkalinity). Both orthophosphate and polyphosphate either increased or had no effect on iron concentrations, except at 300 mg/L CaCO<sub>3</sub>. This observation of phosphate inhibitors influence in stagnant pipes is opposite to common experiences in flowing water conditions, in which polyphosphate addition reduced iron release in non-stagnant conditions (Cohen et al. 1999; Larson 1957).

In another study by Rompre et al. (1999), a blend of ortho-polyphosphates (BOP) at 1 mg PO<sub>4</sub>/L was tested on pilot and full-scale water distribution system. Iron release was reduced with

the application of the BOP under flowing water conditions. However, at reduced flow or stagnant conditions, iron release increased despite the BOP application. Also maintenance of phosphate dose was required to curtail iron release, because when the dose was dropped below 1.0 mg PO<sub>4</sub>/L, iron concentrations increased in effluent measurements. McNeill & Edwards (2000) attempted to correlate total iron release to the amount of phosphate consumed, but no relationship was found. For pipes that received polyphosphate, a sharp increase in iron release was observed when dosing was stopped, which may be explained by iron release from scales into the water. Inspection of the pipe showed less scale buildup than on pipes still receiving polyphosphate.

According to Boffardi (1995), blended phosphate has a synergistic effect; where the polyphosphate controls calcium carbonate scale, orthophosphate protects against copper and lead corrosion. Polyphosphate can prevent the formation of calcium carbonate scales in pipes, with as little concentration as 0.7 mg/L PO<sub>4</sub> (Boffardi and Cognetti 1995). Overdosing polyphosphates can cause old loose deposits, especially iron oxide deposits, to dislodge from pipe surface and disperse, increasing red water problems (Boffardi 1993).

Sarin et al. (2003) investigated iron release from corroded unlined cast-iron pipe under changing pH and alkalinity conditions, as well as orthophosphate addition. They found that raising the pH to 9.5 resulted in a noticeable decrease in iron release over a period of few months (from >1.5 mg/L to <0.3 mg/L). Variations of alkalinity at constant pH levels indicated lower alkalinities often corresponded to higher iron release and visa versa. Dosing orthophosphate at 2-3 mg/L PO<sub>4</sub> to iron pipe system at a pH range of 7.4-7.8 reduced iron levels below 0.2 mg/L. Orthophosphate addition coupled with pH and alkalinity further reduced iron release.

Volk et al. (2000) studied the impact of corrosion control strategies (pH adjustment and phosphate addition) on iron pipes by monitoring corrosion rates, and found corrosion rates were strongly dependent on seasonal variations and water temperature, even with the addition of phosphate. Slight increases in phosphate dose (from 0.9mg PO<sub>4</sub>/L to between 1.5 and 2.0 mg PO<sub>4</sub>/L) were necessary to maintain low corrosion rates, especially during warm periods.

### 5.3 Material and Methods

#### 5.3.1 Pilot Plant Design

A research facility was constructed for investigation of distribution system water quality at the Cypress Creek Water Treatment Facility near Tampa Bay, FL. The facility contained 14 identical pilot distribution systems (PDS) that received the same blended water and were made from increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series (Figure 5-1). The PDSs were constructed of aged pipes that were obtained from existing utility distribution systems to represent the pipe materials used locally. Effluent from each PDS feeds a copper loop that mimicked in-house plumbing system, which included copper pipe material and plumbing fixtures with varying lead content (Figure 5-1). PDSs received blended water and inhibitors for 12-months. The blends were changed quarterly. Inhibitor type and dose to PDSs were constant for the 12-month operational period.



Figure 5-1 Pilot Distribution Systems and Corrosion Loops

### 5.3.2 Inhibitors

The BOP PDSs (1, 2 and 3) received doses 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L as total phosphorous, respectively. The BOP inhibitor was a commercial product that was a blend of 60%-80% orthophosphate and 20%-40% polyphosphate. Similarly, The OP PDSs (4, 5 and 6) received doses 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L as total phosphorous, respectively. Two PDSs (13 and 14) received only NaOH for corrosion inhibition and were used as controls. PDS 13 and 14 received blended water at  $\text{pH}_s$  and  $\text{pH}_s+0.3$ .

### 5.3.3 Source and Blend Waters

Varying blends of three different process waters were used in this study, surface water (SW), groundwater (GW), and desalinated -reverser osmosis- water (RO). The blends were changed every phase to vary water quality, as shown in Table 5-1. Phase I and Phase III have the same blend (WQ1) in order to study the seasonal effects. The average water quality for source waters and the resulting blends are presented in Table 5-2.

Table 5-1 Water Blend Ratios

Phase	Blend	% GW	% SW	% RO
I (Feb – May 2006)	WQ1	62	27	11
II (May - Aug 2006)	WQ2	27	62	11
III (Aug – Nov 2006)	WQ1	62	27	11
IV (Nov 2006 – Feb 2007)	WQ3	40	40	20

Table 5-2 Water Quality of Source and Blended Waters

Parameter	Units	GW	RO	SW	WQ1	WQ2	WQ3
pH		7.8	7.8	7.8	7.9	7.9	8.0
TDS	mg/L	355	285	433	365	388	414
HCO <sub>3</sub>	mg/L as CaCO <sub>3</sub>	211	70	81	163	109	154
Ca	mg/L as CaCO <sub>3</sub>	214	63	227	202	185	206
Mg	mg/L as CaCO <sub>3</sub>	28	6	33	29	28	23
Turbidity	NTU	0.25	0.07	0.26	0.3	0.19	0.21
Cl	mg/L	36	93	51	47	59	95
SO <sub>4</sub>	mg/L	29	2	191	72	112	74
DO	mg/L	7.3	8.2	8.7	8.7	8	8
NH <sub>2</sub> Cl	mg/L Cl <sub>2</sub>	5	5	5	5	6	6

#### 5.3.4 Sampling and Analysis

Daily, weekly and biweekly samples were collected from the influent, effluent, and corrosion shed locations and analyzed in the field laboratory and UCF laboratories. Data was collected throughout the year of operation.

## 5.4 Results and Discussion

### 5.4.1 Iron Release by PDS

Iron concentrations from each PDS influent and corrosion loop effluent were compared. Each PDS experienced a two-day HRT throughout the duration of operations. Both PDS influent and corrosion loop effluent total iron measurements were averaged over the 12-month duration and presented in Figure 5-2 for each PDS. The annual average influent iron concentrations were slightly less than 0.03 mg/L, while the corrosion loop effluent concentrations varied from 0.11 to 0.22 mg/L, depending on the control strategy and the applied dose.

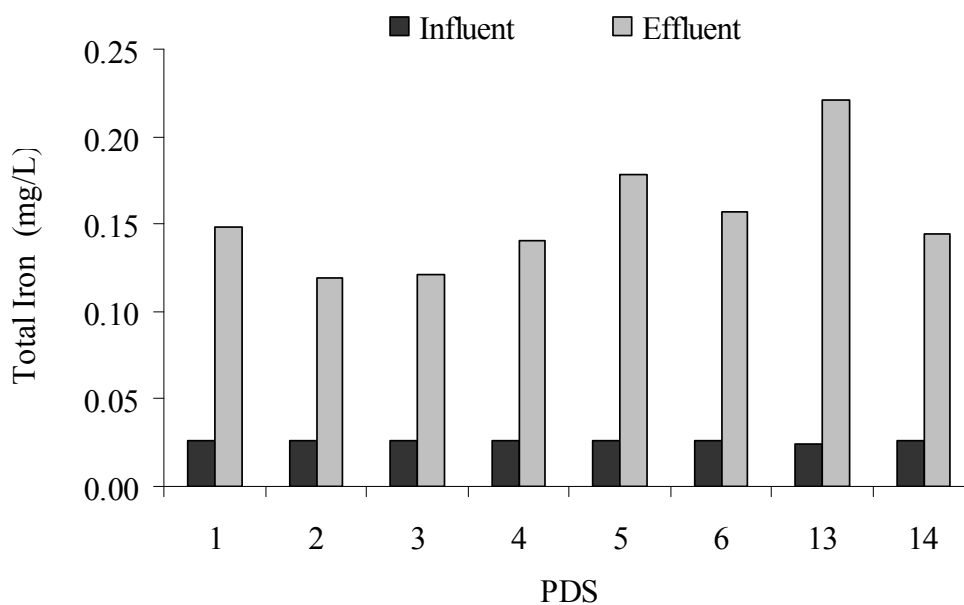


Figure 5-2 Comparison of PDS Influent and Corrosion Loop Effluent Iron Concentration

The significant differences in iron concentrations between influents and effluents were statistically compared using a one-tailed paired-data t-test. All determinations of p-values were

below 0.05, indicating there is sufficient evidence (at 95% confidence level) that effluent concentrations from corrosion loops were greater than PDS influent iron concentrations. This statistical analysis confirmed the release of iron corrosion products from unlined cast iron or galvanized steel pipe materials at 2-day HRT, regardless of which corrosion control strategy was employed (BOP, OP, or pH adjustment). Nonetheless, Medium and high doses of BOP appeared to mitigate total iron release slightly better than other inhibiting conditions, as shown in Figure 5-2.

#### 5.4.2 Statistical Modeling of Iron Release

##### *5.4.2.1 Initial Model Development*

Empirical models were developed to predict total and dissolved copper concentrations in corrosion loops effluent at the end of the hybrid PDSs. Monitored water quality parameters in the PDSs were evaluated using ANOVA procedures to identify statistically significant parameters at 95% confidence level. Dummy variables (0, 1) were utilized in the model to segregate data by individual corrosion control strategy. Non-linear least squares regressions were conducted on all data to estimate parameter exponents and coefficients. A linear correlation matrix of the entire data set revealed some parameters such as sodium and chloride or dissolved oxygen and temperature were confounded. These parameters were eliminated for model development and utilized some relationships developed in earlier work that related iron release to water quality in the absence of inhibitors (Taylor et al. 2005).

The initial form of the model is presented in Equation 5-1. This initial model did not demonstrate sensitivity to the effect of inhibitor dose on iron release, so further modifications were pursued.

$$\text{Iron} = (a * BOP + b * OP + c * pH_s) * Alk^f * Cl^g \quad \text{Equation 5-1}$$

Where *BOP* = *BOP inhibitor dummy variable (0,1)*  
*OP* = *OP inhibitor dummy variable (0,1)*  
*pH<sub>s</sub>* = *pH<sub>s</sub> inhibitor dummy variable (0,1)*  
*Alk* = *alkalinity, mg/L as CaCO<sub>3</sub>*  
*Cl* = *chloride, mg/L*  
*a* = *BOP dummy variable coefficient*  
*b* = *OP dummy variable coefficient*  
*c* = *pH<sub>s</sub> dummy variable coefficient*  
*f* = *Alkalinity exponent*  
*g* = *chloride exponent*

#### 5.4.2.2 Models Development Considering Phosphorous Speciation

The ratio of orthophosphorous (OP) to total phosphorous (TP) was added to the model to evaluate phosphorous speciation; however, OP/TP term was statistically insignificant, and was discarded. Only the total phosphorous term was retained. Sensitivity to phosphorous speciation was still accounted for in the model through the dummy variables, which separated data for the BOP inhibitor from the data for OP inhibitor.

#### 5.4.2.3 Models Development Considering Inhibitor Dose

Model sensitivity to inhibitor dose was achieved by including terms associated with the dose of each inhibitor (i.e. TP) with the dummy variable for that inhibitor. This provided each inhibitor with unique parameter estimation of exponents on the inhibitor dose. As in previous modeling attempts, statistically significant variables were identified and included in the model using ANOVA methods. Non-linear least squares regression provided parameters estimates.



This final modeling modification significantly improved the empirical model's accuracy, especially with respect to inhibitor dose. The general form of the model is depicted in Equation 5-2. Dummy variables shown are those associated with BOP, OP, and pH<sub>s</sub> inhibition.

$$Iron = \left( a * BOP * TP^m + b * OP * TP^n + c * pH_s \right) * Alk^f * Cl^g * Temp^h * Fe_{inf}^i \quad \text{Equation 5-2}$$

Where *TP* = total phosphorous, mg/L  
*SO<sub>4</sub>* = sulfate, mg/L  
*Temp* = Temperature, °C  
*Fe<sub>inf</sub>* = Influent iron, mg/L  
*Alk* = alkalinity, mg/L as CaCO<sub>3</sub>  
*k* = Temperature exponent  
*i* = influent iron exponent  
*m* = TP exponent associated with BOP dummy variable  
*n* = TP exponent associated with OP dummy variable  
 Remaining terms were defined previously in Equation 5-1.

Separate models for each corrosion control strategy were also developed for each inhibitor but were less robust than the combined model as the reduced data set was smaller and several singular models did not converge. Therefore, the approach to develop individual models for each control strategy was abandoned.

#### 5.4.2.4 Empirical Model for Total Iron Concentration

The empirical model developed for total iron concentrations is presented in Equation 5-3. The model suggests that total iron concentrations would decrease with increasing alkalinity, as evident by the negative exponent on the alkalinity term. Both chloride and influent iron have positive exponents, suggesting an increase in iron release with higher chloride or influent iron concentrations. As shown, each inhibitor had a contributing term that was multiplied by a dummy variable in order to adjust the predicted iron concentrations as a function of the inhibitor dose.

$$Total\ Fe = \left( 0.495BOP * TP^{-0.104} + 0.593OP * TP^{0.047} + 0.661pH_s \right) * Alk^{-0.457} * Cl^{0.345} * Fe_{inf}^{0.136}$$

Equation 5-3

The p-values of retained independent variables were: 0.2573 for TP(BOP), 0.5332 for TP(OP), 0.0001 for Alk, 0.0002 for Cl, and 0.0011 for  $Fe_{inf}$ . Total phosphorous terms were retained in the model despite their large p-values ( $>0.05$ ) to include sensitivity to inhibitor dose in the model. HRT was not varied (2 days) and was not used in the model. For the conditions of this work, pH had no significant impact on iron release as stabilization with respect to  $CaCO_3$  was achieved prior to discharge to the PDSs.

Equation 5-3 shows that the coefficient of dummy variables for BOP and OP were 0.495 and 0.593, and the TP exponents were -0.104 and 0.047, respectively. These differences indicate the different effects BOP and OP had on iron release for equivalent phosphorous doses.

Comparison of predicted and actual total iron concentrations is shown in Figure 5-3 for all phases. The straight diagonal line represents perfect agreement between predicted and actual values. The coefficient of determination ( $R^2$ ) was not robust at  $R^2=0.25$ . This value indicates the limited response of iron data to increases in inhibitor dose, which is confirmed in Figure 5-2, where iron release was noticeably higher than influent concentrations across all inhibitors and doses. The model tends to under-predict the higher iron concentrations, especially those exceeding the secondary iron standard of 0.3 mg/L.

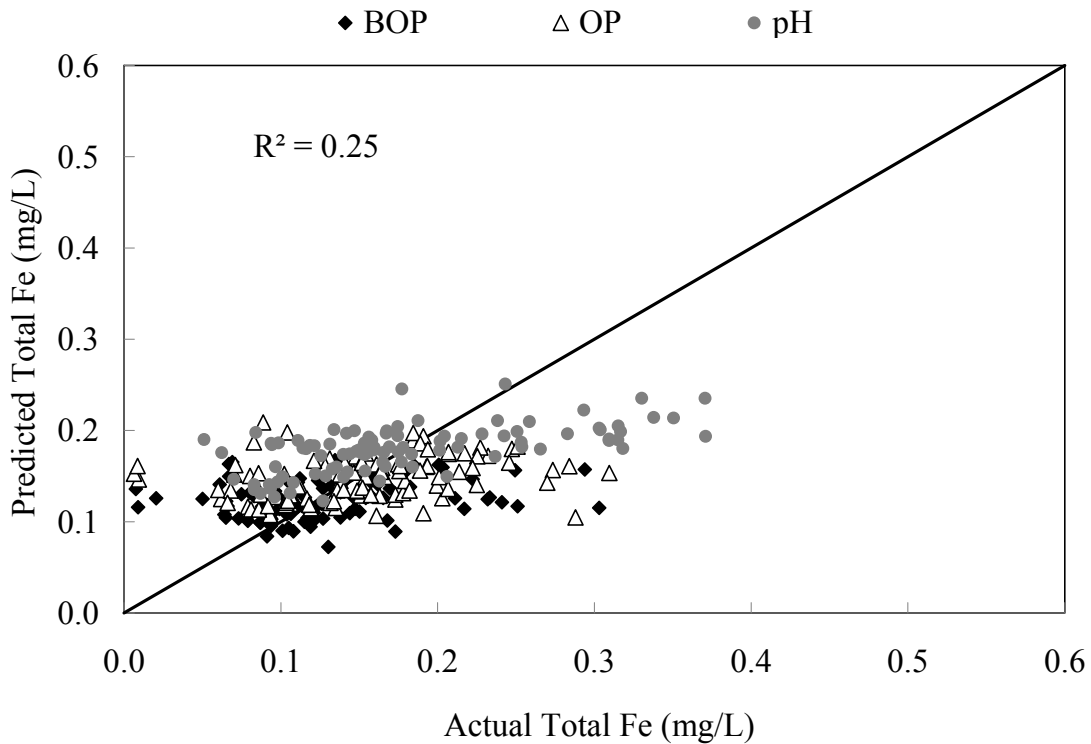


Figure 5-3 Model predicted versus actual total iron concentrations

As shown below in data summary (Table 5-3), particulate iron was the dominant form of iron in the effluent (about 90%). Also, considerations of adverse water quality effects addressed by secondary drinking water standards, namely color (15 color units) and iron (0.3 mg/L) (USEPA 2002), are related to the total iron concentrations. Therefore, it's more relevant to discuss the control and prediction of total iron release than considering dissolved iron. Collected dissolved iron measurements are more appropriate for thermodynamic equilibrium calculations, such as solubility of iron species.

### 5.4.3 Inhibitors Performance Comparison

Summary for the corrosion loop total and dissolved iron concentrations for PDSs treated with BOP, OP, and pH adjustments are presented in Table 5-3, Table 5-4, and Table 5-5, , respectively. Data is segregated by Phase and PDS. Shown are average, maximum, and minimum values observed of iron release. Data for all treatments shows that on average, the majority of the iron was present in the particulate form (overall, particulate iron was about 90% of total iron).

#### 5.4.3.1 Data Summary for BOP Inhibitor

Iron release data from PDS 1-PDS 3 that received the BOP inhibitor is shown in Table 5-3, and suggests that controlling total iron release improved with BOP doses higher than 0.5 mg P/L. Variation in total iron release between phases was limited under the BOP treatment.

Table 5-3 Iron release summary for BOP PDSs

Phase	PDS	Dose	Fe-Diss (mg/L)			Fe-Total (mg/L)		
			Avg	Max	Min	Avg	Max	Min
I	1	0.57	0.05	0.17	0.00	0.14	0.30	0.07
	2	1.08	0.03	0.13	0.00	0.10	0.15	0.06
	3	1.82	0.03	0.17	0.00	0.12	0.25	0.07
II	1	0.57	0.01	0.05	0.00	0.21	0.56	0.07
	2	1.00	0.01	0.02	0.00	0.15	0.25	0.07
	3	1.95	0.01	0.02	0.00	0.15	0.25	0.07
III	1	0.49	0.01	0.03	0.00	0.13	0.22	0.08
	2	0.90	0.01	0.03	0.00	0.11	0.13	0.07
	3	1.73	0.01	0.03	0.00	0.12	0.23	0.08
IV	1	0.68	0.00	0.01	0.00	0.12	0.18	0.01
	2	1.31	0.00	0.02	0.00	0.13	0.21	0.02
	3	2.66	0.01	0.04	0.00	0.09	0.13	0.01
All	1	0.58	0.02	0.17	0.00	0.15	0.56	0.01
	2	1.07	0.01	0.13	0.00	0.12	0.25	0.02
	3	2.03	0.02	0.17	0.00	0.12	0.25	0.01

#### 5.4.3.2 BOP Inhibitor Performance

The model is shown in Equation 5-4, and suggests that total iron release is influenced by alkalinity, chloride, influent iron in the raw water, and total phosphate through BOP dosing,

$$Total\ Fe = 0.495 \times TP^{-0.104} \times Alk^{-0.457} \times Cl^{0.345} \times Fe_{inf}^{0.136} \quad \text{Equation 5-4}$$

Exponents on terms in the model give an indication of the degree of influence each term has on total iron release. The addition of BOP inhibitor controlled the extent of phosphorus concentrations in PDSs, represented by the TP term. The model suggests that BOP addition decreased iron release due to the negative exponent on the TP term. However, the magnitude of the exponent was the smallest in the model, indicating BOP had the least influence on total iron release. This is supported by average iron release data (Table 5-3), which showed little reduction of iron release with increasing dose beyond 1.0 mg P/L.

Figure 5-4 shows separate bars for the average predicted and average actual concentrations of total iron release in each of the BOP PDSs for each phase. Whiskers define the maximum and minimum measured and predicted concentrations. The noticeably high maximum measurement in PDS 1 during Phase II, as shown in the Figure 1-4 is due to a single sample that registered 0.56 mg/L, which was the highest in all samples of the study. This aberration is likely due to iron particles that may have dislodged from the inner pipe surface and was collected in the sample.

Figure 5-4 shows that the model does reasonably well at predicting iron release for the BOP PDSs. The medium BOP dose (1.0 mg P/L) had the best control of total iron release in Phases I and III. Medium and high doses were equally better than the low dose in Phase II,

while the high dose in Phase IV resulted in the least total iron release. Figure 5-4 suggests that decreased total iron release was not always related to increased BOP dose.

The remaining terms in the model (alkalinity, chloride, and influent iron) are related to the water quality of the source water blend. Phase I and III were mostly groundwater, which was characterized by high alkalinity. Phase II utilized a blend with a greater surface water composition than was used in other phases, resulting in a reduced alkalinity (Table 5-2). The increase in iron concentration at reduced alkalinity is consistent with the inclusion of alkalinity in the empirical model with a negative exponent on that variable. Actual total iron release shown in Figure 5-4 supports this statement, where Phase II concentrations were higher than those from Phases I or III.

