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IMPACT OF ZINC ORTHOPHOSPHATE INHIBITOR ON  
DISTRIBUTION SYSTEM WATER QUALITY

by

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B.S. Beijing University of Technology, 2001

M.S. Beijing University of Technology, 2004

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

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Advisor: James S. Taylor

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## **ABSTRACT**

This dissertation consists of four papers concerning impacts of zinc orthophosphate (ZOP) inhibitor on iron, copper and lead release in a changing water quality environment. The mechanism of zinc orthophosphate corrosion inhibition in drinking water municipal and home distribution systems and the role of zinc were investigated.

Fourteen pilot distribution systems (PDSs) which were identical and consisted of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes were used in this study. Changing quarterly blends of finished ground, surface and desalinated waters were fed into the pilot distribution systems over a one year period. Zinc orthophosphate inhibitor at three different doses was applied to three PDSs. Water quality and iron, copper and lead scale formation was monitored for the one year study duration.

The first article describes the effects of zinc orthophosphate (ZOP) corrosion inhibitor on surface characteristics of iron corrosion products in a changing water quality environment. Surface compositions of iron surface scales for iron and galvanized steel coupons incubated in different blended waters in the presence of ZOP inhibitor were investigated using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS). Based on surface characterization, predictive equilibrium models were developed to describe the controlling solid phase and mechanism of ZOP inhibition and the role of zinc for iron release.

The second article describes the effects of zinc orthophosphate (ZOP) corrosion inhibitor on total iron release in a changing water quality environment. Development of empirical models

as a function of water quality and ZOP inhibitor dose for total iron release and mass balances analysis for total zinc and total phosphorus data provided insight into the mechanism of ZOP corrosion inhibition regarding iron release in drinking water distribution systems.

The third article describes the effects of zinc orthophosphate (ZOP) corrosion inhibitor on total copper release in a changing water quality environment. Empirical model development was undertaken for prediction of total copper release as a function of water quality and inhibitor dose. Thermodynamic models for dissolved copper based on surface characterization of scale that were generated on copper coupons exposed to ZOP inhibitor were also developed. Surface composition was determined by X-ray Photoelectron Spectroscopy (XPS).

The fourth article describes the effects of zinc orthophosphate (ZOP) corrosion inhibitor on total lead release in a changing water quality environment. Surface characterization of lead scale on coupons exposed to ZOP inhibitor by X-ray Photoelectron Spectroscopy (XPS) was utilized to identify scale composition. Development of thermodynamic model for lead release based on surface analysis results provided insight into the mechanism of ZOP inhibition and the role of zinc.

This dissertation is dedicated to my parents  
for their unconditional love, understanding and support.

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## **LIST OF ABBREVIATIONS**

AES	Auger Electron Spectroscopy
Alka.	Alkalinity
AMPAC	Advanced Materials Processing and Analysis Center
AO	Aesthetic Objective
AWWA	American Water Works Association
AwwARF	American Water Works Association Research Foundation
BOP	Blended Orthophosphate
BAT	Best Available Technology
CCPP	Calcium Carbonate Precipitation Potential
Cond.	Conductivity
DL	Detection limit
DO	Dissolved oxygen
EDS	Energy Dispersive X-ray Spectroscopy
EPA	Environmental Protection Agency
ESCA	Electron Spectroscopy for Chemical Analysis
GW	Groundwater
HRT	Hydraulic Residence Time
LCR	Lead and Copper Rule
LSI	Langelier Saturation Index
MAC	Maximum Acceptable Concentration

MCF	Material Characterization Facility
MCL	Maximum Contamination Level
MGD	Millions of Gallons per Day
OP	Orthophosphate
PDS	Pilot Distribution System
PVC	Polyvinyl Chloride
RO	Reverse Osmosis
SW	Surface Water
TBW	Tampa Bay Water
TDS	Total Dissolved Solids
UCF	University of Central Florida
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction
ZOP	Zinc Orthophosphate

## **CHAPTER 1 INTRODUCTION**

### **Background**

The Tampa Bay area is facing increasing consumer demand and more stringent environmental and drinking water regulations as with many metropolitan areas. 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 has 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.