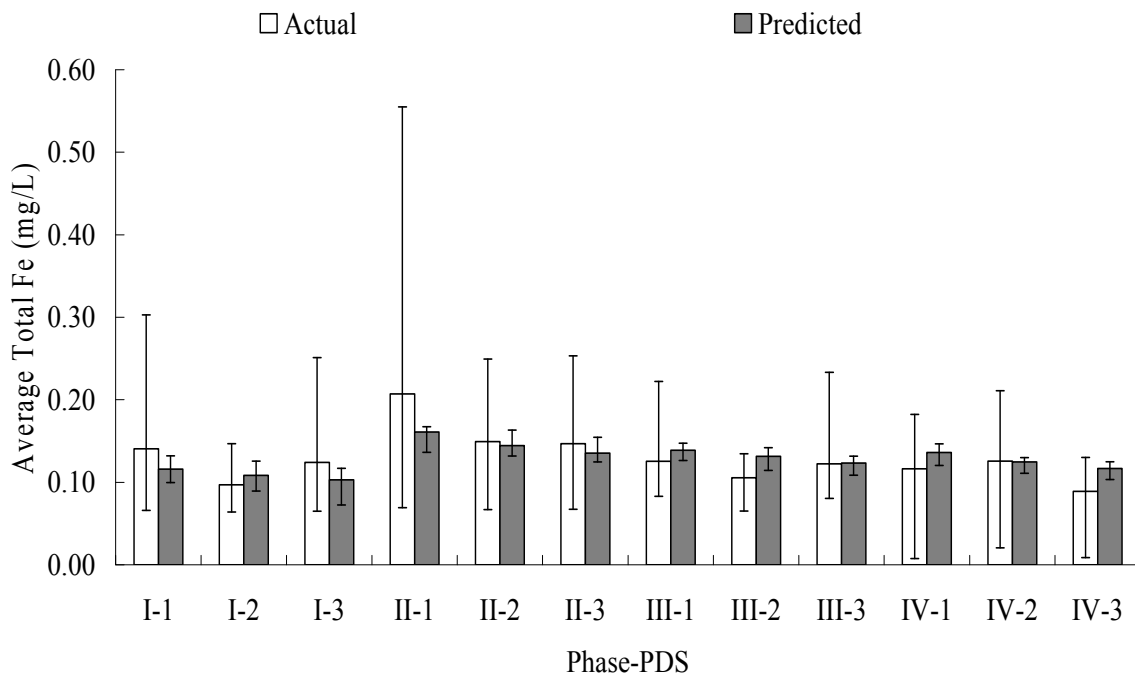


Figure 5-4 Total iron release model summary for BOP PDSs by phase

The model is also sensitive to chloride and influent iron. Chloride has the largest positive exponent in the model, suggesting that an increase in chloride results in increasing total iron release. Phase I had the lowest average chloride concentration among all phases, which would result in lower iron release for that phase. This is supported by the low levels of actual iron release in Phase I as shown in Figure 5-4. Influence of influent iron term is less pronounced than chloride because of its smaller exponent. Also, influent iron concentrations were consistently low, around 0.03 mg/L, so the model is not as sensitive to the influent iron term.

#### 5.4.3.3 Data Summary for OP Inhibitor

For PDSs treated with OP inhibitor, Table 5-4 shows that the lowest overall iron release appeared in Phase I, which corresponded to a water blend enriched in groundwater resulting in the highest alkalinity concentrations. Increasing the OP inhibitor dose showed no improvement in iron release.

Table 5-4 Iron release summary for OP PDSs

Phase	PDS	Dose	Dissolved Fe (mg/L)			Total Fe (mg/L)		
			Avg	Max	Min	Avg	Max	Min
I	4	0.49	0.03	0.11	0.00	0.12	0.20	0.06
	5	1.04	0.03	0.16	0.00	0.14	0.19	0.10
	6	1.84	0.03	0.13	0.00	0.11	0.29	0.06
II	4	0.55	0.00	0.01	0.00	0.16	0.22	0.08
	5	0.90	0.01	0.06	0.00	0.21	0.33	0.10
	6	1.91	0.01	0.03	0.00	0.17	0.24	0.09
III	4	0.54	0.01	0.03	0.00	0.14	0.21	0.10
	5	0.99	0.01	0.03	0.00	0.23	0.31	0.15
	6	1.87	0.01	0.03	0.00	0.14	0.18	0.08
IV	4	0.47	0.00	0.00	0.00	0.13	0.20	0.01
	5	0.82	0.00	0.01	0.00	0.13	0.20	0.01
	6	1.69	0.00	0.01	0.00	0.20	0.51	0.01
All	4	0.51	0.01	0.11	0.00	0.14	0.22	0.01
	5	0.94	0.01	0.16	0.00	0.18	0.33	0.01
	6	1.83	0.01	0.13	0.00	0.16	0.51	0.01

#### 5.4.3.4 OP Inhibitor Performance

The form of the developed model applicable to OP inhibitor is shown in Equation 5-5. The differences between model forms for BOP and OP are in the model coefficient and the exponent on the total phosphorus term. The remaining water quality parameters have the same impact on iron release with both phosphorus inhibitors, because these parameters are related to the water blend, which was consistent across all PDSs in any given Phase.

The model suggests that OP inhibitor application would contribute to iron release by the positive exponent on the total phosphorus term. However, the low exponent on the total phosphorus term makes the model less sensitive to total phosphorus for the OP PDSs. The data agrees closely with this statement, as increasing the dose of OP inhibitor did not offer improved iron control (Table 5-4).

$$Total\ Fe = 0.593 \times TP^{0.047} \times Alk^{-0.457} \times Cl^{0.345} \times Fe_{inf}^{0.136} \quad \text{Equation 5-5}$$

Figure 5-5 shows the average iron release in each of the OP PDSs for each phase compared to the predicted release. The model does reasonably well at predicting iron concentrations for the OP PDSs. Figure 5-5 clearly shows that increasing the dose did not offer improved control of iron release.

The negative exponent on the alkalinity term suggests reduction of iron release by increasing alkalinity, which is related to the source water blend. Figure 5-5 confirms the impact of alkalinity, where Phase I data had the lowest iron release and Phase II had the highest. The model is sensitive to the alkalinity of the blend due to the large magnitudes of exponent and actual concentrations.



As with the BOP form of iron model, the large positive exponent on the chloride term suggests a direct relation to iron release. Phase I had the lowest average chloride concentration, which is another explanation for the low levels of iron observed in Phase I in Figure 5-5. Although influent iron is a significant term in the developed model, its small exponent and consistent low concentrations limited its impact on predicted iron release.

Figure 5-5 shows a wide spread between the maximum and minimum iron concentrations in PDS 6 during Phase IV. This is the result of a single measurement of 0.51 mg/L in the middle of the Phase, and was not related to changes in water quality or operational practices.

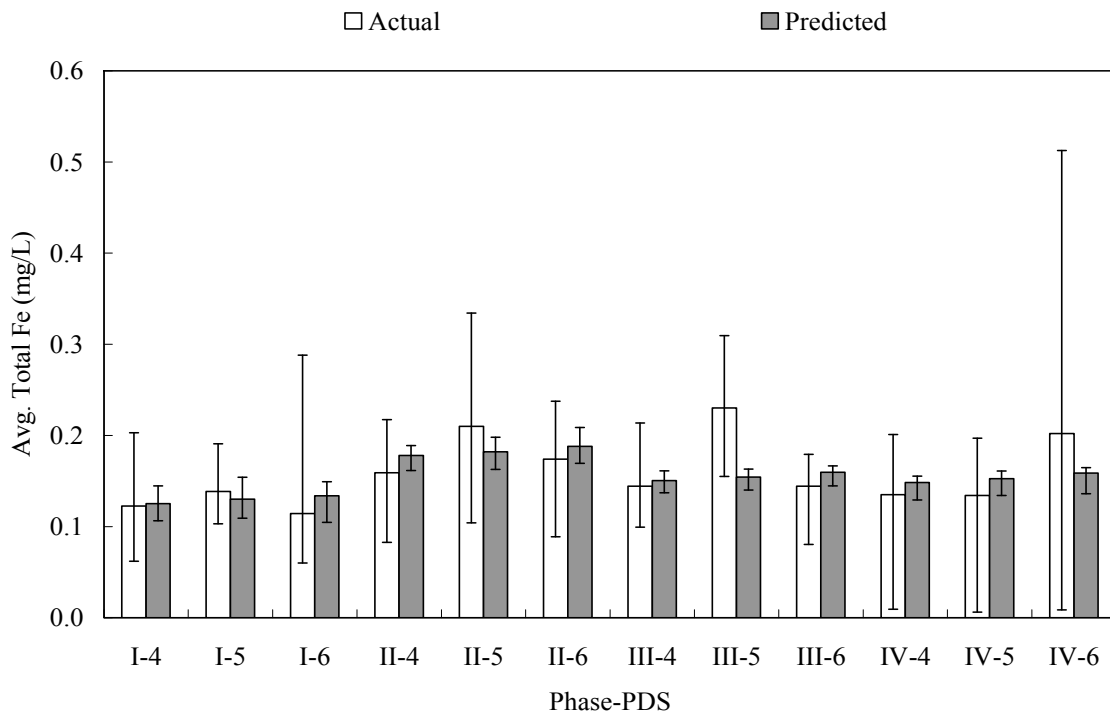


Figure 5-5 Total iron release model summary for OP PDSs by phase

#### 5.4.3.5 Data Summary for pH Control

Table 5-5 shows that pH<sub>s</sub> PDS (PDS13) consistently experienced higher iron release than the pH<sub>s</sub>+0.3 PDS (PDS 14). The lowest iron release appeared in Phase I, which had the highest alkalinity. Phase II had the highest iron release and the lowest alkalinity.

Table 5-5 Iron release summary for pH control PDSs

Phase	PDS	Dissolved Fe (mg/L)			Total Fe (mg/L)		
		Avg	Max	Min	Avg	Max	Min
I	13	0.03	0.11	0.00	0.15	0.20	0.10
	14	0.04	0.18	0.00	0.11	0.21	0.07
II	13	0.02	0.12	0.00	0.28	0.37	0.17
	14	0.03	0.13	0.00	0.19	0.33	0.12
III	13	0.01	0.04	0.00	0.27	0.37	0.16
	14	0.01	0.04	0.00	0.14	0.18	0.09
IV	13	0.00	0.00	0.00	0.19	0.32	0.05
	14	0.00	0.00	0.00	0.14	0.24	0.06
All	13	0.02	0.12	0.00	0.22	0.37	0.05
	14	0.02	0.18	0.00	0.14	0.33	0.06

#### 5.4.3.6 pH Control Performance

The form of the total iron model for the pH control PDSs is shown in Equation 5-6, where all terms were previously defined. The effect of increasing the pH to pH<sub>s</sub>+0.3 is seen in the model by an increase in alkalinity. Increasing pH, and therefore alkalinity, helps in reducing iron release as shown by the negative exponent on the alkalinity term.

$$Total\ Fe = 0.661 \times Alk^{-0.457} \times Cl^{0.345} \times Fe_{inf}^{0.136} \quad \text{Equation 5-6}$$

Figure 5-6 shows the average iron release in the pH control PDSs for each phase compared to the predicted iron release. The maximum and minimum error bars are also shown. The wide spread between maximum and minimum values for PDS 13 confirms the difficulty of controlling iron release at pH<sub>s</sub> (average of 7.7). The model does reasonably well at predicting

iron release for the pH control PDSs. The figure shows that increasing pH consistently offered a reduction in iron release for both predicted and actual concentrations.

Alkalinity depends on pH increase in PDS14 and on groundwater ratio in the blend. Phases I and III were mostly groundwater, which is characterized by high alkalinity. This contributed to the lowest iron release in Phase I, and the highest release in Phase II, as seen in Figure 5-6 for both the observed and predicted release.

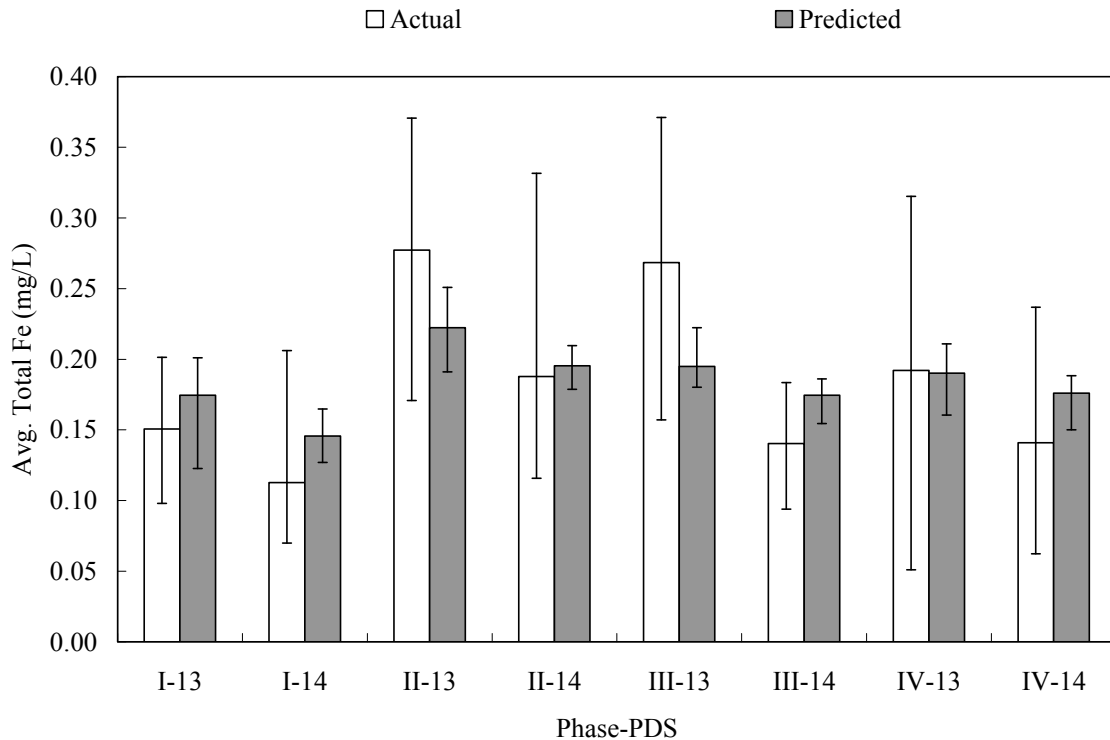


Figure 5-6 Total iron release model summary for pH control PDSs by phase

The positive exponent on the chloride term suggests an increase in chloride would increase iron release. Along with the highest alkalinity, the Phase I blend had the lowest average chloride concentration, offering another suggestion for why Phase I iron release was lower than the other phases. Chloride was much higher in the  $pH_s$  PDSs than the  $pH_s+0.3$  PDSs due to the

maintenance of pH<sub>s</sub> with hydrochloric acid (HCl). The higher chloride levels would contribute to higher iron release in the pH<sub>s</sub> PDS, as suggested by the model and shown in Figure 5-6. Influent iron was relatively constant in the pH control PDSs in all phases. Influent iron concentrations were consistently low, around 0.03 mg/L, so the model was not as sensitive to this term. It should be noted that addition of bicarbonate and hydroxide salts for increasing alkalinity increases the TDS, usually with sodium, in the system. In a previous study (Taylor et al. 2005), the increase in sodium also meant an increase in iron release.

#### *5.4.3.7 Performance Summary*

Evaluation of inhibitors performance so far indicated that control of iron was directly affected by water quality (alkalinity content and pH level). This was evident in empirical modeling, where the exponent on alkalinity term had the largest magnitude. And the coefficient of the pH dummy variable was larger than those of the phosphate-based inhibitors (BOP: 0.495, OP: 0.593, pH: 0.661). This suggests that there was no clear advantage to phosphate inhibitors dosing over elevated pH in PDS14. The data shows that PDS13, maintained at pH<sub>s</sub>, experienced the highest iron release among the examined control strategies

A statistical comparison (one-tailed, paired data t-test for equality of means) was conducted to determine any statistical differences between the elevated pH control (PDS14) and the phosphate inhibitors, as shown in Table 5-6. Several data entries are marked in italic font to indicate the occurrence of an average concentration in a PDS that exceeded the concentration in PDS14. The analysis shows that BOP at medium and high doses (PDS 2 and PDS 3) reduced the composite average iron concentrations, relative to the control strategy of pH elevation. It is

important to note that pH elevation may produce undesirable conditions through excessive deposition of calcium carbonate scale.

Table 5-6 Comparison of phosphate inhibitors to elevated pH control for total iron

Treatment Dose	PDS 14 pH pHs+0.3	PDS 01 BOP Low	PDS 02 BOP Med	PDS 03 BOP High	PDS 04 OP Low	PDS 05 OP Med	PDS 06 OP High	PDS 13 pH pHs
Phase I								
Average	0.113	0.141	0.097	0.124	0.123	0.138	0.114	0.151
Std Dev	0.039	0.067	0.022	0.048	0.042	0.026	0.059	0.031
Count	14	14	14	14	14	14	14	14
Significant difference		No	No	No	No	Yes	No	Yes
p-value		0.103	0.076	0.211	0.205	0.014	0.460	0.008
Phase II								
Average	0.188	0.207	0.149	0.147	0.159	0.210	0.174	0.277
Std Dev	0.068	0.117	0.050	0.053	0.037	0.057	0.040	0.065
Count	13	13	13	13	13	13	13	13
Significant difference		No	No	Yes	No	No	No	Yes
p-value		0.281	0.051	0.039	0.086	0.205	0.268	0.003
Phase III								
Average	0.140	0.125	0.105	0.123	0.144	0.230	0.144	0.268
Std Dev	0.026	0.033	0.019	0.040	0.032	0.043	0.026	0.058
Count	13	13	13	13	13	13	13	13
Significant difference		No	Yes	No	No	Yes	No	Yes
p-value		0.140	<0.001	0.066	0.366	<0.001	0.227	<0.001
Phase IV								
Average	0.141	0.117	0.126	0.089	0.135	0.134	0.202	0.192
Std Dev	0.047	0.053	0.054	0.039	0.057	0.057	0.126	0.087
Count	12	12	12	12	12	12	12	12
Significant difference		Yes	No	Yes	No	No	No	Yes
p-value		0.014	0.096	<0.001	0.294	0.250	0.060	0.006
Composite								
Average	0.145	0.148	0.119	0.121	0.140	0.178	0.157	0.221
Std Dev	0.054	0.081	0.043	0.049	0.044	0.063	0.077	0.081
Count	52	52	52	52	52	52	52	52
Significant difference		No	Yes	Yes	No	Yes	No	Yes
p-value		0.390	<0.001	0.002	0.248	<0.001	0.148	<0.001

#### 5.4.4 Seasonal Impact

The impact of temperature associated with seasonal variation on iron release is illustrated in Table 5-7. Phases I and III had similar water quality since they shared the same source water blend. Also, inhibitors dosing was kept constant across all phases. Six months separate Phases I and III, where Phase I coincided with the winter months, while Phase III was in the summer time. Therefore, the differences in iron release between Phase I and Phase III was primarily related to temperature. Averaged total iron concentrations in Phases I and III for each control strategy are shown in Table 5-7.

Table 5-7 Comparison of averaged iron release and temperature in Phases I and III

Inhibitor	Phase	Avg. Iron Release (mg/L)	Avg. Temperature (°C)
BOP	I	0.12	21.2
	III	0.12	25.3
OP	I	0.13	21.0
	III	0.17	25.4
pH <sub>s</sub>	I	0.15	21.2
	III	0.27	25.3
pH <sub>s</sub> +0.3	I	0.11	21.5
	III	0.14	25.4

For the BOP inhibitor treatment, the averaged total iron release during the warmer months in Phase III was the same as the release in Phase I, as shown in Table 5-7. This suggests that BOP inhibition was able to pacify the impact of seasonal variation on iron release. For OP inhibitor and elevated pH (pH<sub>s</sub>+0.3), warmer conditions in Phase III resulted in slightly higher total iron. Table 5-7 shows that pH<sub>s</sub> treatment was the most sensitive to seasonal variations, with noticeably higher iron release during Phase III.

## 5.5 Conclusion

The impact of phosphate-based corrosion inhibitors and pH adjustments on iron release from hybrid pilot distribution system (PDS) was monitored for a 12-month period. BOP and OP inhibitors were applied at three dose levels to separate PDSs. A pair of PDSs were maintained at two pH levels, respectively ( $\text{pH}_s$  and elevated pH). Source water blends were adjusted every phase to account for effects of water quality variation on iron release in the presence of inhibitors.

Iron was released from PDSs of all treatment strategies (BOP, OP, and pH control), and during all phases. The dominant form of iron in the effluent was particulate (90%). On average, medium and high doses of BOP achieved the least total iron release (around 0.12 mg/L), followed closely by elevated pH at  $\text{pH}_s+0.3$ . The OP inhibitor was not able to control iron release better than elevated pH. Iron concentrations were generally highest under the  $\text{pH}_s$  treatment, almost doubling the average release of BOP treatment (0.22 mg/L).

Iron release was variable between phases for all the control strategies. Water quality variation, primarily alkalinity content associated with changing water blend, played a major role in iron release. Water with higher alkalinity content and/or low chloride levels resulted in less iron concentration. Empirical modeling confirmed the pivotal role of source water quality, where alkalinity had the largest influence on model prediction of iron, followed by chloride.

Temperature variations had a direct impact on iron release. However, BOP inhibitor was the least susceptible treatment to seasonal changes with almost no change in averaged total release.

## 5.6 Acknowledgements

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## 6 COPPER RELEASE MITIGATION BY BLENDED ORTHOPHOSPHATE INHIBITOR AND pH CONTROL IN CHANGING WATER QUALITY ENVIRONMENT

### 6.1 Abstract

Monitoring copper release in a changing water quality environment that consisted of various mixtures of treated groundwater, surface water, and desalinated water showed that dissolved copper was the dominant form in the effluent, at about 88%. Blended orthophosphate (BOP) inhibitor doses of 0.5 to 2.0 mg/L proved beneficial in controlling copper concentrations to an average of below 0.5 mg/L. Control of copper release improved with increasing BOP dose, despite changes in alkalinity. Elevation of pH by 0.3 unit beyond  $pH_s$  (between 7.9 and 8.1) resulted in noticeable decrease in copper concentrations of about 30%, but was more sensitive to higher alkalinity (146 to 151 mg/L as  $CaCO_3$ ) than BOP treatment. Developed empirical models confirmed the importance of BOP inhibitor dose, pH increase, and alkalinity content on copper release. Statistical comparison of the corrosion control strategies proved the advantage of BOP inhibitor, at all doses, over pH elevation in controlling copper release.

## 6.2 Introduction and Background

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. In order to meet drinking water demands, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use. To seek understanding of the issues involved when multiple-source waters are blended, TBW and University of Central Florida (UCF) conducted research regarding the effect of variable finished water quality on distribution system water quality. The capacities of corrosion inhibitors to control these effects, including metal release, were investigated. This study addresses the control of copper release in distribution system by using the corrosion control strategies: blend of ortho/polyphosphate (BOP), and pH adjustments in a changing water quality environment. These strategies are evaluated based on actual observations and empirical models developed to predict copper concentrations, at variant inhibitor dose and water quality conditions.

The EPA's "Lead and Copper Rule" established regulatory action levels for copper at a concentration of 1.3 ppm (USEPA 1991). Since then, research efforts have examined the impact of using phosphate-based corrosion inhibitors on meeting the target level.

Copper release can be controlled by raising pH. A slight pH increase (in 7.0-8.0 range) showed significant reduction in copper release (Edwards et al. 1996), and CO<sub>2</sub> stripping was the recommended method for raising the pH without raising alkalinity, because high concentrations of bicarbonate and carbonate ions can significantly enhance copper release through aqueous complexation (i.e. CuHCO<sub>3</sub><sup>+</sup>, CuCO<sub>3</sub>, Cu(Cu<sub>3</sub>)<sub>2</sub><sup>2-</sup>), especially below pH 8.5 (Edwards et al. 1994; Edwards et al. 1996). On a full-scale demonstration program to control copper corrosion

Duranceau and colleagues (1997) found that addition of phosphate-based inhibitors (blended orthophosphate, zinc orthophosphate, and phosphoric acid) and pH/alkalinity adjustments effectively controlled copper corrosion. However, those inhibitors seemed less effective against pitting corrosion than pH/alkalinity adjustments. pH adjustment to a target of 8.0 provided less variability in copper levels at consumer taps than inhibitor additions (Duranceau 1997). Preventing copper release can be maximized by maintaining high pH and low alkalinity as possible within operational and quality constraints (Xiao et al. 2007). In practice, treating waters with high alkalinity to control copper release by raising pH may be problematic, because hardness in the water would limit the ability to raise the pH without precipitating calcium carbonate (American Water Works Association. and Letterman 1999). Therefore, the use of phosphate-based inhibitors as an alternative treatment was investigated.

Edwards and colleagues (2002; 2001) compared the benefits of orthophosphate vs. polyphosphate in controlling copper corrosion by-product release in aged copper pipes, at variable pH and alkalinity values. Polyphosphate seems to perform less favorably than orthophosphate at comparable concentrations of 1 mg/L as P, due to possible complexation of copper by polyphosphate, increasing soluble copper release. Similarly, Increasing orthophosphate residual to 3 mg/L as PO<sub>4</sub> resulted in a successful decrease of copper level in aged plumbing systems to below the action level of 1.3 mg/L; 90th percentile copper level were reduced to 1.04 mg/L (Schock and Fox 2001)

In stagnant copper pipes, orthophosphate reduced soluble copper concentrations but had little effect on particulate copper, while dosing with polyphosphate resulted in high levels of particulate copper, probably due to formation of copper-phosphate solid (McNeill and Edwards 2004). In another study, copper release was noticeably reduced equally by orthophosphate and

polyphosphate dosing. Yet, polyphosphate resulted in higher soluble copper concentrations after stagnation, which is attributed to the complexation of copper by polyphosphate (Edwards et al. 2001).

Two inorganic phosphates,  $\text{Na}_2\text{PO}_4$  and  $\text{Na}_5\text{P}_3\text{O}_{10}$ , were tested for controlling copper corrosion in aqueous media (Souissi and Triki 2007). Both phosphate inhibitors reduced copper mass loss compared to no inhibitor addition in corrosive conditions.

Dartmann et. al.(2004) used copper loops to study the effect of orthophosphate inhibitor on drinking water while varying pH. Without orthophosphate, high pH water showed a decrease in copper concentration. When orthophosphate is dosed, copper concentrations decreased further in the higher pH water, while the same dose increased copper concentration in lower pH water. Conversely, Dodrill and Edwards (1995) found in a survey of utilities that phosphate inhibitors mitigated copper release well at pH below 7.8, even with high alkalinity. However, at pH above 7.8, inhibitors had variable and adverse effects on copper release.

Two suggested mechanisms for influence of orthophosphate on copper corrosion(Dartmann et al. 2004): (1) Orthophosphate reduced  $\text{O}_2$  consumption by the copper, resulting in less copper being oxidized and going into solution. (2) Conversely, the addition of orthophosphate hindered copper precipitation and the formation of a surface layer. Orthophosphate can decrease or increase copper concentration depending on which mechanisms is more dominant, which could be influenced by pH.

Previous research efforts on the same pilot plant used in this study examined copper release in distribution systems with changing water quality, but without inhibitors addition. Results showed that copper release was affected mainly by alkalinity and pH (Taylor 2005). Sulfate, silica, and temperature were also significant factors.

## 6.3 Material and Methods

### 6.3.1 Pilot Plant Design

A research facility was constructed for investigation of distribution system water quality at the Cypress Creek Water Treatment Facility near Tampa Bay, FL. The facility contains 14 identical pilot distribution systems (PDS) that receive the same blended water and consist of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series (Figure 6-1). The PDSs were constructed of aged pipes that were obtained from existing utility distribution systems to represent the pipe materials in local distribution system. Effluent from each PDS feeds a copper loop that mimics in-house plumbing system, which includes copper pipe material and plumbing fixtures with varying lead content. PDSs receive blended water and inhibitors for 12-month duration divided into four consecutive phases (each phase is approximately three months). Inhibitor doses to PDSs are kept constant for the 12-month duration, however, blended water is varied every phase.



Figure 6-1 Copper Loops

### 6.3.2 Inhibitors

Every three PDSs were dosed with one inhibitor at varying concentrations; so PDSs 01, 02 and 03 were fed with the BOP (blended orthophosphate) inhibitor at doses 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L as total phosphorous (TP), respectively. The BOP inhibitor used is a commercial product that is a blend of orthophosphate and polyphosphate. PDS13 received blended water at pH equal to  $pH_s$ , while PDS14 received blended water at elevated pH of approximately  $pH_s+0.3$ . These inhibition strategies were kept constant throughout all four phases of operation.

### 6.3.3 Source and Blend Waters

Varying blends of three different process waters were used in this study, surface water (SW), groundwater (GW), and desalinated -reverser osmosis- water (RO). Blending ratio was changed every phase to achieve variability in water quality, as shown in Table 6-1. Phase I and Phase III had the same blend (WQ1) in order to study the seasonal temperature effects. The average water quality for source waters and the resulting blends are presented in Table 6-2

Table 6-1 Water Blend Ratios

Phase	Blend	% GW	% SW	% RO
I (Feb – May 2006)	WQ1	62	27	11
II (May - Aug 2006)	WQ2	27	62	11
III (Aug – Nov 2006)	WQ1	62	27	11
IV (Nov 2006 – Feb 2007)	WQ3	40	40	20

Table 6-2 Water Quality of Source and Blended Waters



Parameter	Units	GW	RO	SW	WQ1	WQ2	WQ3
pH		7.8	7.8	7.8	7.9	7.9	8.0
TDS	mg/L	355	285	433	365	388	414
HCO <sub>3</sub>	mg/L as CaCO <sub>3</sub>	211	70	81	163	109	154
Ca	mg/L as CaCO <sub>3</sub>	214	63	227	202	185	206
Mg	mg/L as CaCO <sub>3</sub>	28	6	33	29	28	23
Turbidity	NTU	0.25	0.07	0.26	0.3	0.19	0.21
Cl	mg/L	36	93	51	47	59	95
SO <sub>4</sub>	mg/L	29	2	191	72	112	74
DO	mg/L	7.3	8.2	8.7	8.7	8	8
NH <sub>2</sub> Cl	mg/L Cl <sub>2</sub>	5	5	5	5	6	6

#### 6.3.4 Sampling and Analysis

Weekly and biweekly samples were collected and analyzed in the field laboratory and at the UCF laboratories. Samples collected from influent, effluent, and corrosion lines for each PDS were analyzed for many physical and chemical parameters associated with water quality and metal release. Data collection was done for one year of operation to account for the effect of seasonal variations on water quality.

### 6.4 Results and Discussion

Examination of copper release data include measurements from PDSs exposed to BOP and pH adjustment control strategies. These are labeled PDS1, PDS2, and PDS3 for BOP treatment, and PDS13 and PDS14 for pH adjustment.

#### 6.4.1 Statistical Modeling of Copper Release

##### *6.4.1.1 Initial Model Development*

Empirical models were developed to predict total and dissolved copper concentrations in output of the hybrid PDSs (in corrosion loops effluent). Monitored water quality parameters in the PDSs were evaluated using ANOVA procedures to identify statistically significant

parameters. Estimations of these parameters were determined using non-linear least squares regression techniques, where independent variables that are not significant at 95% confidence level were eliminated from the model. Data from all 14 PDSs and all four phases were used in the regression.

Dummy variables were utilized in the model to segregate data by individual corrosion control strategy. The dummy variables are ones and zeros to indicate the presence or absence of any of the corrosion control strategies. Non-linear least squares regression were completed on the entire data set to estimate all parameters exponents and dummy variables coefficients. A linear correlation matrix of the entire data set revealed that several parameters were confounded, for example, sodium and chloride were confounded, and dissolved oxygen was confounded with temperature. Selected parameters were eliminated to remove confounding effects and overcome associated convergence issues in parameters estimation. So, sodium was eliminated in favor of chloride, dissolved oxygen was eliminated in favor of temperature, and sulfate were removed in favor of alkalinity. The ANOVA procedure was utilized to retain significant variables in the empirical model in a step-wise fashion (based on 95% confidence level). The remaining candidate independent variables that were considered were pH, alkalinity, and chloride. This initial model, however, did not demonstrate sensitivity to the effect of inhibitor dose on copper release. Therefore, further modifications were pursued.

#### *6.4.1.2 Consideration of Phosphorous Speciation*

In order to account for the difference in phosphorous speciation in BOP inhibitor, a term was added as the ratio of orthophosphorous (OP) to total phosphorous (TP). However, this model modification was not productive as the ratio (OP/TP) was found to be statistically insignificant, and thus only one term was retained for phosphorous (TP).

### 6.4.1.3 Consideration of Inhibitor Dose

Model sensitivity to inhibitor dose was achieved by including terms associated with the dose of the inhibitor (i.e. TP) with the dummy variable for that inhibitor. This provided unique parameter estimation of exponents on the inhibitor dose. As in previous modeling attempts, statistically significant variables were identified and included in the model using ANOVA methods. Non-linear least squares regression provided parameters estimates. This final modeling modification significantly improved the empirical model's accuracy, especially with respect to inhibitor dose. The general form of the model is depicted in Equation 6-1. Dummy variables shown are only those associated with inhibitors of interest in this paper, namely BOP, and pH control.

$$\text{Copper} = (a * BOP * TP^b + c * pH_s) * pH^d * Alk^f * Cl^g \quad \text{Equation 6-1}$$

Where *BOP* = BOP inhibitor dummy variable (0,1)  
*pH<sub>s</sub>* = pH control dummy variable (0,1)  
*TP* = total phosphorous, mg/L  
*pH* = -Log(H<sup>+</sup>)  
*Alk* = alkalinity, mg/L as CaCO<sub>3</sub>  
*Cl* = chloride, mg/L  
*a* = BOP dummy variable coefficient  
*c* = pH<sub>s</sub> dummy variable coefficient  
*d* = pH exponent  
*f* = Alkalinity exponent  
*g* = chloride exponent  
*b* = TP exponent associated with BOP dummy variable

Attempting to develop a separate model for each corrosion control strategy proved unproductive compared to one that incorporated all 14 PDSs.

### 6.4.1.4 Empirical Model for Total Copper Concentration

The empirical model developed for total copper concentrations is presented in Equation 6-2. The model includes dummy variables for inhibitors of interest in this paper, namely BOP and pH control. Other inhibitors used in the project are not shown for convenience, since their

dummy variables would have values of zero in the presence of BOP or pH treatments, and because they are not addressed in this discussion.

The model suggests that total copper concentrations will decrease with increasing pH, as evident by the negative exponent on the pH term. Both alkalinity and chloride have positive exponents, suggesting an increase in copper release with higher alkalinity and chloride concentrations. A term for total phosphorous (TP) is multiplied by the BOP dummy variable in order to adjust the predicted copper concentrations as a function of the BOP inhibitor dose.

$$Total\ Cu = (6.13BOP * TP^{-0.174} + 16.7pH_s) * pH^{-3.48} * Alk^{0.569} * Cl^{0.394} \quad \text{Equation 6-2}$$

The p-values of retained independent variables shown in Equation 5-3 are: 0.0337 for TP, < 0.0001 for pH, < 0.0001 for Alk, and < 0.0001 for Cl.

Comparison of total copper model predictions to actual total copper concentrations is shown in Figure 5-3 for all phases. The straight diagonal line represents perfect agreement between predicted and actual values. The coefficient of determination ( $R^2$ ) was acceptable at  $R^2=0.68$ . This value indicates the reasonable response of copper data to increases in BOP inhibitor dose or pH adjustments, and to variations of alkalinity or chloride. The model tends to under-predict higher copper concentrations, especially those above 2.0 mg/L.

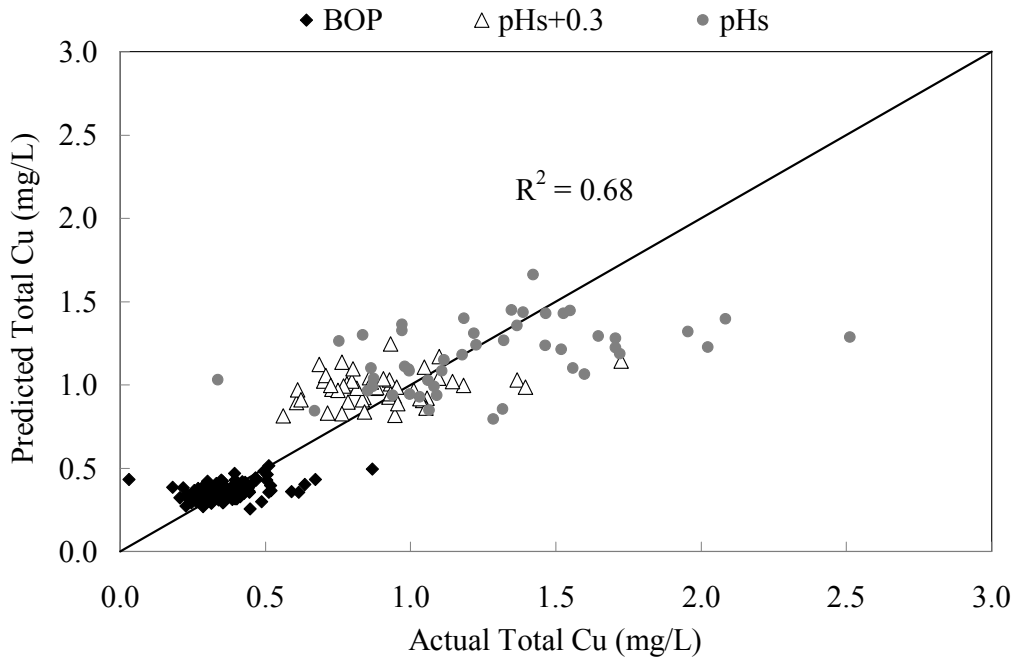


Figure 6-2 Model predicted versus actual total copper concentrations

#### 6.4.1.5 Empirical Model for Dissolved Copper Concentration

Another model for dissolved copper concentrations was also developed in the same manner as the total copper model. The model is presented in Equation 6-3, where all the terms were previously defined. Because the majority of copper is in the dissolved form (88%), both dissolved and total copper models are very similar.

$$Dissolved\ Cu = (0.302BOP * TP^{-0.140} + 0.831pH_s) * pH^{-2.48} * Alk^{0.713} * Cl^{0.421} \quad \text{Equation 6-3}$$

The model suggests that higher alkalinity and/or chloride levels would result in increased dissolved copper concentrations, as evident by the positive exponents on their terms. In contrast, pH elevation would reduce copper concentrations. The negative exponent on the model variable that quantifies the BOP inhibitor dose (TP) suggests a reduction in dissolved copper release with increasing inhibitor dose.

A comparison between the observed and predicted dissolved copper concentrations is presented in Figure 6-3. As with the total copper model, the dissolved copper model fits the data reasonably well, with an  $R^2$  of 0.61. The p-values of the retained variables in the model are: 0.1150 for TP, 0.0007 for pH, <0.0001 for Alk, and <0.0001 for Cl.

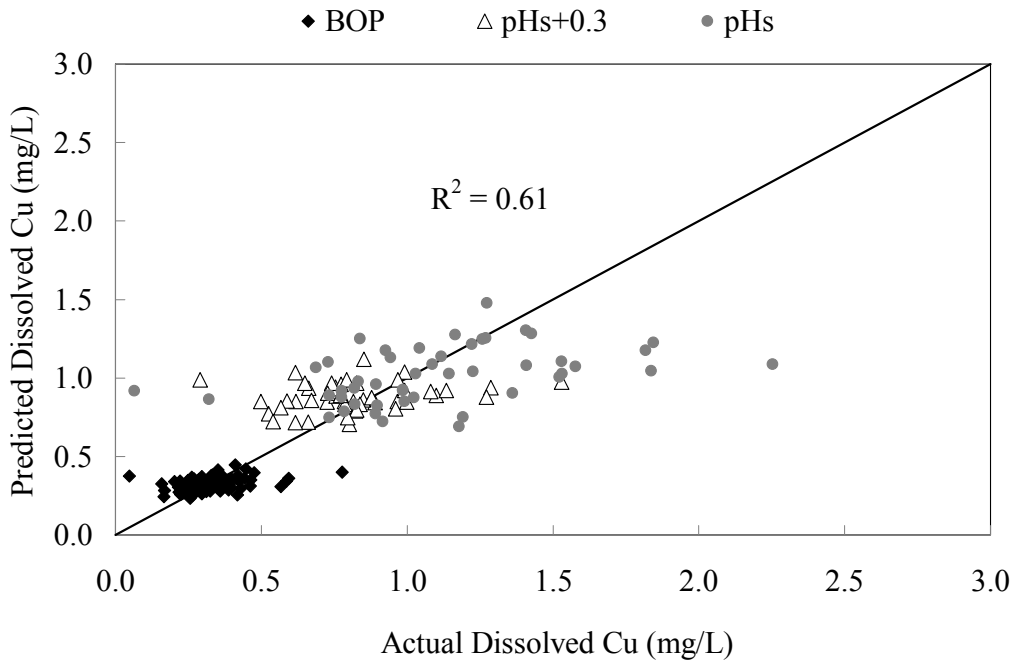


Figure 6-3 Model predicted versus actual dissolved copper concentrations

#### 6.4.2 Controlling Copper Release with BOP Inhibitor Addition

##### 6.4.2.1 Data Summary for BOP Inhibitor

Summary data for the corrosion loop total and dissolved copper concentrations, for PDSs treated with BOP inhibitor, is presented in Table 6-3. Data is segregated by Phase and by PDS, showing average, maximum, and minimum values observed of copper release for each PDS in every phase. As was mentioned earlier, the data shows that the majority of the copper is found in the dissolved form (about 88%). The data also suggests that increasing BOP inhibitor dose

improves the control of copper release. Water quality data for the independent variables in the empirical model, in addition to temperature data, is summarized in Table 6-4.

Table 6-3 Copper release summary for BOP PDSs

Phase	PDS	Dose	Dissolved Cu (mg/L)			Total Cu (mg/L)		
			Avg	Max	Min	Avg	Max	Min
I	1	0.57	0.36	0.46	0.05	0.40	0.52	0.03
	2	1.08	0.34	0.46	0.29	0.36	0.41	0.30
	3	1.82	0.33	0.43	0.22	0.37	0.62	0.23
II	1	0.57	0.35	0.57	0.16	0.43	0.59	0.18
	2	1.00	0.29	0.40	0.25	0.33	0.43	0.29
	3	1.95	0.24	0.32	0.17	0.27	0.33	0.21
III	1	0.49	0.38	0.51	0.26	0.43	0.57	0.30
	2	0.90	0.30	0.37	0.20	0.32	0.40	0.22
	3	1.73	0.26	0.33	0.22	0.29	0.35	0.23
IV	1	0.68	0.35	0.78	0.03	0.45	0.87	0.27
	2	1.31	0.31	0.59	0.20	0.37	0.67	0.25
	3	2.66	0.29	0.59	0.17	0.32	0.63	0.20
All	1	0.58	0.36	0.78	0.03	0.43	0.87	0.03
	2	1.07	0.31	0.59	0.20	0.34	0.67	0.22
	3	2.03	0.28	0.59	0.17	0.31	0.63	0.20

Table 6-4 Average influent water quality parameters for BOP PDSs

PDS	Phase	pH	Alkalinity (mg/L as CaCO <sub>3</sub> )	Chloride (mg/L)	Temperature (°C)
1	I	8.1	162	43.2	21.3
	II	7.9	106	67.5	26.1
	III	8.0	151	63.3	25.3
	IV	7.9	123	57.3	21.4
2	I	8.0	163	43.7	21.2
	II	7.9	106	67.7	26.3
	III	8.0	151	64.2	25.5
	IV	7.9	125	57.5	21.3
3	I	8.0	163	44.0	21.1
	II	7.8	106	68.6	26.0
	III	8.0	151	65.7	25.6
	IV	7.8	125	58.8	21.3

#### 6.4.2.2 Analysis of BOP Inhibitor Performance

When applying the developed total copper model to PDSs receiving BOP inhibitor, coefficients for dummy variables of other inhibitors have zero values, reflecting the absence of other inhibition strategies. The resulting model is shown in Equation 6-4. Total copper release is influenced by total phosphate, pH value, alkalinity, and chloride.

$$Total\ Cu = 6.13 * TP^{-0.174} * pH^{-3.48} * Alk^{0.569} * Cl^{0.394} \quad \text{Equation 6-4}$$

Exponents on terms in the model give an indication of the degree of influence each term has on total copper release. The addition of BOP inhibitor controls the extent of phosphorus concentrations in PDSs, represented by the TP term. The model suggests that BOP addition decreases copper release due to the negative exponent on the TP term. However, the magnitude of the exponent is the smallest in the model.