Zinc orthophosphate has been widely used for many years as a reliable, known and safe chemical. The EPA Lead and Copper Rule (1991) identified zinc orthophosphate as a ‘best available technology’ (BAT) to minimize the leaching of lead from water lines and brass fixtures into the drinking water. There is however little knowledge on the effect of variable water quality on the capability of zinc orthophosphate to function in a distribution system. Hence, the capabilities of zinc orthophosphate to offset the adverse effects of changing finished water quality on distribution system water quality was investigated over a one year period and utilized a 8500 ft<sup>2</sup> (800 m<sup>2</sup>) research facility that was constructed for the project.

### **Research Objectives**

The primary goal of the dissertation is to determine or gain insight into the mechanism of zinc orthophosphate corrosion inhibition in drinking water municipal and home distribution systems in a changing water quality environment.

Specific to this objective are ZOP impacts on total and dissolved lead, copper and iron release with reference to:

- Water quality impacts.
- The role of Zn.
- Development of mathematical models that describe the impact of ZOP inhibitor on metal release in distribution system



### **Research Approach**

This dissertation consists of four papers concerning impacts of zinc orthophosphate (ZOP) inhibitor on iron, copper and lead release in a changing water quality environment. The document is comprised of seven chapters. The first chapter presents the introduction of this dissertation. Chapter 2 reviews the technologies and presents current research efforts for corrosion inhibitors especially for ZOP inhibitor. The theoretical background involved is also introduced in this chapter. Chapter 3 introduces project facilities, experimental approach and the major analytical techniques. Chapter 4 presents the first paper entitled “Effects of zinc orthophosphate (ZOP) corrosion inhibitor on surface characteristics of iron corrosion products in a changing water quality environment”. Chapter 5 presents the second paper entitled “Effects of zinc orthophosphate (ZOP) corrosion inhibitor on total iron release in a changing water quality environment”. Chapter 6 presents the third paper entitled “Effects of zinc orthophosphate (ZOP) corrosion inhibitor on total copper release in a changing water quality environment”. Chapter 7 presents the forth paper entitled “Effects of zinc orthophosphate (ZOP) corrosion inhibitor on total lead release in a changing water quality environment”.

## **CHAPTER 2 LITERATURE REVIEW**

### **Theory**

#### **Fundamental corrosion**

All corrosion reactions in drinking water system are fundamentally redox reactions and involve electron transfer. Three fundamental conditions must exist to realize corrosion. Interfering or eliminating any one of these will reduce or eliminate corrosion. These three fundamental conditions are:

- There must be a potential difference between the species (typically a metal and another metal or water).
- There must be a means of electron transfer between the species involved in the corrosion reaction (electron connection).
- There must a means of electron return (ground).

The use of dissimilar metals in drinking water systems is minimized to the extent possible during design and installation. The focus of corrosion control in drinking water systems is typically through the use of corrosion inhibitions or producing a calcium carbonate scale that essentially short circuits the corrosion reaction as is possible in a given system. Hence, the effects of major inorganic ions and organic solutes that effect precipitation are important considerations in the investigation of corrosion.

## Water quality

### *Alkalinity, pH, and calcium hardness*

Langelier Saturation Index (LSI) is the most widely used index in the water treatment field, which combined the effect of pH on the equilibrium solubility of  $\text{CaCO}_3$ . It is preferable to let  $\text{LSI} > 0$  to form a  $\text{CaCO}_3$  scale to protect the iron surface from being corroded.  $\text{pH}_s$  is the pH at which  $\text{CaCO}_3$  is saturated, and the  $\text{CaCO}_3$  scale should neither be dissolved nor deposited.

$$\text{LSI} = \text{pH} - \text{pH}_s \quad (\text{Equation 2.1})$$

$\text{LSI} > 0$ ,            *water is supersaturated,  $\text{CaCO}_3$  scale tends to be formed;*  
 $\text{LSI} = 0$ ,            *$\text{CaCO}_3$  is in equilibrium, neither dissolved, nor deposited;*  
 $\text{LSI} < 0$ ,           *water is under saturated,  $\text{CaCO}_3$  scale tends to be dissolved.*

$$\text{pH}_s = -\log\left(\frac{K'_2}{K'_s}\right) - \log[\text{Ca}^{2+}] - \log[\text{HCO}_3^-] \quad (\text{Equation 2.2})$$

Where,  $K'_2$  is the second dissociation constants for carbonic acid corrected for temperature and ionic strength.  $K'_s$  is the solubility constant for calcium carbonate corrected for temperature and ionic strength.

Calcium Carbonate Precipitation Potential (CCPP) represents the quantity of  $\text{CaCO}_3$  that could precipitate on the pipe surface. It is calculated as shown in Equation 2.3. A positive CCPP denotes over saturation, and that much of  $\text{CaCO}_3$  (mg/L) should precipitate. A negative CCPP indicates under saturation, and that much of  $\text{CaCO}_3$  (mg/L) should dissolve.

$$\text{CCPP} = 50045 \cdot [\text{TALK}_i - \text{TALK}_{eq}] \quad (\text{Equation 2.3})$$

The use of calcium carbonate precipitation is limited to the availability of calcium and alkalinity for precipitation. Too much of either causes excessive precipitation, turbidity and interference with operation of valves; whereas too little makes precipitation nearly impossible or requires such a high pH that other undesirable effects can occur.

### *Chloride and sulfate*

Chloride and sulfate may cause increased iron corrosion by reacting with metals in solution and causing them soluble, or interfering with the formation of normal oxide, hydroxide, or hydroxycarbonate film. Larson index is sometimes used to predict corrosion problem, which should be less than 0.2 or 0.3.

$$LarsonIndex = \frac{2[SO_4^{2-}] + [Cl^-]}{[HCO_3^-]} \quad (\text{Equation 2.4})$$

### *Temperature*

Theoretically, electrode potential is proportional to absolute temperature, therefore the corrosion rate will increase with temperature. By changing solubility, temperature can influence the precipitation of different solid phases or transform the identities of corrosion products, which may result in more or less corrosion rate.

### *TDS (Conductivity)*

A high TDS will increase the conductivity of the water, which can increase the ability of water to complete the electrochemical circuit and then the corrosion current. It may also affect

the formation of protective film. TDS will also affect ionic strength and complex or precipitate formation; however TDS in drinking water is typically less than 500 mg/L, which minimizes the effect of ionic strength.

## **Surface characterization techniques**

### *XPS*

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique, which is based upon the photoelectric effect. (O'Connor, D.J., Sexton, B.A. & Smart, R.S. 1992) Each atom in the surface has core electron with the characteristic binding energy that is conceptually, not strictly, equal to the ionization energy of that electron. When an X-ray beam directs to the sample surface, the energy of the X-ray photon is adsorbed completely by the core electron of an atom. If the photon energy,  $h\nu$ , is large enough, the core electron will then escape from the atom and emit out of the surface. The emitted electron with the kinetic energy of  $E_k$  is referred to as the photoelectron. The binding energy of the core electron is given by the Einstein relationship:

$$E_b = h\nu - E_k - \phi \quad \text{(Equation 2.5)}$$

Where  $h\nu$  is the X-ray photon energy (for monochromatic Al K $\alpha$ ,  $h\nu = 1486.6\text{eV}$ );  $E_k$  is the kinetic energy of photoelectron, which can be measured by the energy analyzer; and  $\phi$  is the work function induced by the analyzer, about 4~5eV. Since the work function can be compensated artificially, it is eliminated, giving the binding energy as follows:

$$E_b = h\nu - E_k \quad \text{(Equation 2.6)}$$

For insulating samples, once the photoelectrons are emitted out of the sample surface, a positive charge zone will establish quickly in the sample surface. As a result, the sample surface acquires a positive potential (varying typically from several volts to tens of volts) and the kinetic energies of core electrons are reduced by the same amount,  $C$ .

$$E_b = h\nu - (E_k - C) \quad (\text{Equation 2.7})$$

It can be seen that the surface charging results in the shift of the XPS peaks to higher binding energy. In this case, the binding energy has to be calibrated with an internal reference peak. The C 1s peak from the adventitious carbon-based contaminant, with the binding energy of 284.8eV, is commonly used as the reference for calibration. In order to neutralize the surface charge during data acquisition, a low-energy electron flood gun is used to deliver the electrons to the sample surface. The electron flood gun can be tuned to provide the right current to push the XPS peaks back to the real position.