Figure 6-4 shows separate bars for the average predicted and average actual concentrations of total copper release in each of the BOP PDSs for each phase. Whiskers define the maximum and minimum measured and predicted concentrations. The model does reasonably well at predicting copper release for the BOP PDSs, where model predictions follow the decreasing trend of copper concentrations with increasing BOP dose. However, the model slightly over-predicts total copper release for the medium and high BOP doses (PDS 02 and 03) in Phases II, III, and IV. The low BOP dose (PDS 01) shows less discrepancy between actual and predicted concentrations. Both Table 6-3 and Figure 6-4 show the consistent benefit of increasing BOP dose in controlling total copper release, irrespective of phase changes.

The noticeably high maximums for all BOP PDSs during Phase IV, as shown in Figure 6-4, are attributed to isolated high copper measurements in the first week of Phase IV (after switching the water blend). These maximum values were almost twice the average in all of



Phase IV. For example, the first copper measurement from PDS 01 was 0.87 mg/L, while the overall average for PDS 01 was only 0.45 mg/L for Phase IV. It appears that switching to a blend with lower pH and lower alkalinity in Phase IV compared to Phase III (Table 6-4) caused a spike in copper concentrations for all the BOP PDSs. However, control of copper release was quickly restored by the second measurement of Phase IV.

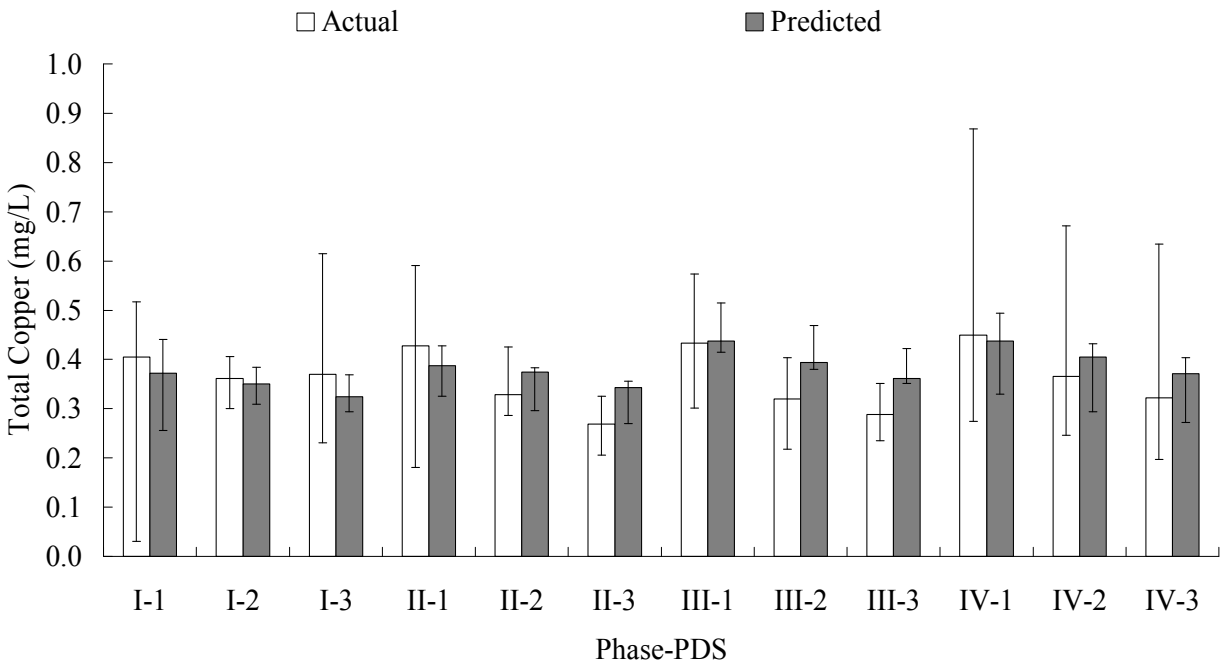


Figure 6-4 Total copper release model summary for BOP PDSs by phase

The remaining terms in the model (pH, alkalinity, and chloride) are related to the water quality of the source water blend. The groundwater component in water blend is the lowest in Phase II (27%) compared to the other Phases, as shown in Table 6-1. The larger groundwater component in Phases I, III, and IV, resulted in higher alkalinity levels compared to Phase II (Table 6-4). The average total copper concentrations for all BOP PDSs in Phases I through IV are 0.38 mg/L, 0.34 mg/L, 0.35 mg/L, and 0.38 mg/L, respectively. This increase in copper release in phases with higher alkalinity is consistent with the inclusion of alkalinity in the model

with a positive exponent on the variable. Figure 6-4 supports this conclusion, where copper release in Phase II is slightly lower than other Phases.

Total copper model is most sensitive to pH because its exponent has the greatest magnitude in the model, suggesting a noticeable change in copper release with a slight change in pH. However, average variation in pH between phases for all three BOP PDSs was limited to a pH range of 0.3. So even though the magnitude of the pH exponent is noticeably larger than other exponent in Equation 6-4, variations in actual pH values were minimal compared to alkalinity values, and therefore, the total impact of pH on actual copper release was less than that of alkalinity under BOP treatment for the four phases.

The model is also sensitive to chloride, where it has a positive exponent in the model but a smaller magnitude than exponents of both pH and alkalinity. This suggests that an increase in chloride results in an increase in total copper release, but not to the extent caused by an increase in alkalinity.

### 6.4.3 Controlling Copper Release with pH Control

#### *6.4.3.1 Data Summary for pH Control*

Summary data for the corrosion loop total and dissolved copper concentrations from the pH control PDSs is presented in Table 6-5. Similar to BOP copper data, dissolved copper constitutes the majority of copper release in the pH PDSs (88%). The data also suggests that increasing pH improves the control of copper release, since copper concentrations in the pH<sub>s</sub> PDS (PDS13) is significantly greater than the concentrations for the elevated pH treatment (PDS14). Water quality data for the independent variables in the empirical model for copper release is summarized in Table 6-6.

Table 6-5 Iron release summary for pH control PDSs

Phase	PDS	Dissolved Cu (mg/L)			Total Cu (mg/L)		
		Avg	Max	Min	Avg	Max	Min
I	13	0.95	1.41	0.69	1.04	1.52	0.75
	14	0.89	1.29	0.29	1.00	1.37	0.76
II	13	1.04	1.53	0.73	1.16	1.71	0.67
	14	0.73	1.24	0.13	0.82	1.34	0.21
III	13	1.32	1.84	0.84	1.48	2.08	0.97
	14	0.79	1.13	0.62	0.85	1.14	0.69
IV	13	1.14	2.25	0.06	1.41	2.51	0.34
	14	0.83	1.53	0.50	0.93	1.72	0.56
All	13	1.11	2.25	0.06	1.27	2.51	0.34
	14	0.81	1.53	0.13	0.90	1.72	0.21

Table 6-6 Average influent water quality parameters for pH PDSs

PDS	Phase	pH	Alkalinity (mg/L as CaCO <sub>3</sub> )	Chloride (mg/L)	Temperature (°C)
13	I	7.8	146	64.2	21.3
	II	7.9	92	82.8	26.4
	III	7.7	149	88.4	25.3
	IV	7.6	119	68.1	21.0
14	I	8.0	164	43.2	21.2
	II	7.9	106	65.1	26.5
	III	8.1	151	64.8	25.6
	IV	7.9	125	57.9	21.3

#### 6.4.3.2 Analysis of pH Control Performance

The form of the total copper model for the pH control PDSs is shown in Equation 6-5, reflecting the absence of other inhibition strategies. The negative exponent on pH in the model suggests that increasing pH is beneficial in controlling copper release. However, any elevation of pH between PDS13 and PDS14 is accompanied by an increase in alkalinity. The model suggests the increase in copper release with increasing alkalinity (positive exponent).

$$Total\ Cu = 16.7 * pH^{-3.48} * Alk^{0.569} * Cl^{0.394} \quad \text{Equation 6-5}$$

Figure 6-5 shows the average copper release in the pH control PDSs for each phase compared to the model prediction. The maximum and minimum error bars are also shown. The model does reasonably well at predicting iron release for the pH control PDSs. The figure confirms that elevating the pH in PDS14 consistently offers a reduction in copper release for both the observed data and the predictions by the model.

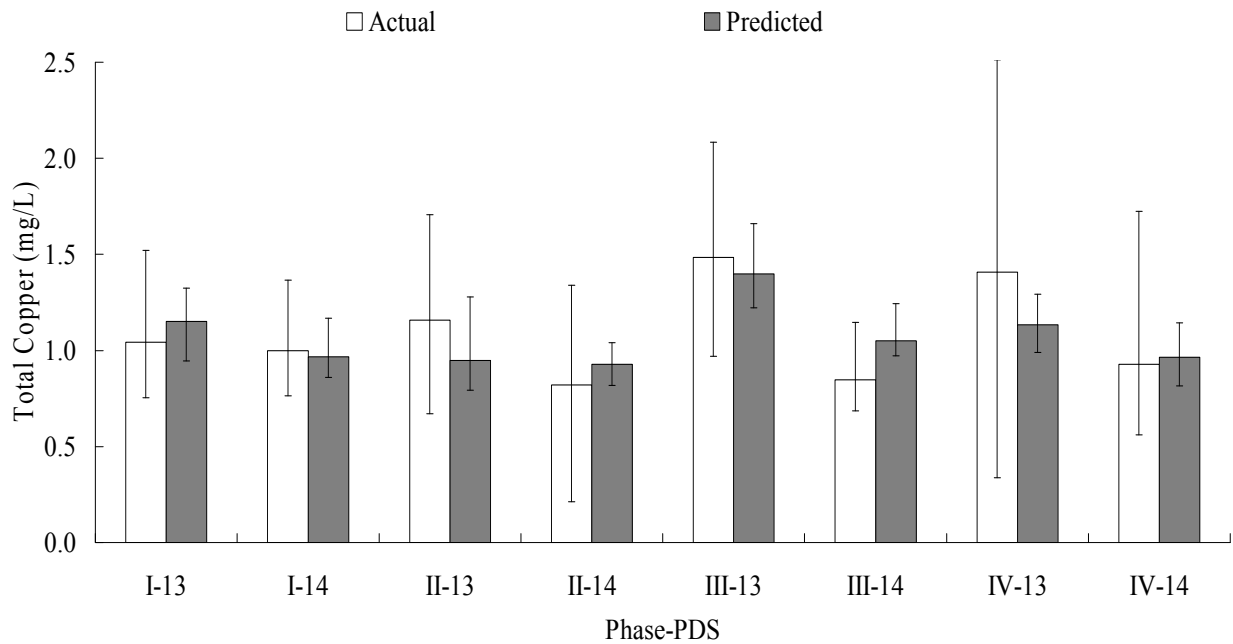


Figure 6-5 Total copper release model summary for pH control PDSs by phase

Alkalinity does depend on pH increase in PDS14, but mostly on groundwater ratio in the blend. For PDS14, the greater alkalinity was experienced in Phase I (Table 6-6), which coincides with the greater average copper concentrations (1.0 mg/L). Similarly, the minimum average copper release in PDS14 was observed in Phase II (0.82 mg/L), which had the lowest alkalinity level of all Phases. The model confirmed the negative impact of alkalinity on copper release by predicting higher copper concentrations in phases with larger groundwater component (Phases I and III), and lower concentrations in Phase II, as shown in Figure 6-5. For PDS13, the

maximum average concentration of copper was observed in Phase III, corresponding with a high alkalinity blend.

The effect of pH on copper release is clear when comparing PDS13 and PDS14 observations. The target pH for PDS13 was  $\text{pH}_s$ , while PDS14 was targeted at 0.3 unit above  $\text{pH}_s$ . The pH for both PDSs remained relatively stable across all phases. Actual data in Table 6-5 clearly shows that copper release is more sensitive to pH elevation than alkalinity changes, as seen by the consistently lower copper concentrations in PDS14 than PDS13. Elevation of pH in PDS14 proved beneficial in controlling copper below the action level of 1.3 mg/L on average in any phase. PDS13, however, exceeded the action level on average in two phases (Phases III and IV).

Equation 6-5 shows the direct impact of chloride on copper release, where higher chloride concentrations would lead to greater copper release. This is confirmed by observing the minimum average copper concentrations during Phase I, which had the lowest chloride concentrations (Table 6-6). PDS13 experienced higher chloride concentrations, with the associated adverse effect on copper release, due to the addition of hydrochloric acid (HCl) to maintain pH at  $\text{pH}_s$ .

#### 6.4.4 Performance Comparison

Performance evaluation of corrosion control strategies so far demonstrated the ability of BOP inhibitor and pH elevation to mitigate copper release. Elevation of the pH by 0.3 units was shown to significantly reduce copper concentrations (almost 30%) relative to operation at  $\text{pH}_s$ . Annual average corrosion loop concentrations for PDS13 and PDS14 were 1.27 and 0.90 mg Cu/L respectively. The advantage of increasing pH in copper release control is illustrated in Figure 6-6. The addition of BOP inhibitor consistently controlled copper release to below 1.0

mg/L, in spite of the dose or Phase of operation. Overall, the BOP inhibitor reduced copper release by about 70%, compared to the release from PDS13. BOP was more effective in mitigating copper release with increasing inhibitor dose, as shown in Figure 6-7.

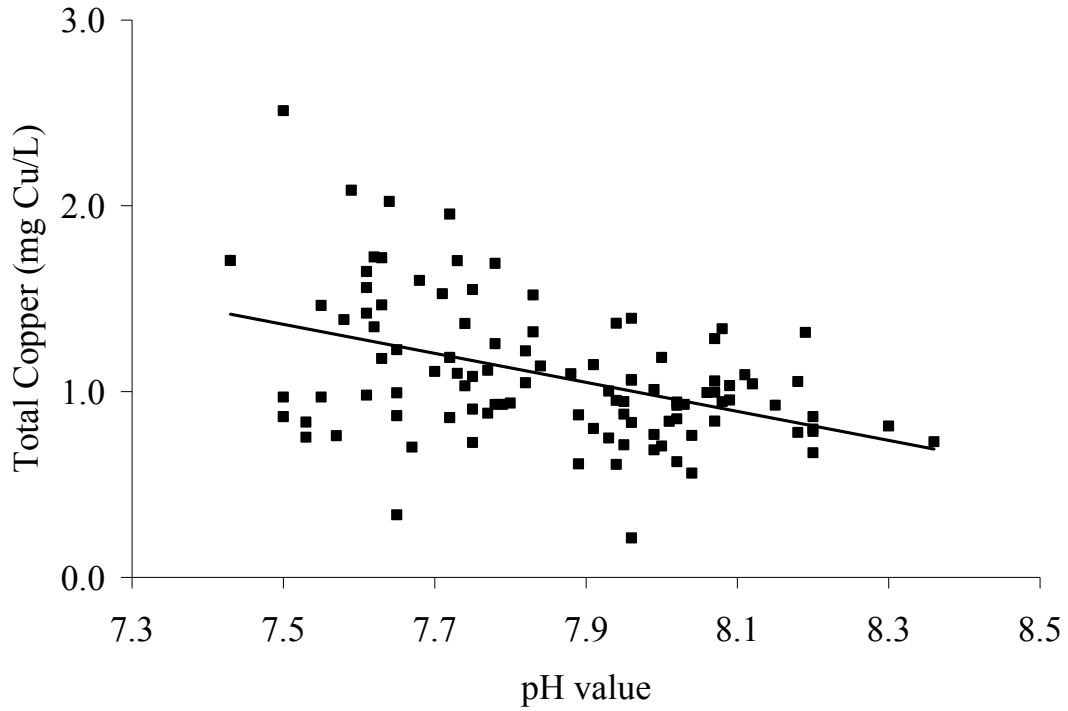


Figure 6-6 Observations of actual copper release in pH control PDSs (PDS13 and PDS14) from all phases.

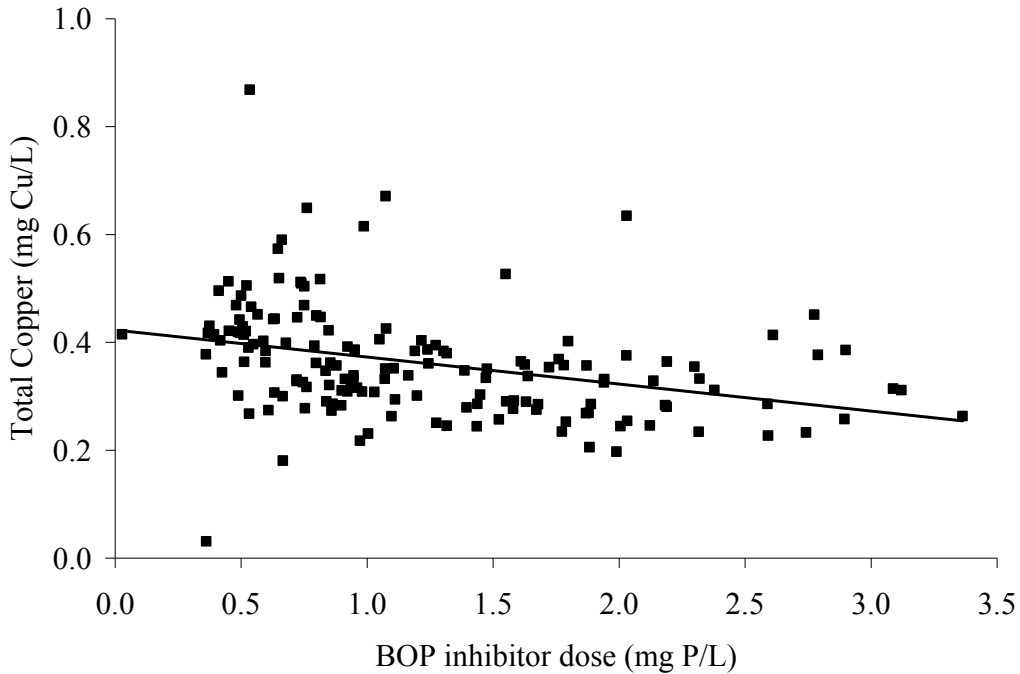


Figure 6-7 impact of increasing dose on actual copper release in BOP inhibitor PDSs (PDS 01 through PDS 03) from all phases.

A statistical comparison (one-tailed, paired data t-test for equality of means) was conducted to determine statistical differences by phase between the pH<sub>s</sub> control (PDS13), the elevated pH treatment (PDS14), and the different BOP inhibitor doses, as shown in Table 6-7. The analysis illustrated a statistically significant benefit for pH elevation in four out of five comparisons (Phases II, III, IV, and composite). Also, BOP inhibitor addition was statistically beneficial compared to pH<sub>s</sub> control at all doses in all phases, including phases with elevated alkalinity associated with large groundwater components in the blend (Phase I and Phase II). It is note worthy that pH elevation may produce undesirable conditions through excessive deposition of calcium carbonate scale, which may not be encountered with BOP inhibitor.

Table 6-7 Comparison of phosphate inhibitors to elevated pH control for total iron

Treatment Dose	PDS 13 pH pHs	PDS 14 pH pHs+0.3	PDS 01 BOP Low	PDS 02 BOP Med	PDS 03 BOP High
Phase I					
Average	1.042	0.999	0.405	0.362	0.370
Std Dev	0.200	0.161	0.125	0.029	0.085
Count	14	14	14	14	14
Significant difference		No	Yes	Yes	Yes
p-value		0.231	<0.001	<0.001	<0.001
Phase II					
Average	1.158	0.820	0.427	0.328	0.269
Std Dev	0.297	0.254	0.098	0.041	0.031
Count	13	13	13	13	13
Significant difference		Yes	Yes	Yes	Yes
p-value		<0.001	<0.001	<0.001	<0.001
Phase III					
Average	1.484	0.846	0.434	0.320	0.288
Std Dev	0.298	0.135	0.073	0.050	0.038
Count	13	13	13	13	13
Significant difference		Yes	Yes	Yes	Yes
p-value		<0.001	<0.001	<0.001	<0.001
Phase IV					
Average	1.408	0.928	0.449	0.366	0.322
Std Dev	0.574	0.342	0.166	0.123	0.121
Count	12	12	12	12	12
Significant difference		Yes	Yes	Yes	Yes
p-value		<0.001	<0.001	<0.001	<0.001
Composite					
Average	1.266	0.900	0.428	0.344	0.313
Std Dev	0.396	0.238	0.117	0.070	0.084
Count	52	52	52	52	52
Significant difference		Yes	Yes	Yes	Yes
p-value		<0.001	<0.001	<0.001	<0.001



## 6.5 Conclusion

The impact of BOP corrosion inhibitors and pH adjustments on copper release from hybrid pilot distribution system (PDS) was monitored for a 12-month period, divided into four equal phases. BOP was applied at three dose levels to separate PDSs. Two PDSs were maintained at two pH levels,  $\text{pH}_s$  and  $\text{pH}_s+0.3$ , respectively. Source water blends fed into the system were adjusted every phase to account for the effects of water quality variation on copper release in the presence of inhibitors.