The core electron of an element has a unique binding energy, which seems like a "fingerprint". Thus almost all elements except for hydrogen and helium can be identified via measuring the binding energy of its core electron. Furthermore, the binding energy of core electron is very sensitive to the chemical environment of element. The same atom is bonded to the different chemical species, leading to the change in the binding energy of its core electron. The variation of binding energy results in the shift of the corresponding XPS peak, ranging from 0.1eV to 10eV. This effect is termed as "chemical shift", which can be applied to studying the chemical status of element in the surface. Therefore, XPS is also known as electron spectroscopy for chemical analysis (ESCA).

Since the number of photoelectron of an element is dependent upon the atomic concentration of that element in the sample, XPS is used to not only identify the elements but also quantify the chemical composition. After the value of peak intensity (the peak area after background removal) is obtained, the atomic concentration of an element,  $C_i$ , can be expressed as:

$$C_i = \frac{I_i / S_i}{\sum_i I_i / S_i} \quad (\text{Equation 2.8})$$

Where  $I_i$  is the peak intensity for element  $i$ , and  $S_i$  is the sensitivity factor for the peak  $i$ .



Figure 2.1 5400 ESCA X-ray Photoelectron Spectroscope

## *SEM/EDS*

In scanning electron microscopy (SEM), an electron beam is scanned across a sample's surface. When the electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample's elemental composition. The three signals which provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons, and X-rays.

Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology. A high resolution image can be obtained because of the small diameter of the primary electron beam.

Backscattered electrons are primary beam electrons which are 'reflected' from atoms in the solid. The contrast in the image produced is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Because these electrons are emitted from a depth in the sample, the resolution in the image is not as good as for secondary electrons.

Interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. The emitted X-ray has an energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis (Energy Dispersive X-ray Spectroscopy or EDS). EDS can provide rapid qualitative, or with adequate standards, 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.

A 4.0kV×5000 image of zinc orthophosphate ( $\text{Zn}_3(\text{PO}_4)_3$ ) solid captured in this study is presented in Figure 2.2. SEM JEOL 6400 F that was used for SEM and EDS scans is shown in Figure 2.3.

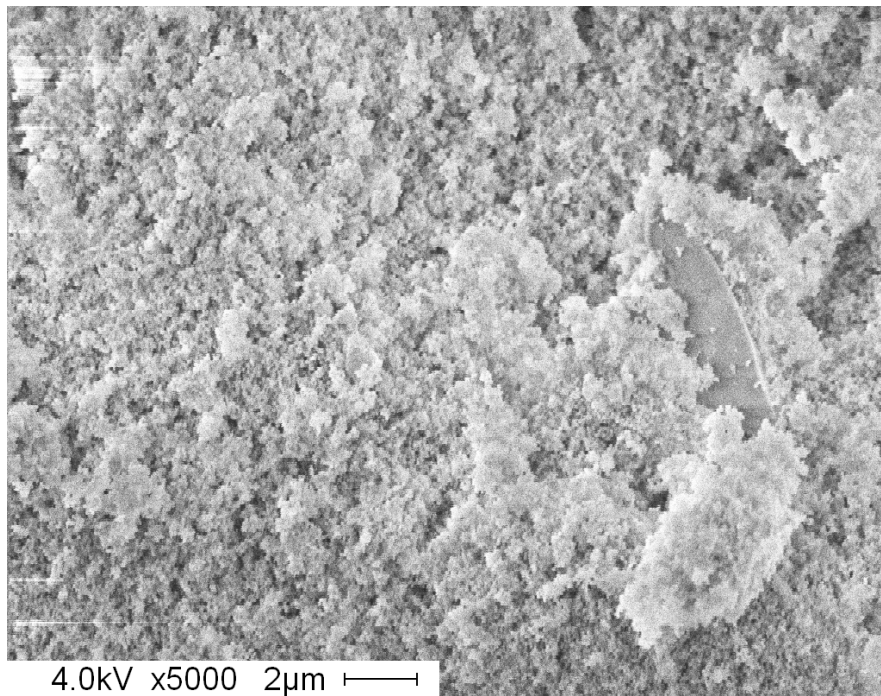


Figure 2.2 SEM analysis for ZOP precipitation (4.0kV×5000)