Monitoring copper release under all control strategies showed that the dominant form of copper in the effluent was dissolved, at about 88%. All doses of BOP inhibitor proved beneficial in controlling copper concentrations below the action level of 1.3 mg/L. Copper release was controlled better with increasing dose. Elevation of pH beyond  $\text{pH}_s$  resulted in noticeable decrease in copper concentrations of about 30%. Copper release from PDS with elevated pH was more sensitive to higher alkalinity values than release from PDSs treated with BOP inhibitor.

Developed empirical models predicted actual release reasonably well, and confirmed the importance of BOP inhibitor dose, pH level, and alkalinity content of the source water. Statistical comparison of the corrosion control strategies proved the advantage of BOP inhibitor at all dose over pH control in controlling copper release.

## 6.6 Acknowledgements

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## 7 IMPACT OF BLENDED ORTHOPHOSPHATE INHIBITOR ON LEAD RELEASE AND LEAD CORROSION SCALES IN PIPE DISTRIBUTION SYSTEMS IN CHANGING WATER QUALITY ENVIRONMENT

### 7.1 Abstract

Blended orthophosphate (BOP) inhibitor mitigated lead release below action level, and consistently outperformed pH elevation, in all water quality conditions. X-ray Photoelectron Spectroscopy (XPS) analysis identified lead dioxide ( $\text{PbO}_2$ ), lead oxide ( $\text{PbO}$ ), cerussite ( $\text{PbCO}_3$ ), and hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ) as the corrosion products in the scale of lead/tin coupons exposed to BOP inhibitor. XPS and Scanning Electron Microscopy (SEM) analysis suggested cerussite or hydrocerussite is the controlling solid phase of lead release. Thermodynamic models for cerussite and hydrocerussite grossly over predicted actual concentrations. Solubility and equilibrium relationships suggested the possibility of a lead orthophosphate solid that would describe the effectiveness of BOP inhibitor, although no lead-phosphate solid was detected by surface analysis. BOP inhibitor appears to have mitigated lead release by forming a surface film between lead scale and the bulk water.

## 7.2 Introduction and Background

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. In order to meet drinking water demands, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use. To seek understanding of the issues involved when multiple-source waters are blended, TBW and University of Central Florida (UCF) conducted research regarding the effect of variable finished water quality on distribution system water quality. The capacities of corrosion inhibitors to control these effects, including metal release, were investigated. This study examines the impact of blended ortho-polyphosphate inhibitor (BOP) on lead corrosion scale and lead release in distribution system in a changing water quality environment. This investigation includes surface characterization of lead coupons and monitoring of actual release at varying inhibitor dose. Additionally, empirical models are developed for predicting lead release at various water quality conditions and inhibitor doses.

The EPA's "Lead and Copper Rule" established regulatory action levels for lead at a concentration of 15 ppb (USEPA 1991). Since then, research efforts have examined the impact of using phosphate-based corrosion inhibitors, such as BOP, on meeting this target level.

Lead pipes were first used in plumbing because the material is ductile and can be bent to desired shapes easily. However, later health concerns related to corrosion by-products in drinking water reduced the use of lead in water piping and emphasized the need to control lead release into drinking water at the tap (James M. Montgomery Consulting Engineers. 1985).

The form of lead in water depends strongly on pH, under typical water conditions. At lower pH, the dissolved plumbic ion ( $\text{Pb}^{2+}$ ) is the most stable form, while at neutral pH, lead

carbonate (cerussite  $\text{PbCO}_3$ ) is more favored (James M. Montgomery Consulting Engineers. 1985). At higher pH values, hydrocerussite  $\text{Pb}_2(\text{OH})_2(\text{CO}_3)_2$  or the hydroxide  $\text{Pb}(\text{OH})_2$  are the dominant forms of lead. As pH decreases below pH 8, the solubility of lead increases dramatically for a fixed alkalinity.

Surface characterization of lead coupons in distribution system receiving variable source water blends indicated that  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ,  $\text{PbCO}_3$ , and  $\text{PbO}$  were the major lead corrosion products (Tang et al. 2006a; Taylor 2005). These findings were obtained from previous research efforts on the same pilot plant utilized in this current research, without inhibitors (Taylor 2005). Hydrocerussite ( $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ) content on coupons, determined by XPS analysis, was linearly correlated with lead release, suggesting that  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  may be the solid phase controlling lead release. An equilibrium model of hydrocerussite indicated that pH and alkalinity have a major effect on predicted lead release (Tang et al. 2006a). When lead coupons were exposed to BOP inhibitor, two distinct surface layers formed: a bottom layer composed of small particles (salt-like morphology), and a top layer that showed three-dimensional growth (Vesecky et al. 1997). An XPS analysis of lead coupons indicated that orthophosphate inhibited lead release by reacting directly with the lead surface, whereas polyphosphates reacted with divalent ions in the water (i.e. calcium ions) and developed a protective barrier on the lead surface (Boffardi and Sherbondy 1991).

The magnitude of pH effect on lead solubility is dependant on the dissolved inorganic carbon (DIC) concentration in the water. Higher DIC concentrations can affect orthophosphate film formation and the optimum pH at which the film forms due to the interconnected roles of phosphate solubility and carbonate complexation (Schock 1989).

Comparing the impacts of orthophosphate and polyphosphate on lead release was examined by several authors. In stagnant pipes, both orthophosphate and polyphosphate reduced lead particulate species, which was significant fraction of corrosion by-product release, although polyphosphate increased soluble lead concentrations (McNeill and Edwards 2004). Other studies also showed that polyphosphate application increased soluble lead release in plumbing systems (Boffardi and Sherbondy 1991; Holm and Schock 1991), even at various alkalinity and pH values (Edwards and McNeil 2002). Conversely, orthophosphate dosing typically reduced soluble lead release during stagnation in pure lead pipes (Edwards and McNeil 2002).

The ability of polyphosphate to complex lead may reduce free Pb in water, which promotes the dissolution of lead and lead scale compounds, such as cerussite ( $\text{PbCO}_3$ ) and Hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), during stagnation periods (Edwards et al. 2001; Holm and Schock 1991). That is why elevated Pb concentrations are found when polyphosphates are used.

Similar results were obtained by Atassi et. al. (2004) who found that orthophosphate was more effective (at 1 mg/L) than polyphosphate, but equally effective as blended ortho-polyphosphate (BOP) in controlling lead levels. Higher temperatures resulted in moderate increases in lead levels, while short term variations in phosphate inhibitors feed showed no impact on lead levels. All pipe loops had a visible white powdery deposit that increased with higher orthophosphate dose.

In another study comparing orthophosphate, polyphosphate, BOP, and stannous chloride ( $\text{SnCl}_2$ ), all inhibitors performed better than no-action alternative (control) at reducing lead release with various degrees (Hozalski et al. 2005). The ranking of inhibitors based on total lead concentrations, from lowest to highest, in the tested pipe loops was as follows: orthophosphate< $\text{SnCl}_2$ <BOP<polyphosphate<control



## 7.3 Material and Methods

### 7.3.1 Pilot Plant Design

A research facility was constructed for investigation of distribution system water quality at the Cypress Creek Water Treatment Facility near Tampa Bay, FL. The facility contained 14 identical pilot distribution systems (PDS) that received the same blended water and were made from increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series. The PDSs were constructed of aged pipes that were obtained from existing utility distribution systems to represent the pipe materials in local distribution system. Effluent from each PDS feeds a copper loop that mimicked in-house plumbing system, which included copper pipe material and plumbing fixtures with varying lead content. PDSs received blended water and inhibitors for 12-months. The blends were changed quarterly. Inhibitor type and dose to PDSs were constant for the 12-month operational period.

### 7.3.2 Inhibitors

The BOP PDSs (1, 2 and 3) received doses 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L as total phosphorous, respectively. The BOP inhibitor was a commercial product that was a blend of 60%-80% orthophosphate and 20%-40% polyphosphate. Two PDSs (13 and 14) received only NaOH for corrosion inhibition and were used as controls. PDS 13 and 14 received blended water at  $\text{pH}_s$  and  $\text{pH}_s+0.3$ .

### 7.3.3 Source and Blend Waters

Varying blends of three different process waters were used in this study, surface water (SW), groundwater (GW), and desalinated -reverser osmosis- water (RO). The blends were

changed every phase to vary water quality, as shown in Table 7-1. Phase I and Phase III had the same blend (WQ1) in order to study the seasonal effects. The average water quality for source waters and the resulting blends are presented in Table 7-2.

Table 7-1 Water Blend Ratios

Phase	Blend	% GW	% SW	% RO
I (Feb – May 2006)	WQ1	62	27	11
II (May - Aug 2006)	WQ2	27	62	11
III (Aug – Nov 2006)	WQ1	62	27	11
IV (Nov 2006 – Feb 2007)	WQ3	40	40	20

Table 7-2 Water Quality of Source and Blended Waters

Parameter	Units	GW	RO	SW	WQ1	WQ2	WQ3
pH		7.8	7.8	7.8	7.9	7.9	8.0
TDS	mg/L	355	285	433	365	388	414
HCO <sub>3</sub>	mg/L as CaCO <sub>3</sub>	211	70	81	163	109	154
Ca	mg/L as CaCO <sub>3</sub>	214	63	227	202	185	206
Mg	mg/L as CaCO <sub>3</sub>	28	6	33	29	28	23
Turbidity	NTU	0.25	0.07	0.26	0.3	0.19	0.21
Cl	mg/L	36	93	51	47	59	95
SO <sub>4</sub>	mg/L	29	2	191	72	112	74
DO	mg/L	7.3	8.2	8.7	8.7	8	8
NH <sub>2</sub> Cl	mg/L Cl <sub>2</sub>	5	5	5	5	6	6

#### 7.3.4 Lead Coupons and Surface Characterization

Surface characterization was conducted using new lead/tin coupons that were housed inside a cradle in a trailer, which received PDS effluent and was also used for an Electro Noise (EN) investigation. Coupons in the EN trailer were limited to only 1.0 mg/L as total P, resulting in a single coupon per phase.

Surface characterization was performed on coupons using X-ray Photoelectron Spectroscopy (XPS). Some of the coupons were analyzed as well by scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The XPS spectra patterns

identify chemical components of the top surface of the corrosion layer. SEM visually magnifies the physical structure of the scale surface. EDS identifies the elemental composition of the corrosion layer pictured in the magnified image obtained by SEM.

#### 7.3.5 Sampling and Analysis

Daily, weekly and biweekly samples were collected from the influent, effluent, and corrosion shed locations and analyzed in the field laboratory and UCF laboratories, following procedures of Standard Methods (American Public Health Association. et al. 1998). Data was collected throughout the year of operation

### 7.4 Results and Discussion

#### 7.4.1 Control of Lead Release with BOP Inhibitor Addition

Table 7-3 provides summary data for the corrosion loop total and dissolved lead concentrations for PDS 01 to PDS 03 that received the BOP. This data is segregated by phase and by PDS and lists the average, maximum, and minimum values observed for lead concentrations.

Table 7-3 Lead release summary for BOP PDSs

Phase	PDS	Dose	Dissolved Pb (mg/L)			Total Pb (mg/L)		
			Avg	Max	Min	Avg	Max	Min
I	1	0.57	0.000	0.003	0.000	0.003	0.017	0.000
	2	1.08	0.000	0.001	0.000	0.001	0.009	0.000
	3	1.82	0.001	0.007	0.000	0.001	0.011	0.000
II	1	0.57	0.000	0.001	0.000	0.002	0.009	0.000
	2	1.00	0.000	0.001	0.000	0.001	0.003	0.000
	3	1.95	0.000	0.000	0.000	0.001	0.006	0.000
III	1	0.49	0.000	0.001	0.000	0.001	0.003	0.000
	2	0.90	0.000	0.001	0.000	0.001	0.001	0.000
	3	1.73	0.000	0.000	0.000	0.000	0.001	0.000
IV	1	0.68	0.000	0.001	0.000	0.001	0.002	0.000
	2	1.31	0.000	0.001	0.000	0.001	0.001	0.000
	3	2.66	0.000	0.001	0.000	0.000	0.001	0.000
All	1	0.58	0.000	0.003	0.000	0.002	0.017	0.000
	2	1.07	0.000	0.001	0.000	0.001	0.009	0.000
	3	2.03	0.000	0.007	0.000	0.001	0.011	0.000

These results suggest there is a possible decrease in total lead release with increasing BOP dose, especially between low and medium doses. Data from Phase I showed the greatest variability for all BOP PDSs. The majority of the lead was often present in a particulate form, especially for those cases with the greatest lead concentration. Many of the dissolved lead measurements were below the detection limit of analysis. Water quality variations through phase change showed no clear impact on lead release in Table 7-3 with BOP inhibitor application.

On average, BOP inhibitor controlled lead release consistently better than elevated pH treatment (PDS14) in every phase, as shown in Table 7-4. BOP PDSs and PDS14 had similar water quality characteristics, except for the inhibitor addition.

Table 7-4 Comparison of averaged observed lead release from BOP inhibitor PDSs to pH<sub>s</sub>+0.3

Phase	Inhibitor	Average Release (mg/L)		% Ratio to pH <sub>s</sub> +0.3	
		Dissolved Pb	Total Pb	Dissolved Pb	Total Pb
I	pH <sub>s</sub> +0.3	0.001	0.003		
	BOP	0.000	0.001	29%	45%
II	pH <sub>s</sub> +0.3	0.004	0.008		
	BOP	0.000	0.001	6%	8%
III	pH <sub>s</sub> +0.3	0.005	0.010		
	BOP	0.000	0.001	6%	7%
IV	pH <sub>s</sub> +0.3	0.001	0.003		
	BOP	0.000	0.001	30%	19%

#### 7.4.2 Lead Surface Characterization by XPS

Coupons used for XPS analyses were inserted into the pilot distribution systems (PDS) at the beginning of each phase of pilot plant operation, and then retrieved at the end of the phase. The XPS scanning consists of a two-step process, where an initial “survey” scan was performed to identify all possible elements present on the coupon. A survey scan, conducted over a broad range of energy levels, was useful for confirming the presence or absence of elements on the surface. In contrast, a “high resolution” scan, conducted over a narrow range of energy levels was useful for establishing the chemical states present for a given element. High resolution spectra were shifted along the energy axis to conform to a 284.6 eV adventitious carbon (C 1s) standard.

The elements are indicated on the survey by pronounced peaks above the background of the survey, and these peaks are then selected individually for the high resolution scan for each element. Elements of interest, such as those associated with inhibitors, coupon material, or water quality, were analyzed. Possible compounds associated with a given element were determined through deconvolution of the high resolution scans. A typical survey scan for lead/tin coupons is

shown in Figure 7-1. Peaks were typically pronounced for the lead, tin, oxygen, carbon, calcium, silica, phosphorus, and zinc.

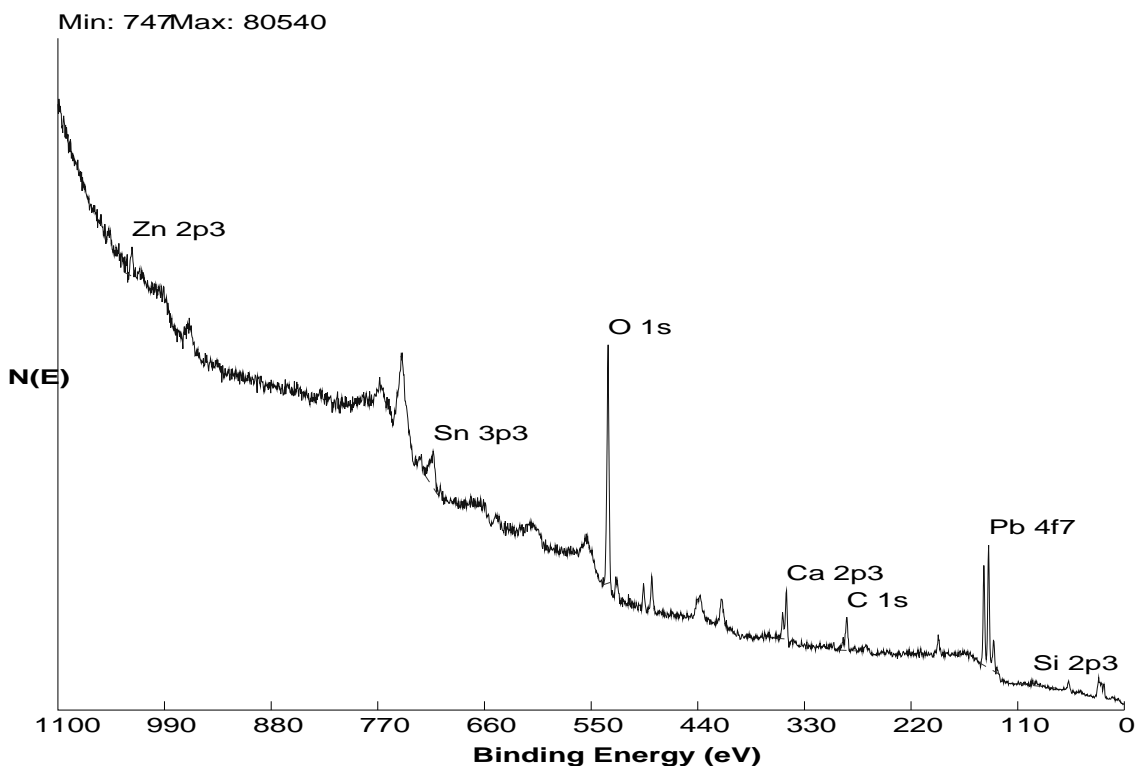


Figure 7-1 XPS survey scan for lead/tin coupon

#### 7.4.2.1 Identification of Lead Scale Corrosion Products

Deconvolution of the lead high resolution scans identified  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  (hydrocerussite),  $\text{PbCO}_3$  (cerussite),  $\text{PbO}$ , and  $\text{PbO}_2$  as the lead corrosion products composing the scale on lead coupons exposed to the BOP inhibitor. Figure 7-2 shows a deconvoluted scan for a lead coupon. The same products were previously identified by XRD and verified by XPS, in the absence of inhibitors (Taylor 2005). Binding energies for these lead compounds were consistent with those used by Tang et. al. (2006a) and were 137.4, 137.7, 138.1, and 138.7 eV for  $\text{PbO}_2$ ,  $\text{PbO}$ ,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , and  $\text{PbCO}_3$ , respectively.

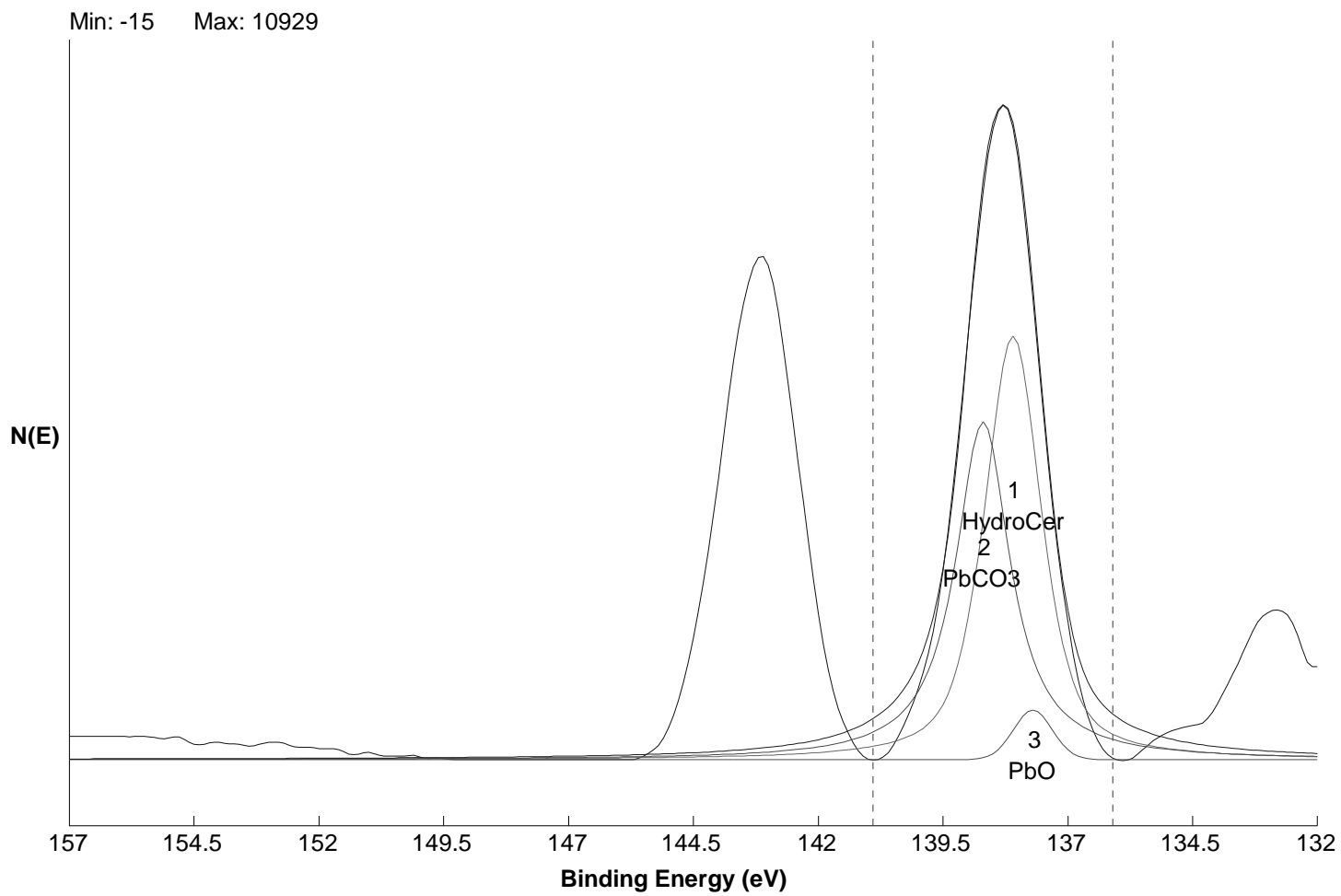


Figure 7-2 Deconvolution of lead for coupon exposed to BOP during Phase IV

Consideration of the lead compounds  $\text{PbO}_2$ ,  $\text{PbO}$ ,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , and  $\text{PbCO}_3$  were sufficient to describe the high resolution peaks for all lead/tin coupons. This implies that introducing the BOP inhibitor into the system did not significantly change the composition of the lead corrosion products. The percent content and composition variations of corrosion products on lead coupons exposed to BOP are illustrated in (Figure 7-3). Cerussite and hydrocerussite were the dominant solid forms of lead on the surface, in all phases. Presence of both  $\text{PbO}$  and  $\text{PbO}_2$  was more prominent in Phases I and III than in Phases II and IV. Phases I and III had similar water quality, with higher alkalinity than Phases II and IV (Table 7-2). Conversely, composition variations of cerussite and hydrocerussite between phases did not follow a clear trend.