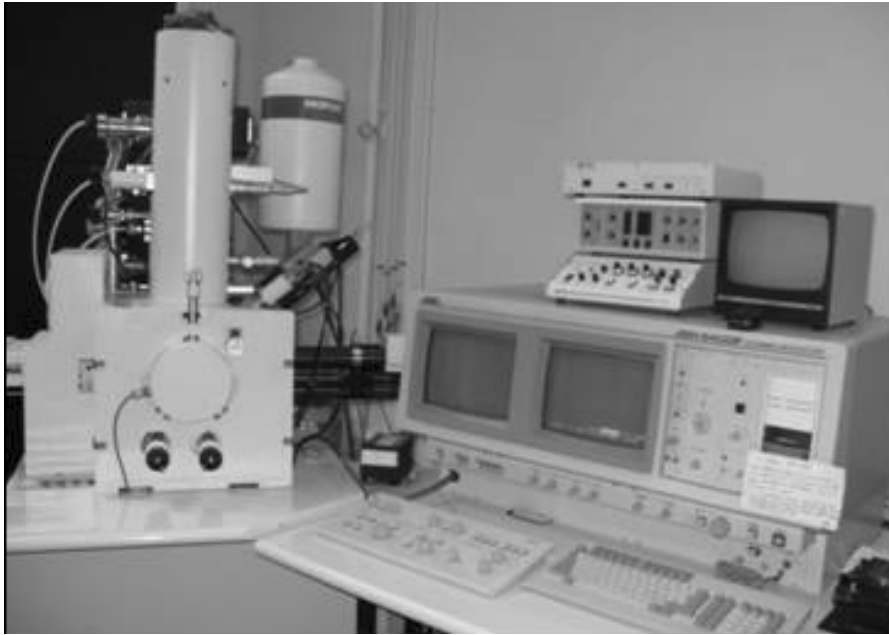


Figure 2.3 JEOL 6400F Scanning Electron Microscopy

### **Corrosion**

Corrosions are processes that deteriorate materials by chemical reactions with their environment. It obeys the laws of thermodynamics and leads to changes in the properties of materials (Taylor, J.S., et al 2001).

Corrosion of iron pipes in a distribution system can cause three distinct problems. First, pipe mass is lost through oxidation to soluble iron species or iron-bearing scale. Second, the scale can accumulate as large tubercles that increase head loss and decrease water capacity. Finally, the release of soluble or particulate iron corrosion by-products to the water leads to consumer complaints of "red water" at the tap. (McNeill, L.S. & Edwards, M. 2001)

Corrosion can also lead to unacceptable levels of copper and lead being introduced into drinking water, which in turn can have deleterious effects on human health. Increasing awareness

of the presence and potential health impacts of corrosion products in drinking water has led the US Environmental Protection Agency to mandate action levels (90<sup>th</sup> percentile concentration) of 0.015 mg/L for lead and 1.3 mg/L for copper (Pontius, F.W. 1991). Canadian drinking water guideline levels (Health and Welfare Canada 1996) are 0.01 mg/L maximum acceptable concentration (MAC) for lead, on a flushed sample, and 1.0 mg/L aesthetic objective (AO) for copper.

Corrosion can also have negative impacts on the environment. Copper are toxic to fish and microorganisms at quite low concentrations and may pose a threat to receiving waters and sewage treatment plants. Corrosion leads to premature failure of plumbing and piping systems and can cause problems such as metallic tasting water and staining of plumbing fixtures, clothing, and human hair. (Churchill, D.M., et al 2000)

### **Phosphate Inhibitors**

#### **Introduction and application history**

Phosphate inhibitors have been used for more than 60 years to prevent scale buildup and to control pipe corrosion. About 1934, lime or soda ash was first added to water in order to raise the pH value to eliminate red water problems. It was soon found that the reduction was accomplished by precipitating the corrosion products in place of tubercles rather than by decreasing the rate of corrosion. Lime was then added on purpose to help calcium carbonate scale covering the corroding pipe surfaces. However, the difficulty experienced in practice was that most of the scale would precipitate in transmission mains, leaving the main part of the system unprotected and even decreasing flow rates in the transmission mains.