Phosphate was found in all phases; however, lead deconvolution did not identify a lead compound that incorporated phosphorus. It appears that the phosphorus constituents detected were not directly incorporated into the surface scale, but rather formed a surface film that contributed to inhibition.



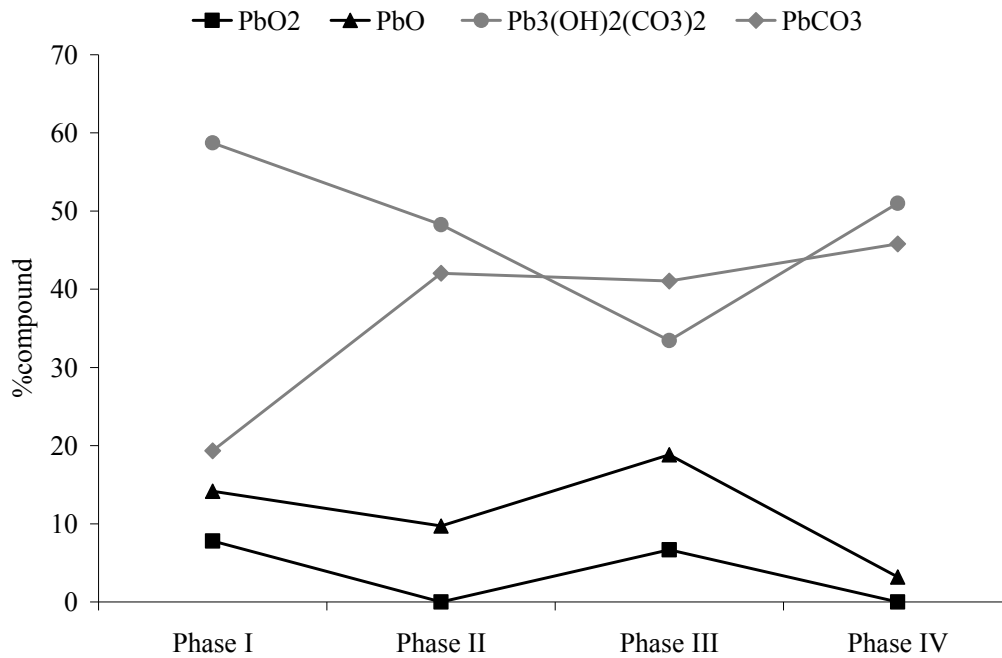


Figure 7-3 Variations of composition of identified compounds on lead coupons for BOP inhibitor

#### 7.4.2.2 Correlation between Lead Corrosion Products and lead release

Relationships between actual lead release and the composition of lead scale compounds were examined. Lead release and hydrocerussite composition had a positive correlation ( $R^2=0.48$ ), suggesting the possible increase of lead release with increasing hydrocerussite content, as illustrated in Figure 7-4. Cerussite was negatively correlated with lead release ( $R^2=0.97$ ), suggesting a decrease in lead release with more cerussite content on lead surface, as shown in Figure 7-5. Composition of both PbO and PbO<sub>2</sub> had no significant correlation with lead concentrations. These correlations imply that either cerussite or hydrocerussite may be the controlling solid phase of lead release.

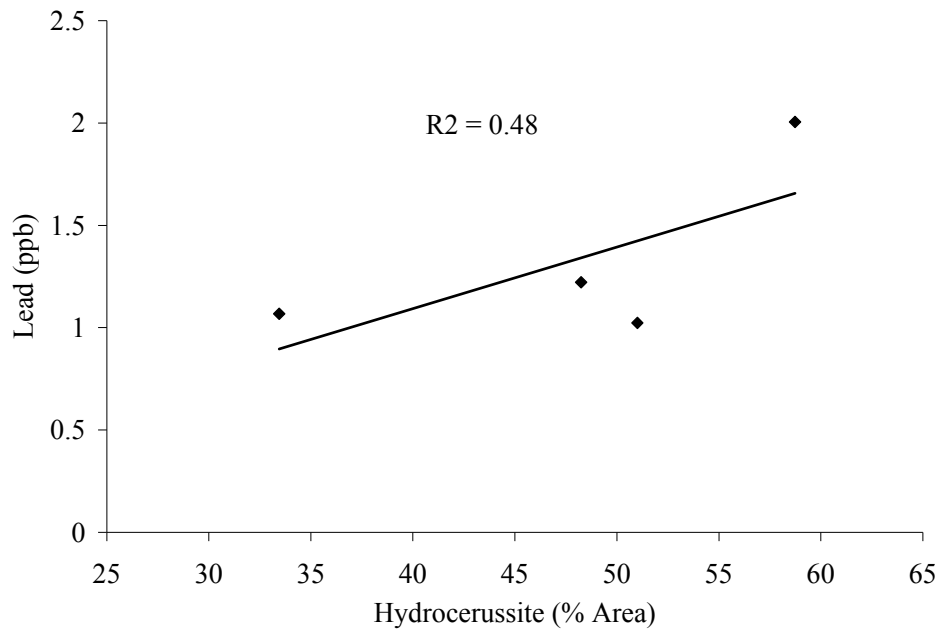


Figure 7-4 Correlation between hydrocerussite composition on BOP coupons and lead release

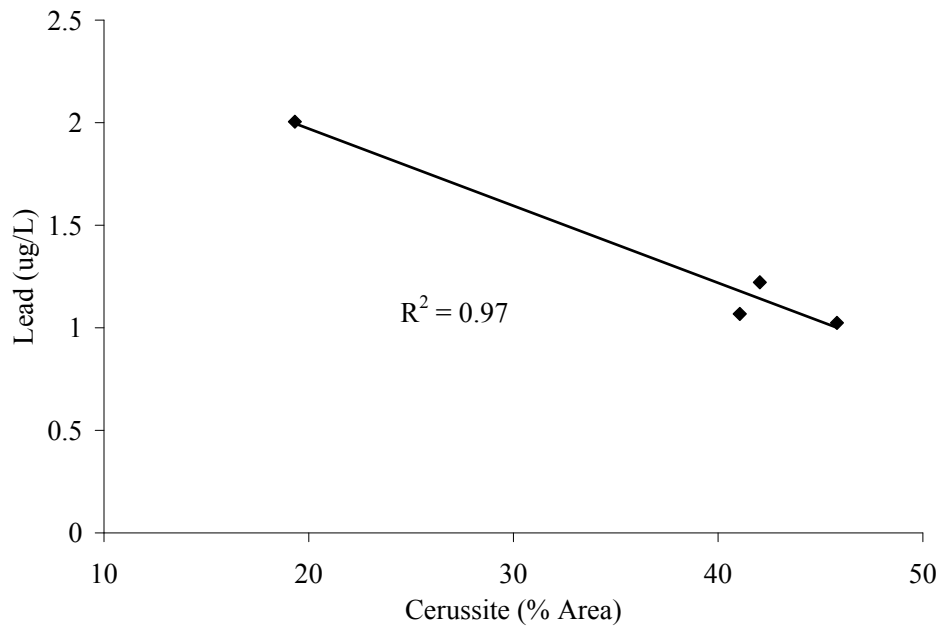


Figure 7-5 Correlation between cerussite composition on BOP coupons and lead release

### 7.4.3 Lead Surface Characterization by SEM/EDS

In addition to employing XPS, lead corrosion surfaces were further characterized by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Representative images obtained from SEM/EDS analysis of coupons incubated in BOP inhibitor are presented in Figure 7-6 and Figure 7-7. Figure 7-6 shows a coupon exposed to BOP high dose in Phase II. Phase II is characterized by the highest average sulfate and lowest alkalinity among all phases (Table 7-2). The left image shows general scale with two distinct growth areas in the center and at the bottom right. The image on the right is a detailed view of a growth area, showing a mixture of pencil or needle-like crystals along with polygonal plate crystals. The polygonal plates were proposed to be hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ) (Korshin et al. 2000). These plates were not scattered randomly but were heavily concentrated in distinct growth areas. The needle-like structures were identified as cerussite (Liu et al. 2006).

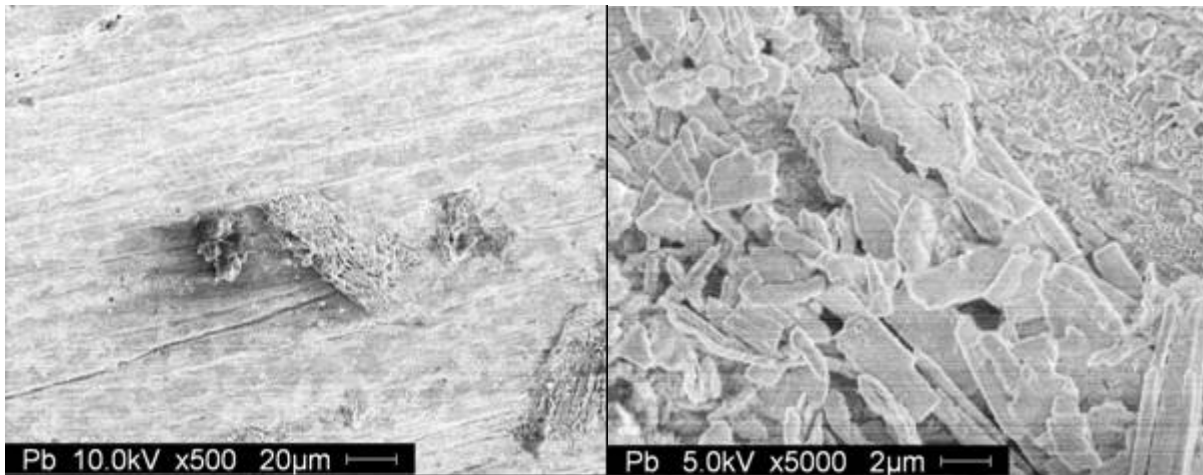


Figure 7-6 SEM images of Lead-Tin coupon incubated in high BOP dose during phase II.

Figure 7-7 shows images of a lead coupon exposed to Phase III (left image), and Phase IV (right image). Numerous small pits appear as dark spots in the images. Both coupons showed a scale which was amorphous and whitish in color, which gave the lead-tin surface a grey shade.

Only a general scale without any distinct growth was observed in the scanned area of the coupon. EDA identified Pb, Sn and Ca as major components with smaller amounts of Si and P.

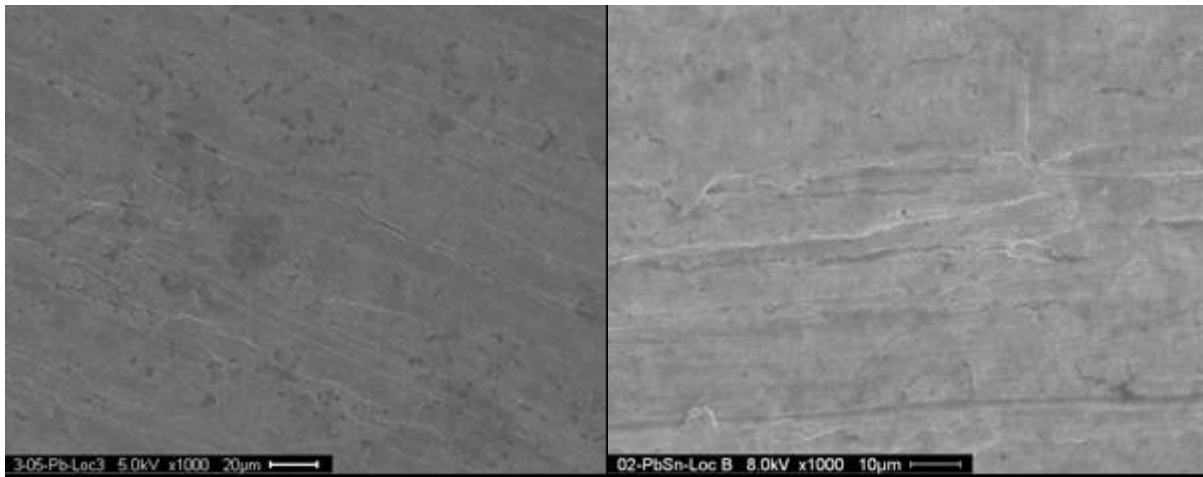
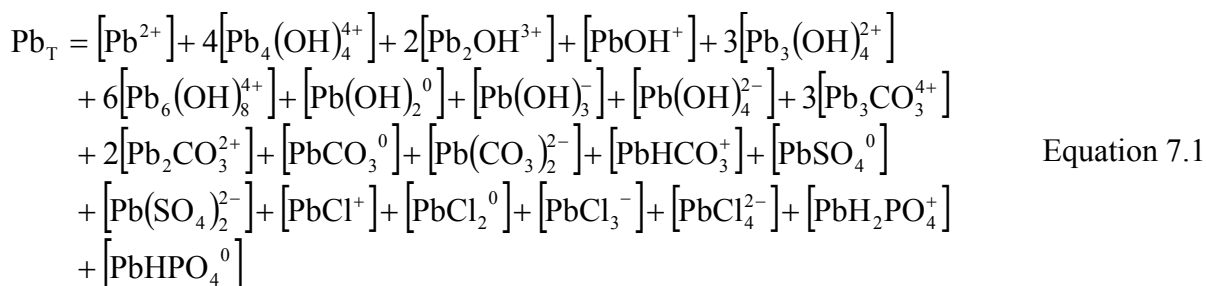


Figure 7-7 SEM images of Lead-Tin coupon incubated in medium BOP dose during phases III and IV.

#### 7.4.4 Thermodynamic Modeling of Lead Release

Lead release from pipe surfaces may be predicted by the solubility of solid phases formed within the corrosion scales using thermodynamic models. Such models are limited to the soluble species, and would be expected to under predict total lead release given significant particulate lead is present. Hydrocerussite ( $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ), and cerussite ( $\text{PbCO}_3$ ) were assumed as controlling solid phases for thermodynamic modeling based on XPS analysis and SEM images. Modeling approach was similar to that used by Tang et. al. (2006a), and resulted in the model shown in Equation 7.1, with the inclusion of possible lead-phosphate complexes.



The complexes considered within Equation 7.1 demonstrate the various water quality dependencies governing lead release. The speciation of dissolved lead suggests such water quality parameters as alkalinity, chloride, sulfate, and phosphate may promote further lead release.

The results from the thermodynamic modeling are shown in Table 7-5. Modeled releases from either cerussite or hydrocerussite grossly over predicted actual concentrations. This implies either the existence of a different controlling solid phase or the formation of a chemical barrier promoted by the presence of BOP.

Table 7-5 Lead thermodynamic modeling of BOP

Phase	Actual Lead Release (mg/L)		Modeled Lead Release (mg/L)		
	Diss Pb	Total Pb	Hydroxypyromorphite	Hydrocerussite	Cerussite
I	0.000	0.001	0.064	0.181	0.200
II	0.000	0.001	0.041	0.176	0.202
III	0.000	0.001	0.064	0.181	0.200
IV	0.000	0.001	0.049	0.187	0.201
All	0.000	0.001	0.056	0.182	0.200

Although the XPS analysis of the 4 lead/tin coupons exposed to BOP indicated the presence of small amounts of phosphate on all coupons, the analysis was inadequate in identifying a phosphate compound. The presence of a less soluble lead-phosphate compound would explain the decrease in lead release with the application of BOP. Postulating the presence of a lead-phosphate solid, the equilibrium model was applied assuming hydroxypyromorphite

( $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ) as the controlling solid phase. Conditions within a water distribution system would likely favor hydroxypyromorphite as a stable lead orthophosphate form (Schock 1989). The hydroxypyromorphite model still over predicted actual release as shown in Table 7-5, but was more accurate than both hydrocerussite and cerussite models.

The solubility limit of lead, without complexation, when considering hydrocerussite and hydroxypyromorphite is shown in Figure 7-8 at an alkalinity of 100 mg/L as  $\text{CaCO}_3$  and phosphate of 1.0 mg/L as P. The solubility diagram suggests that at equilibrium, hydroxypyromorphite was the solubility limiting solid during the study. Dissolved lead was significantly decreased when applying the thermodynamic model as seen in Table 7-5. The decrease in dissolved lead indicates that the lead orthophosphate solid could explain the improvement observed with BOP inhibitor application.

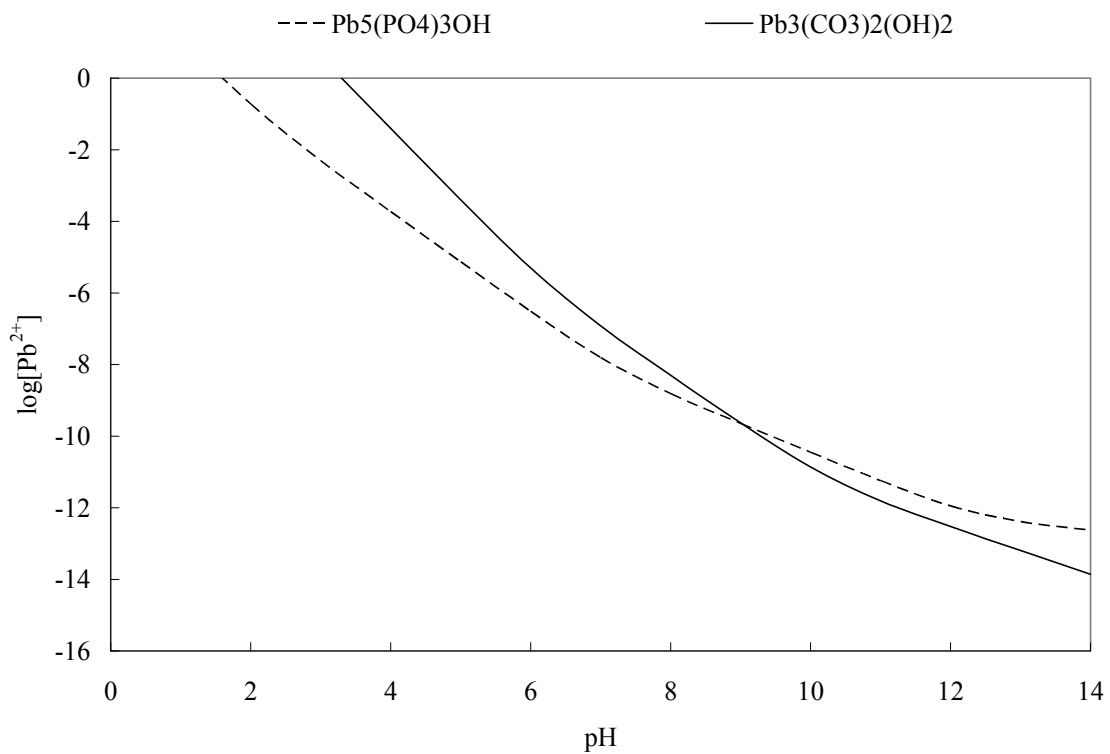


Figure 7-8 Solubility limit of lead for medium dose BOP inhibitor

## 7.5 Conclusion

The impact of BOP inhibitor on lead release and corrosion scales was examined in pipe distribution system with changing water quality conditions by varying source water blends. On average, BOP inhibitor consistently mitigated lead release below action level, and outperformed pH elevation, in all phases. Resulting corrosion scales on lead coupons were analyzed by XPS and SEM to gain insight into the controlling solid phase and mechanism of lead release with BOP inhibition.

Lead corrosion products found in the scale of lead/tin coupons consisted of lead dioxide ( $\text{PbO}_2$ ), lead oxide ( $\text{PbO}$ ), cerussite ( $\text{PbCO}_3$ ), or hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ). XPS analysis found cerussite and hydrocerussite to be the dominant lead corrosion products in all phases of operation. SEM imaging confirmed the presence of cerussite and hydrocerussite on lead coupons. Therefore, cerussite and hydrocerussite were assumed to be the controlling solid phases of lead release. No lead-phosphate solids were detected by surface analysis. BOP inhibitor may have mitigated lead release by forming a surface film between lead scale and the bulk water.

Thermodynamic models for cerussite and hydrocerussite were developed to predict lead release; however, both models grossly over predicted actual concentrations. Solubility and equilibrium relationships suggested the possibility of a lead orthophosphate solid that would describe the effectiveness of BOP inhibitor.

## 7.6 Acknowledgements

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## 8 CONCLUSIONS

This research effort examined the impact of BOP inhibitor on iron, copper, and lead corrosion in pipe distribution system, with changing water quality conditions by varying source water blends. The ability of BOP inhibitor to control metal release was compared to other corrosion control strategies. The effect of BOP on corrosion scale products were examined by surface characterization techniques.

### 8.1 Iron Corrosion Scales under BOP treatment

Resulting iron corrosion scales on iron and galvanized steel coupons were analyzed by XPS and SEM to gain insight into the controlling solid phase and mechanism of iron release with BOP inhibition. Ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), hydrated ferric oxide ( $\text{FeOOH}$ ) and ferric phosphate ( $\text{FePO}_4$ ) were the major corrosion products identified in the surface scale on coupons incubated in BOP inhibitor and were found to be uniformly distributed throughout the coupon scales. Deposition of  $\text{FePO}_4$  was attributed to inhibitor addition as no phosphate scale was detected in the pH inhibited coupons. This suggested BOP inhibitor may produce a solid phosphate film which could be barriers to iron release from pipe materials and consequently inhibit iron release. Variation of phase water quality did not significantly affect the distribution of solid iron forms in the films. This suggests that BOP inhibitor hindered the impact of variations in water quality that otherwise might adversely affect iron release.

Thermodynamic models for identified corrosion compounds were developed to predict iron release. Although ferric phosphate ( $\text{FePO}_4$ ) solid was present under BOP treatment,  $\text{FePO}_4$

model grossly under-predicted iron concentrations and was ruled out as the controlling solid phase of iron release. A siderite ( $\text{FeCO}_3$ ) thermodynamic model that incorporates possible iron-phosphate complexes should good agreement with actual data, with slight over prediction of actual iron release. This suggests that dissolved iron release is not solely dependent on  $\text{FeCO}_3$  but rather may depend on  $\text{FePO}_4$  or other iron phosphate solids that may form and reduce iron release with BOP inhibitor addition.

## 8.2 Controlling Iron Release

Iron was released from PDSs of all treatment strategies (BOP, OP, and pH control), and during all phases. The dominant form of iron in the effluent was particulate (90%). On average, medium and high doses of BOP achieved the least total iron release (around 0.12 mg/L), followed closely by elevated pH at  $\text{pH}_s+0.3$ . The OP inhibitor was not able to control iron release better than elevated pH. Iron concentrations were generally highest under the pHs treatment, almost doubling the averaged release of BOP treatment (0.22 mg/L).

Iron release was variable between phases for all the control strategies. Water quality variation, primarily alkalinity content associated with changing water blend, played a major role in iron release. Water with higher alkalinity content and/or low chloride levels resulted in less iron concentration. Empirical modeling confirmed the pivotal role of source water quality, where alkalinity had the largest influence on model prediction of iron, followed by chloride. Temperature variations had a direct impact on iron release. However, BOP inhibitor was the least susceptible treatment to seasonal changes with almost no change in averaged total release.

### 8.3 Controlling Copper Release

Monitoring copper release under all control strategies showed that the dominant form of copper in the effluent was dissolved, at about 88%. All doses of BOP inhibitor proved beneficial in controlling copper concentrations below the action level of 1.3 mg/L. Copper release was controlled better with increasing dose. Elevation of pH beyond  $pH_s$  resulted in noticeable decrease in copper concentrations of about 30%. Copper release from PDS with elevated pH was more sensitive to higher alkalinity values than release from PDSs treated with BOP inhibitor.

Developed empirical models predicted actual release reasonably well, and confirmed the importance of BOP inhibitor dose, pH level, and alkalinity content of the source water. Statistical comparison of the corrosion control strategies proved the advantage of BOP inhibitor at all dose over pH control in controlling copper release.

### 8.4 Impact of BOP on Lead Corrosion

The impact of BOP inhibitor on lead release and corrosion scales was examined in pipe distribution system with changing water quality conditions by varying source water blends. On average, BOP inhibitor consistently mitigated lead release below action level, and outperformed pH elevation, in all phases. Resulting corrosion scales on lead coupons were analyzed by XPS and SEM to gain insight into the controlling solid phase and mechanism of lead release with BOP inhibition.

Lead corrosion products found in the scale of lead/tin coupons consisted of lead dioxide ( $PbO_2$ ), lead oxide ( $PbO$ ), cerussite ( $PbCO_3$ ), or hydrocerussite ( $Pb_3(CO_3)_2(OH)_2$ ). XPS analysis found cerussite and hydrocerussite to be the dominant lead corrosion products in all phases of

operation. SEM imaging confirmed the presence of cerussite and hydrocerussite on lead coupons. Therefore, cerussite and hydrocerussite were assumed to be the controlling solid phases of lead release. No lead-phosphate solids were detected by surface analysis. BOP inhibitor may have mitigated lead release by forming a surface film between lead scale and the bulk water. Thermodynamic models for cerussite and hydrocerussite were developed to predict lead release; however, both models grossly over predicted actual concentrations. Solubility and equilibrium relationships suggested the possibility of a lead orthophosphate solid that would describe the effectiveness of BOP inhibitor.

APPENDIX A: METAL RELEASE DATA

## A.1 IRON DATA

Table A-1 Iron (total) in Corrosion Loops from Phase I

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 4</b> mg/L	<b>PDS 5</b> mg/L	<b>PDS 6</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
01/30/06	0.120	0.119	0.105	0.161	0.191	0.288	0.127	0.087
02/04/06	0.241	0.099	0.144	0.173	0.163	0.112	0.098	0.101
02/12/06	0.138	0.147	0.251	0.138	0.145	0.154	0.177	0.165
02/19/06	0.303	0.121	0.168	0.106	0.136	0.111	0.134	0.122
02/26/06	0.088	0.092	0.094	0.097	0.151	0.140	0.142	0.163
03/05/06	0.066	0.064	0.065	0.062	0.106	0.060	0.111	0.070
03/12/06	0.126	0.094	0.117	0.203	0.173	0.153	0.178	0.108
03/19/06	0.217	0.079	0.087	0.079	0.103	0.068	0.184	0.083
03/26/06	0.115	0.101	0.173	0.093	0.135	0.081	0.175	0.096
04/02/06	0.094	0.073	0.127	0.086	0.103	0.066	0.140	0.083
04/09/06	0.118	0.087	0.091	0.104	0.117	0.087	0.154	0.093
04/16/06	0.138	0.108	0.130	0.119	0.132	0.092	0.169	0.106
04/23/06	0.104	0.093	0.094	0.118	0.134	0.105	0.201	0.093
05/01/06	0.100	0.081	0.093	0.178	0.149	0.085	0.119	0.206

Table A-2 Iron (total) in Corrosion Loops from Phase II

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 4</b> mg/L	<b>PDS 5</b> mg/L	<b>PDS 6</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
05/09/06	0.170	0.109	0.232	0.133	0.161	0.131	0.215	0.121
05/16/06	(a)							
05/23/06	0.190	0.093	0.105	0.121	0.139	0.135	0.300	0.309
05/30/06	0.135	0.185	0.179	0.184	0.191	0.184	0.238	0.332
06/06/06	0.169	0.139	0.131	0.167	0.191	0.166	0.281	0.147
06/15/06	0.069	0.067	0.067	0.083	0.104	0.089	0.177	0.116
06/20/06	0.555	0.174	0.253	0.185	0.210	0.160	0.171	0.259
06/26/06	0.294	0.249	0.162	0.217	0.232	0.207	0.243	0.166
07/03/06	0.171	0.107	0.111	0.144	0.208	0.169	0.272	0.158
07/11/06	0.203	0.159	0.124	0.207	0.247	0.189	0.371	0.167
07/18/06	0.130	0.124	0.103	0.138	0.237	0.171	0.351	0.175
07/25/06	0.201	0.162	0.137	0.154	0.251	0.227	0.330	0.175
08/01/06	0.232	0.213	0.178	0.187	0.334	0.238	0.317	0.159
08/08/06	0.175	0.157	0.127	0.148	0.225	0.194	0.338	0.156
08/16/06	(a)							

(a) Free chlorine burn this week; no samples collected.



Table A-3 Iron (total) in Corrosion Loops from Phase III

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 4</b> mg/L	<b>PDS 5</b> mg/L	<b>PDS 6</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
08/21/06	0.222	0.106	0.080	0.128	0.175	0.121	0.251	0.094
08/28/06	0.139	0.088	0.083	0.133	0.155	0.117	0.204	0.114
09/04/06	0.096	0.086	0.233	0.102	0.193	0.151	0.228	0.150
09/11/06	0.131	0.104	0.104	0.127	0.238	0.148	0.293	0.156
09/18/06	0.112	0.108	0.099	0.147	0.222	0.141	0.309	0.152
09/25/06	0.129	0.128	0.120	0.153	0.250	0.167	0.318	0.166
10/02/06	0.132	0.135	0.154	0.214	0.273	0.165	0.371	0.183
10/09/06	0.124	0.110	0.129	0.099	0.262	0.148	0.303	0.153
10/16/06	0.111	0.096	0.107	0.138	0.309	0.152	0.283	0.131
10/23/06	0.114	0.115	0.123	0.148	0.217	0.160	0.304	0.153
10/29/06	0.083	0.065	0.147	0.199	0.270	0.080	0.157	0.097
11/05/06	0.123	0.125	0.106	0.136	0.203	0.148	0.254	0.143
11/13/06	0.115	0.105	0.106	0.152	0.225	0.179	0.213	0.133
11/20/06	(a)							

(a) Free chlorine burn this week; no samples collected.

Table A-4 Iron (total) in Corrosion Loops from Phase IV

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 4</b> mg/L	<b>PDS 5</b> mg/L	<b>PDS 6</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
11/27/06	0.061	0.075	0.050	0.070	0.086	0.071	0.116	0.126
12/04/06	0.145	0.153	0.120	0.168	0.197	0.220	0.242	0.237
12/11/06	0.136	0.211	0.111	0.166	0.164	0.193	0.168	0.144
12/17/06	0.081	0.076	0.061	0.111	0.102	0.124	0.188	0.098
12/24/06	0.007	0.020	0.009	0.009	0.006	0.009	0.051	0.062
12/30/06	0.067	0.069	0.042	0.074	0.089	0.513	0.084	0.094
01/08/07	0.142	0.157	0.105	0.176	0.176	0.246	0.266	0.160
01/15/07	0.133	0.125	0.092	0.143	0.108	0.143	0.253	0.148
01/22/07	0.182	0.165	0.124	0.201	0.189	0.284	0.315	0.156
01/29/07	0.181	0.170	0.130	0.189	0.176	0.249	0.315	0.202
02/05/07	0.105	0.150	0.120	0.157	0.182	0.207	0.167	0.129
02/12/07	0.158	0.134	0.103	0.155	0.133	0.166	0.140	0.135

Table A-5 Summary of Phase I and II Iron (dissolved) in Corrosion Loops

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	0.052	0.033	0.033	0.030	0.028	0.031	0.030	0.036
Minimum	0.000	0.003	0.002	0.000	0.002	0.000	0.001	0.003
Maximum	0.173	0.131	0.166	0.111	0.158	0.130	0.106	0.181
Std Dev	0.057	0.038	0.043	0.035	0.043	0.041	0.030	0.047
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	0.010	0.006	0.005	0.004	0.008	0.005	0.025	0.030
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	0.049	0.024	0.020	0.015	0.055	0.028	0.116	0.134
Std Dev	0.014	0.008	0.007	0.005	0.015	0.008	0.032	0.038
Count	13	13	13	13	13	13	13	13

Table A-6 Summary of Phase III and IV Iron (dissolved) in Corrosion Loops

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	0.008	0.009	0.008	0.008	0.009	0.007	0.011	0.008
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	0.029	0.034	0.029	0.026	0.026	0.027	0.041	0.037
Std Dev	0.008	0.010	0.008	0.008	0.009	0.008	0.014	0.012
Count	13	13	13	13	13	13	13	13
<b>Phase IV</b>								
Average	0.003	0.004	0.013	0.001	0.002	0.001	0.004	0.002
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	0.011	0.016	0.044	0.003	0.009	0.006	0.029	0.003
Std Dev	0.003	0.005	0.012	0.001	0.003	0.002	0.008	0.001
Count	12	12	12	12	12	12	12	12

Table A-7 Summary of Phase I and II Influent Total Iron

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	0.028	0.028	0.028	0.027	0.028	0.027	0.027	0.029
Minimum	0.009	0.008	0.003	0.008	0.011	0.007	0.005	0.010
Maximum	0.090	0.118	0.127	0.090	0.090	0.090	0.083	0.090
Std Dev	0.022	0.028	0.031	0.021	0.021	0.022	0.018	0.021
Count	13	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	0.025	0.026	0.026	0.026	0.027	0.026	0.018	0.020
Minimum	0.015	0.015	0.014	0.014	0.017	0.013	0.012	0.016
Maximum	0.038	0.040	0.035	0.038	0.045	0.045	0.025	0.028
Std Dev	0.008	0.010	0.008	0.009	0.010	0.011	0.004	0.004
Count	7	7	7	7	7	7	10	10

Table A-8 Summary of Phase III and IV Influent Total Iron

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	0.029	0.028	0.027	0.029	0.030	0.027	0.029	0.030
Minimum	0.022	0.019	0.020	0.022	0.021	0.020	0.020	0.021
Maximum	0.036	0.040	0.035	0.040	0.039	0.035	0.039	0.039
Std Dev	0.005	0.007	0.006	0.006	0.007	0.006	0.006	0.006
Count	7	7	7	7	7	7	13	13
<b>Phase IV</b>								
Average	0.021	0.020	0.020	0.020	0.020	0.019	0.022	0.022
Minimum	0.015	0.014	0.014	0.014	0.013	0.012	0.015	0.014
Maximum	0.037	0.027	0.028	0.028	0.028	0.028	0.035	0.037
Std Dev	0.008	0.006	0.005	0.006	0.006	0.006	0.007	0.007
Count	6	6	6	6	6	6	12	12

## A.2 COPPER DATA

Table A-9 Copper (total) in Corrosion Loops from Phase I

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
01/30/06	0.51	0.39	0.62	0.99	0.76
02/05/06	0.03	0.36	0.23	1.00	0.95
02/12/06	0.47	0.39	0.41	0.85	0.88
02/19/06	0.45	0.40	0.36	0.84	0.79
02/26/06	0.36	0.34	0.33	0.75	0.93
03/05/06	0.42	0.41	0.35	0.87	1.06
03/12/06	0.40	0.33	0.36	1.06	0.84
03/19/06	0.49	0.38	0.38	1.18	1.01
03/26/06	0.27	0.35	0.40	1.22	1.04
04/02/06	0.42	0.30	0.28	1.12	1.18
04/09/06	0.45	0.35	0.36	1.23	1.10
04/16/06	0.44	0.34	0.36	1.52	1.05
04/23/06	0.44	0.36	0.36	0.99	1.03
05/01/06	0.52	0.37	0.39	0.97	1.37

Table A-10 Copper (total) in Corrosion Loops from Phase II

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
05/09/06	0.36	0.29	0.29	1.28	0.95
05/16/06	(a)				
05/23/06	0.41	0.33	0.33	1.14	0.93
05/30/06	0.18	0.31	0.21	0.67	0.21
06/06/06	0.47	0.32	0.29	1.00	0.83
06/15/06	0.59	0.43	0.23	1.32	1.34
06/20/06	0.51	0.31	0.24	1.69	0.93
06/26/06	0.52	0.32	0.25	1.71	0.94
07/03/06	0.44	0.39	0.28	1.26	0.88
07/11/06	0.47	0.36	0.29	1.09	0.86
07/18/06	0.42	0.33	0.29	1.06	0.76
07/25/06	0.40	0.30	0.28	0.87	0.70
08/01/06	0.38	0.29	0.27	1.03	0.71
08/08/06	0.40	0.29	0.25	0.94	0.61
08/16/06	(a)				

Table A-11 Copper (total) in Corrosion Loops from Phase III

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
08/21/06	0.51	0.39	0.35	1.32	0.93
08/28/06	0.43	0.28	0.27	0.97	0.69
09/04/06	0.42	0.31	0.34	1.18	0.78
09/11/06	0.41	0.32	0.29	1.42	0.86
09/18/06	0.43	0.32	0.26	1.35	0.81
09/25/06	0.42	0.33	0.28	1.37	0.80
10/02/06	0.40	0.33	0.28	1.47	0.93
10/09/06	0.34	0.27	0.24	1.55	0.73
10/16/06	0.50	0.35	0.29	1.71	0.80
10/23/06	0.39	0.29	0.23	1.39	0.71
10/29/06	0.30	0.22	0.25	1.53	0.77
11/05/06	0.57	0.40	0.33	2.08	1.14
11/13/06	0.51	0.35	0.33	1.96	1.05
11/20/06	(a)				

Table A-12 Copper (total) in Corrosion Loops from Phase IV

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
11/27/06	0.87	0.67	0.63	2.51	1.72
12/04/06	0.45	0.36	0.31	1.72	0.95
12/11/06	0.50	0.38	0.38	1.65	1.10
12/17/06	0.42	0.33	0.31	1.56	0.91
12/24/06	0.33	0.38	0.26	1.46	0.75
12/30/06	0.65	0.53	0.45	2.02	1.39
01/08/07	0.38	0.30	0.26	1.08	0.73
01/15/07	0.33	0.25	0.23	0.98	0.61
01/22/07	0.45	0.36	0.31	1.60	0.96
01/29/07	0.31	0.26	0.20	1.11	0.62
02/05/07	0.27	0.25	0.23	0.87	0.56
02/12/07	0.42	0.31	0.28	0.34	0.84

Table A-13 Summary of Phase I and II Copper (dissolved) in Corrosion Loops

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	0.36	0.34	0.33	0.46	0.38	0.26	0.95	0.89
Minimum	0.05	0.29	0.22	0.41	0.26	0.16	0.69	0.29
Maximum	0.46	0.46	0.43	0.57	0.48	0.38	1.41	1.29
Std Dev	0.11	0.04	0.05	0.05	0.06	0.06	0.20	0.23
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	0.35	0.29	0.24	0.33	0.28	0.21	1.04	0.73
Minimum	0.16	0.25	0.17	0.13	0.15	0.10	0.73	0.13
Maximum	0.57	0.40	0.32	0.49	0.38	0.28	1.53	1.24
Std Dev	0.09	0.04	0.04	0.08	0.05	0.04	0.27	0.25
Count	13	13	13	13	13	13	13	13

Table A-14 Summary of Phase III and IV Copper (dissolved) in Corrosion Loops

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	0.38	0.30	0.26	0.36	0.29	0.19	1.32	0.79
Minimum	0.26	0.20	0.22	0.29	0.24	0.14	0.84	0.62
Maximum	0.51	0.37	0.33	0.44	0.37	0.26	1.84	1.13
Std Dev	0.07	0.04	0.04	0.05	0.04	0.03	0.30	0.14
Count	13	13	13	13	13	13	13	13
<b>Phase IV</b>								
Average	0.35	0.31	0.29	0.34	0.32	0.21	1.14	0.83
Minimum	0.03	0.20	0.17	0.20	0.19	0.12	0.06	0.50
Maximum	0.78	0.59	0.59	0.63	0.56	0.34	2.25	1.53
Std Dev	0.17	0.12	0.12	0.12	0.11	0.06	0.61	0.31
Count	12	12	12	12	12	12	12	12

# LEAD DATA

Table A-15 Lead (total) in Corrosion Loops from Phase I

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
01/30/06	0.004	0.002	0.001	0.000	0.000
02/05/06	0.000	0.003	0.005	0.002	0.010
02/12/06	0.002	0.011	0.002	0.009	0.000
02/19/06	0.000	0.000	0.000	0.017	0.000
02/26/06	0.000	0.000	0.001	0.000	0.000
03/05/06	0.000	0.000	0.000	0.000	0.000
03/12/06	0.000	0.000	0.000	0.000	0.000
03/19/06	0.000	0.000	0.000	0.000	0.001
03/26/06	0.000	0.000	0.001	0.007	0.000
04/02/06	0.000	0.003	0.003	0.001	0.002
04/09/06	0.005	0.015	0.012	0.001	0.003
04/16/06	0.001	0.016	0.001	0.002	0.000
04/23/06	0.004	0.001	0.013	0.001	0.009
05/01/06	0.000	0.016	0.001	0.001	0.013

Table A-16 Lead (total) in Corrosion Loops from Phase II

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
05/09/06	0.000	0.000	0.000	0.000	0.000
05/16/06	(a)				
05/23/06	0.006	0.000	0.000	0.007	0.005
05/30/06	0.001	0.001	0.006	0.001	0.002
06/06/06	0.002	0.001	0.000	0.009	0.004
06/15/06	0.006	0.003	0.000	0.013	0.007
06/20/06	0.009	0.001	0.000	0.015	0.006
06/26/06	0.003	0.001	0.000	0.005	0.004
07/03/06	0.001	0.000	0.000	0.015	0.005
07/11/06	0.001	0.001	0.000	0.024	0.017
07/18/06	0.001	0.000	0.000	0.016	0.023
07/25/06	0.000	0.000	0.000	0.009	0.018
08/01/06	0.000	0.000	0.000	0.022	0.012
08/08/06	0.000	0.000	0.000	0.015	0.004
08/16/06	(a)				

Table A-17 Lead (total) in Corrosion Loops from Phase III

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
08/21/06	0.002	0.001	0.000	0.034	0.010
08/28/06	0.000	0.000	0.000	0.040	0.009
09/04/06	0.001	0.000	0.001	0.031	0.005
09/11/06	0.002	0.001	0.000	0.059	0.013
09/18/06	0.002	0.001	0.000	0.056	0.036
09/25/06	0.001	0.000	0.000	0.041	0.015
10/02/06	0.003	0.001	0.001	0.064	0.013
10/09/06	0.001	0.000	0.000	0.022	0.015
10/16/06	0.002	0.001	0.000	0.016	0.006
10/23/06	0.001	0.001	0.001	0.028	0.005
10/29/06	0.001	0.001	0.000	0.013	0.003
11/05/06	0.001	0.001	0.000	0.005	0.001
11/13/06	0.001	0.001	0.000	0.010	0.002
11/20/06	(a)				

Table A-18 Lead (total) in Corrosion Loops from Phase IV

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
11/27/06	0.001	0.000	0.000	0.009	0.014
12/04/06	0.001	0.000	0.000	0.008	0.004
12/11/06	0.001	0.001	0.000	0.006	0.003
12/17/06	0.000	0.000	0.000	0.002	0.001
12/24/06	0.000	0.000	0.000	0.001	0.001
12/30/06	0.001	0.001	0.001	0.006	0.003
01/08/07	0.001	0.001	0.000	0.000	0.002
01/15/07	0.001	0.001	0.001	0.004	0.003
01/22/07	0.002	0.001	0.001	0.006	0.004
01/29/07	0.001	0.001	0.000	0.004	0.002
02/05/07	0.000	0.000	0.000	0.002	0.001
02/12/07	0.001	0.000	0.000	0.001	0.003



Table A-19 Summary of Phase I and II Lead (dissolved) in Corrosion Loops

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	0.000	0.000	0.001	0.000	0.000	0.000	0.003	0.001
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	0.003	0.001	0.007	0.002	0.002	0.001	0.008	0.006
Std Dev	0.001	0.000	0.002	0.001	0.001	0.000	0.003	0.002
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	0.000	0.000	0.000	0.001	0.000	0.000	0.005	0.004
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Maximum	0.001	0.001	0.000	0.001	0.000	0.001	0.010	0.011
Std Dev	0.000	0.000	0.000	0.001	0.000	0.000	0.003	0.003
Count	13	13	13	13	13	13	13	13

Table A-20 Summary of Phase III and IV Lead (dissolved) in Corrosion Loops

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	0.000	0.000	0.000	0.001	0.000	0.000	0.017	0.005
Minimum	0.000	0.000	0.000	0.001	0.000	0.000	0.003	0.001
Maximum	0.001	0.001	0.000	0.002	0.001	0.001	0.035	0.022
Std Dev	0.000	0.000	0.000	0.001	0.000	0.000	0.011	0.006
Count	13	13	13	13	13	13	13	13
<b>Phase IV</b>								
Average	0.000	0.000	0.000	0.001	0.000	0.000	0.002	0.001
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	0.001	0.001	0.001	0.004	0.001	0.001	0.007	0.005
Std Dev	0.000	0.000	0.000	0.001	0.000	0.000	0.002	0.001
Count	12	12	12	12	12	12	12	12

## APPENDIX B: INHIBITOR FEED DATA

Table B-1 Influent Phosphorus (total) during Phase I

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
01/30/06	0.74	0.92	0.99	0.09	0.60
02/05/06	0.36	0.60	1.00	0.07	0.08
02/12/06	0.54	1.24	2.61	0.23	0.23
02/19/06	0.82	1.27	2.30	0.05	0.10
02/26/06	0.51	0.95	1.94	0.08	0.08
03/05/06	0.50	1.05	1.72	0.09	0.11
03/12/06	0.42	0.95	1.78	0.09	0.14
03/19/06	ND	1.19	2.03	0.05	0.06
03/26/06	0.53	1.11	1.80	0.12	0.13
04/02/06	0.39	0.67	0.75	0.11	0.11
04/09/06	0.80	1.39	2.19	0.13	0.13
04/16/06	0.63	1.16	1.87	0.12	0.13
04/23/06	0.49	0.88	1.63	0.15	0.15
05/01/06	0.81	1.76	2.90	0.17	0.17

Table B-2 Influent Phosphorus (total) during Phase II

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
05/09/06	0.85	1.44	2.59	0.14	0.14
05/16/06	(a)				
05/23/06	0.03	1.07	1.94	0.03	0.03
05/30/06	0.67	0.98	1.88	0.04	0.02
06/06/06	0.75	0.94	1.89	0.02	0.02
06/15/06	0.66	1.08	2.32	0.02	0.07
06/20/06	0.74	0.92	2.01	0.02	0.02
06/26/06	0.65	0.76	1.79	0.02	0.02
07/03/06	0.63	0.95	1.67	0.02	0.02
07/11/06	0.48	0.80	1.55	0.02	0.04
07/18/06	0.37	0.94	1.58	0.02	0.03
07/25/06	0.68	1.20	2.18	0.02	0.02
08/01/06	0.36	0.84	1.88	0.00	0.00
08/08/06	0.59	1.11	2.12	ND	0.02
08/16/06	(a)			0.14	0.14

Table B-3 Influent Phosphorus (total) during Phase III

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
08/21/06	0.45	0.79	1.47	0.03	0.04
08/28/06	0.37	0.90	1.87	0.03	0.03
09/04/06	0.52	0.90	1.64	0.03	0.03
09/11/06	0.51	0.96	1.68	0.04	0.04
09/18/06	0.51	0.85	1.52	0.05	0.05
09/25/06	0.49	0.72	1.58	0.04	0.04
10/02/06	0.55	0.72	1.39	0.04	0.05
10/09/06	0.42	0.86	1.44	0.04	0.04
10/16/06	0.41	0.84	1.63	0.04	0.04
10/23/06	0.53	0.86	1.77	0.05	0.05
10/29/06	0.49	0.97	2.03	0.05	0.05
11/05/06	0.65	1.22	2.32	0.04	0.04
11/13/06	0.52	1.07	2.14	0.06	0.05
11/20/06	(a)				

Table B-4 Influent Phosphorus (total) during Phase IV

<b>Date</b>	<b>PDS 1</b> mg/L	<b>PDS 2</b> mg/L	<b>PDS 3</b> mg/L	<b>PDS 13</b> mg/L	<b>PDS 14</b> mg/L
11/27/06	0.53	1.07	2.03	0.05	0.07
12/04/06	0.57	1.24	2.38	0.03	0.03
12/11/06	0.75	1.30	2.79	0.05	0.06
12/17/06	0.85	1.47	3.12	0.02	0.02
12/24/06	0.74	1.32	3.36	0.03	0.03
12/30/06	0.76	1.55	2.77	0.04	0.13
01/08/07	0.60	1.45	2.89	0.04	0.04
01/15/07	0.91	1.27	2.74	0.21	0.20
01/22/07	0.72	1.61	3.09	0.02	0.01
01/29/07	0.63	1.10	1.99	0.05	0.05
02/05/07	0.61	1.32	2.59	0.04	0.04
02/12/07	0.45	1.03	2.19	0.06	0.06

Table B-5 Summary of Phase I and II Effluent Phosphorus (total)

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	0.67	1.36	2.09	0.53	0.86	1.60	0.12	0.11
Minimum	0.51	0.94	0.36	0.37	0.62	0.53	0.05	0.05
Maximum	0.90	3.59	5.05	1.41	1.48	2.32	0.25	0.24
Std Dev	0.13	0.67	1.10	0.28	0.26	0.44	0.06	0.06
Count	13	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	0.59	1.00	1.72	0.47	0.80	1.62	0.03	0.03
Minimum	0.32	0.80	0.45	0.38	0.50	0.96	0.00	0.00
Maximum	1.10	1.91	2.23	0.57	0.95	2.13	0.16	0.15
Std Dev	0.20	0.28	0.44	0.07	0.12	0.30	0.04	0.04
Count	13	13	13	13	13	13	13	13

Table B-6 Summary of Phase III and IV Effluent Phosphorus (total)

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	0.44	0.86	1.65	0.49	0.88	1.74	0.04	0.04
Minimum	0.39	0.70	1.37	0.40	0.77	1.58	0.01	0.01
Maximum	0.52	1.03	2.04	0.53	1.01	1.85	0.05	0.08
Std Dev	0.04	0.10	0.22	0.04	0.07	0.07	0.01	0.02
Count	13	13	13	13	13	13	12	12
<b>Phase IV</b>								
Average	0.62	1.13	2.38	0.45	0.81	1.55	0.06	0.05
Minimum	0.47	0.94	1.95	0.38	0.64	1.48	0.01	0.02
Maximum	0.77	1.38	2.75	0.57	0.93	1.68	0.20	0.20
Std Dev	0.11	0.12	0.31	0.06	0.07	0.06	0.05	0.05
Count	12	12	12	12	12	12	12	12

## APPENDIX C: WATER QUALITY DATA

Table C-1 Summary of Phase I and II Influent Alkalinity

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>
<b>Phase I</b>								
Average	162	163	163	164	164	163	146	164
Minimum	156	158	152	157	158	153	119	157
Maximum	167	168	168	169	169	170	168	169
Std Dev	3.8	3.1	4.3	3.3	3.6	5.0	16.6	3.9
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	106	106	106	106	107	107	92	106
Minimum	96	99	98	98	101	99	84	98
Maximum	112	112	112	114	113	116	99	114
Std Dev	6.4	5.0	5.5	5.5	4.8	6.4	4.7	4.6
Count	7	7	7	7	7	7	9	10

Table C-2 Summary of Phase III and IV Influent Alkalinity

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>
<b>Phase III</b>								
Average	151	151	151	152	152	151	149	151
Minimum	148	147	146	149	149	148	139	142
Maximum	155	154	154	155	154	154	158	154
Std Dev	2.6	2.3	2.8	2.0	1.5	2.0	6.1	3.3
Count	7	7	7	7	7	7	13	13
<b>Phase IV</b>								
Average	123	125	125	125	125	125	119	125
Minimum	120	122	122	121	122	122	108	118
Maximum	129	132	133	132	132	132	131	132
Std Dev	3.2	3.7	4.1	3.9	3.7	3.4	5.6	3.3
Count	6	6	6	6	6	6	12	12

Table C-3 Summary of Phase I and II Effluent Alkalinity

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>
<b>Phase I</b>								
Average	166	163	163	163	162	163	147	163
Minimum	159	159	159	158	145	157	126	153
Maximum	193	169	169	169	169	169	168	169
Std Dev	8.3	2.7	2.7	3.2	5.9	3.3	13.6	4.4
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	108	107	107	108	106	106	97	106
Minimum	102	99	100	101	99	100	88	98
Maximum	114	112	114	113	111	113	103	114
Std Dev	4.4	4.4	4.8	4.5	4.5	4.9	5.7	4.7
Count	7	7	7	7	7	7	9	10

Table C-4 Summary of Phase III and IV Effluent Alkalinity

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>	mg/L CaCO <sub>3</sub>
<b>Phase III</b>								
Average	153	153	152	153	153	152	149	151
Minimum	147	148	147	149	148	149	143	147
Maximum	156	156	156	157	156	156	157	157
Std Dev	3.1	2.8	2.9	2.7	2.7	2.6	4.1	2.6
Count	7	7	7	7	7	7	13	13
<b>Phase IV</b>								
Average	126	126	126	126	126	125	123	125
Minimum	122	120	122	120	122	119	115	120
Maximum	132	133	133	132	133	132	140	131
Std Dev	3.5	4.3	3.8	3.9	3.9	4.3	6.3	2.9
Count	6	6	6	6	6	6	12	12



Table C-5 Summary of Phase I and II Influent Calcium

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	76.5	76.9	76.5	77.1	77.4	76.9	77.5	77.4
Minimum	69.2	72.3	71.8	72.4	72.2	72.1	72.3	71.9
Maximum	84.0	86.1	82.7	83.0	84.6	84.3	88.3	84.2
Std Dev	4.6	4.8	4.2	4.0	4.4	4.0	4.5	4.3
Count	13	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	74.2	71.8	72.9	74.1	72.9	72.0	71.7	72.1
Minimum	71.8	65.9	67.5	70.1	69.2	57.4	66.2	65.9
Maximum	77.7	76.6	77.6	76.2	75.0	81.5	75.8	79.5
Std Dev	2.0	3.6	4.0	2.2	2.0	7.6	3.3	4.3
Count	7	7	7	7	7	7	11	10

Table C-6 Summary of Phase III and IV Influent Calcium

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	75.8	75.3	77.8	78.3	76.9	78.7	74.8	77.7
Minimum	71.8	68.1	74.7	74.1	72.9	74.0	72.4	70.1
Maximum	77.9	80.8	87.0	88.3	78.7	88.2	78.8	83.7
Std Dev	2.1	3.9	4.1	4.7	1.9	4.5	2.0	4.0
Count	7	7	7	7	7	7	13	13
<b>Phase IV</b>								
Average	60.9	60.0	59.1	59.5	59.4	61.4	57.1	57.7
Minimum	52.0	50.8	51.2	51.4	52.3	51.9	46.9	50.0
Maximum	70.4	69.4	66.1	68.8	67.0	70.7	67.9	67.2
Std Dev	8.7	7.6	6.7	7.5	7.4	8.6	7.0	5.8
Count	6	6	6	6	6	6	12	12

Table C-7 Summary of Phase I and II Influent Chloride

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase I</b>								
Average	43.4	43.7	44.0	43.2	43.1	43.2	64.2	43.2
Minimum	38.0	39.0	39.2	38.4	39.0	38.6	38.5	37.6
Maximum	56.2	55.6	57.8	56.9	55.8	56.3	98.0	55.2
Std Dev	4.8	4.8	4.8	4.9	4.6	5.0	16.9	4.6
Count	13	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	67.5	67.7	68.6	67.2	67.4	67.8	82.8	65.1
Minimum	49.3	49.6	49.8	49.4	49.5	49.3	58.9	49.0
Maximum	89.2	90.1	90.9	87.3	89.0	89.6	109.3	78.8
Std Dev	12.6	12.8	13.0	12.3	12.6	12.9	18.0	8.5
Count	7	7	7	7	7	7	9	11

Table C-8 Summary of Phase III and IV Influent Chloride

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	mg/L <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Phase III</b>								
Average	63.3	64.2	65.7	63.6	62.8	65.0	88.4	64.8
Minimum	50.6	52.9	55.8	51.3	51.1	53.3	73.8	50.2
Maximum	74.1	74.8	75.8	73.5	73.0	74.8	123.0	72.5
Std Dev	8.1	8.2	7.6	7.9	8.0	7.8	13.3	7.8
Count	7	7	7	7	7	7	13	13
<b>Phase IV</b>								
Average	57.3	57.5	58.8	56.6	56.4	57.9	68.1	57.9
Minimum	44.2	45.0	46.0	43.9	44.5	45.1	49.2	43.6
Maximum	65.4	67.1	68.8	65.6	64.6	67.5	87.4	64.8
Std Dev	7.7	7.7	8.0	7.8	7.1	8.1	11.6	6.4
Count	6	6	6	6	6	6	12	12

Table C-9 Summary of Phase I and II Influent pH

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>
<b>Phase I</b>								
Average	8.0	7.9	7.9	8.0	8.0	7.9	7.7	7.9
Minimum	7.7	7.7	7.8	7.8	7.8	7.8	7.5	7.6
Maximum	8.9	8.2	8.1	8.2	8.2	8.1	8.1	8.2
Std Dev	0.3	0.1	0.1	0.1	0.1	0.1	0.2	0.2
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.9
Minimum	7.7	7.7	7.7	7.7	7.7	7.6	7.4	7.7
Maximum	8.1	8.0	8.0	8.0	8.2	8.0	8.2	8.1
Std Dev	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1
Count	13	13	13	13	13	13	13	13

Table C-10 Summary of Phase III and IV Influent pH

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>
<b>Phase III</b>								
Average	8.0	8.0	8.0	8.0	8.0	7.9	7.7	8.0
Minimum	7.8	7.8	7.7	7.8	7.8	7.7	7.6	7.8
Maximum	8.4	8.3	8.3	8.3	8.3	8.3	7.8	8.4
Std Dev	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
Count	13	13	13	13	13	13	13	13
<b>Phase IV</b>								
Average	7.8	7.8	7.8	7.8	7.8	7.8	7.6	7.9
Minimum	7.5	7.6	7.5	7.6	7.6	7.6	7.5	7.6
Maximum	8.0	8.0	7.9	8.0	8.0	8.1	7.8	8.1
Std Dev	0.15	0.12	0.14	0.14	0.13	0.14	0.07	0.14
Count	12	12	12	12	12	12	12	12

Table C-11 Summary of Phase I and II Effluent pH

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>
<b>Phase I</b>								
Average	8.1	8.0	7.8	8.0	8.0	8.0	7.8	8.0
Minimum	7.9	7.9	7.4	7.9	7.9	7.9	7.5	7.9
Maximum	8.8	8.2	8.2	8.2	8.2	8.3	8.1	8.2
Std Dev	0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	7.7	7.7	7.7	7.8	7.7	7.7	7.6	7.8
Minimum	7.6	7.6	7.6	7.6	7.6	7.5	7.4	7.7
Maximum	7.9	7.9	7.8	7.9	7.9	7.8	7.8	8.2
Std Dev	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Count	13	13	13	13	13	13	13	13

Table C-12 Summary of Phase III and IV Effluent pH

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>	pH <sub>3</sub>
<b>Phase III</b>								
Average	7.9	7.9	7.9	7.9	7.9	7.9	7.7	8.0
Minimum	7.8	7.8	7.8	7.8	7.8	7.7	7.6	7.8
Maximum	8.2	8.1	8.1	8.2	8.1	8.1	7.8	8.1
Std Dev	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1
Count	13	13	13	13	13	13	13	13
<b>Phase IV</b>								
Average	7.8	7.8	7.7	7.8	7.8	7.7	7.7	7.8
Minimum	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.6
Maximum	7.9	7.9	7.8	7.9	7.9	7.8	7.8	8.0
Std Dev	0.09	0.09	0.08	0.11	0.09	0.08	0.06	0.11
Count	12	12	12	12	12	12	12	12

Table C-13 Summary of Phase I and II Influent Temperature

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	°C	°C	°C	°C	°C	°C	°C	°C
<b>Phase I</b>								
Average	21.3	21.2	21.1	21.0	21.0	20.9	21.3	21.2
Minimum	10.5	10.6	11.7	10.4	10.9	11.5	11.8	11.3
Maximum	27.2	27.4	27.4	27.3	27.4	27.2	27.3	27.4
Std Dev	4.7	4.6	4.6	4.8	4.7	4.7	4.5	4.6
Count	14	14	14	14	14	14	14	14
<b>Phase II</b>								
Average	26.1	26.3	26.0	25.6	26.0	26.0	26.4	26.5
Minimum	23.6	23.3	23.4	22.1	23.0	23.2	22.1	23.6
Maximum	28.5	28.9	29.1	28.5	28.6	29.0	29.7	29.0
Std Dev	2.2	2.4	2.6	2.7	2.3	2.4	2.6	1.7
Count	7	7	7	7	7	7	9	10

Table C-14 Summary of Phase III and IV Influent Temperature

	<b>PDS 1</b>	<b>PDS 2</b>	<b>PDS 3</b>	<b>PDS 4</b>	<b>PDS 5</b>	<b>PDS 6</b>	<b>PDS 13</b>	<b>PDS 14</b>
	°C	°C	°C	°C	°C	°C	°C	°C
<b>Phase III</b>								
Average	25.3	25.5	25.6	25.6	25.6	25.8	25.3	25.6
Minimum	20.6	20.8	20.7	20.7	20.6	20.7	19.9	20.7
Maximum	28.3	28.2	29.0	28.4	28.9	28.8	28.3	28.1
Std Dev	2.6	2.4	2.6	2.5	2.7	2.7	2.4	2.2
Count	7	7	7	7	7	7	13	13
<b>Phase IV</b>								
Average	21.4	21.3	21.3	21.2	21.0	21.2	21.0	21.3
Minimum	17.1	16.8	16.8	16.8	16.8	16.7	15.6	16
Maximum	23.8	23.7	23.5	23.6	23.4	23.3	24	24
Std Dev	2.4	2.5	2.4	2.4	2.3	2.4	3.1	2.8
Count	6	6	6	6	6	6	12	12

## APPENDIX D: XPS ANALYSIS

Table D-1 Percentage Composition of Corrosion Products on Iron Coupons

Inhibitor	Compound	Area%			
		Phase 1	Phase 2	Phase 3	Phase 4
BOP	Fe <sub>2</sub> O <sub>3</sub>	21%	24%	29%	28%
	Fe <sub>3</sub> O <sub>4</sub>	32%	18%	41%	33%
	FePO <sub>4</sub>	29%	0%	12%	16%
	FeOOH	13%	51%	14%	9%
	Satellite	5%	7%	5%	15%
pH	Fe <sub>2</sub> O <sub>3</sub>	10%	10%	9%	9%
	Fe <sub>3</sub> O <sub>4</sub>	52%	38%	21%	34%
	FePO <sub>4</sub>	0%	0%	0%	0%
	FeOOH	29%	45%	60%	49%
	Satellite	9%	8%	10%	9%
pHs	Fe <sub>2</sub> O <sub>3</sub>	14%	8%	13%	14%
	Fe <sub>3</sub> O <sub>4</sub>	57%	29%	15%	42%
	FePO <sub>4</sub>	0%	0%	0%	0%
	FeOOH	20%	48%	64%	36%
	Satellite	9%	15%	8%	9%
pHs+0.3	Fe <sub>2</sub> O <sub>3</sub>	6%	12%	5%	4%
	Fe <sub>3</sub> O <sub>4</sub>	47%	46%	27%	26%
	FePO <sub>4</sub>	0%	0%	0%	0%
	FeOOH	37%	42%	56%	61%
	Satellite	9%	0%	13%	9%

Table D-2 Percentage Composition of Corrosion Products on Galvanized Steel Coupons

Inhibitor	Compound	Area%			
		Phase 1	Phase 2	Phase 3	Phase 4
BOP	Fe <sub>2</sub> O <sub>3</sub>	43%	40%	10%	7%
	Fe <sub>3</sub> O <sub>4</sub>	11%	16%	21%	20%
	FeOOH	13%	18%	30%	42%
	FePO <sub>4</sub>	34%	20%	39%	31%
	Satellite Peak	0%	6%	0%	0%
pH	Fe <sub>2</sub> O <sub>3</sub>	51%	39%	8%	9%
	Fe <sub>3</sub> O <sub>4</sub>	28%	23%	17%	26%
	FeOOH	8%	16%	54%	53%
	FePO <sub>4</sub>	0%	0%	0%	0%
	Satellite Peak	14%	22%	21%	12%
pHs	Fe <sub>2</sub> O <sub>3</sub>	49%	39%	7%	0%
	Fe <sub>3</sub> O <sub>4</sub>	35%	28%	15%	41%
	FeOOH	4%	11%	55%	48%
	FePO <sub>4</sub>	0%	0%	0%	0%
	Satellite Peak	13%	22%	22%	11%
pHs+0.3	Fe <sub>2</sub> O <sub>3</sub>	52%	40%	8%	19%
	Fe <sub>3</sub> O <sub>4</sub>	22%	18%	19%	12%
	FeOOH	12%	21%	54%	57%
	FePO <sub>4</sub>	0%	0%	0%	0%
	Satellite Peak	15%	21%	19%	13%