Phosphate compounds like sodium hexametaphosphate were then introduced to prevent excess calcite precipitation in drinking water distribution systems (Hoover, C.P. & Rice, O. 1939). In the 1940s, hexametaphosphate gained popularity as a “wonder chemical” that supposedly offered simultaneous control of calcite precipitation and corrosion. By 1957, more than 1,500 municipalities were feeding this glassy phosphate for corrosion control (Kleber, J.P. 1965).

The most common types of phosphate inhibitors used today include hexametaphosphate (polyphosphate), orthophosphate, zinc orthophosphate, zinc metaphosphate, bimetallic phosphate (sodium zinc or potassium zinc phosphate) and blends of orthophosphoric acid and polyphosphate.

A nationwide utility survey conducted in 2001 (McNeill, L.S. & Edwards, M. 2002) reported that 56% of all responding utilities add phosphate inhibitors in 2001, 84% of utilities currently dose inhibitors to control lead and copper, 50% for iron corrosion or red water. Around 30% of water utilities reported using orthophosphate or zinc orthophosphate inhibitor. Results from a 1999 survey by American Water Works Company Inc. found that 72% of its 185 utilities were using phosphate products (Casale, R.J. 2001). Also in Europe such as Germany, the continuous dosage of corrosion inhibitors to the central distribution network was successfully applied for many years (Hater, W., et al 2003).

## **Beneficial effects**

Numerous studies found that phosphate based inhibitors especially orthophosphate inhibitors could prevent corrosion related problems and iron, copper and lead release. However, the mechanism proposed varies widely.

### *Iron*

The results of a water-distribution corrosion study conducted for the City of Yellowknife, Northwest Territories, Canada indicated that sodium hexametaphosphate was a effective for iron release control (Facey, R.M. & Smith, D.W. 1995).

Corrosion inhibitors were studied in water with adjusted pH and alkalinity. That study measured corrosion using pipe coupons. The results of the weight loss determinations from the pipe inserts indicated that all of the inhibitors, particularly the zinc orthophosphate, worked very favorably with copper; however, for cast iron coupons, it offered no additional benefit over that obtained from simple pH and alkalinity adjustment (MacQuarrie, D., Mavinic, D. & Neden, D. 1997).

According to Linda (Maddison, L.A., Gagnon, G.A. & Eisnor, J.D. 2001), at both pilot and full-scale distribution systems, polyphosphate inhibitors provided better corrosion protection than pH adjustment treatment.

Another study was conducted in 2002 to evaluate the effect of orthophosphate and several polyphosphates on the properties of Fe particles and suspensions. The results of this study also showed polyphosphates and orthophosphate can alter properties of Fe particles and suspensions and reduced suspension turbidity (Lytle, D.A. & Snoeyink, V.L. 2002).

Pilot scale studies showed the beneficial use of phosphate based inhibitors to minimize the corrosion of iron pipes and its subsequent increased effectiveness on chlorine disinfection, allowing a better control of distribution system biofilms (LeChevallier, M.W., et al 1993). The same author also found that the use of phosphate based corrosion inhibitors was associated with lower coliform levels (LeChevallier, M.W., Welch, N.J. & Smith, D.B. 1996). The reduction in coliform occurrences following application of corrosion inhibitors was because inhibitors reduce three things: the microbial habitat by reducing the mass or corrosion products on pipe surfaces, the adsorption capacity of iron oxides and the disinfectant demand of existing corrosion products and the pipe surfaces (Besner, M.C., et al 2002).

### *Copper*

Dodrill and Edwards conducted a survey of about 360 utilities to examine their strategies in controlling lead and copper release. For copper, the survey showed that at high pH, copper release was reduced with and without inhibitors. At  $\text{pH} < 7.8$ , copper release was high at high alkalinity, but inhibitor use mitigated that release well (Dodrill, D.M. & Edwards, M. 1995).

According to Edwards, moderate (1mg/l as P) doses of polyphosphate or orthophosphate generally decreased copper release in pipe rig tests of >3 years duration. The orthophosphate acted to reduce the solubility of copper solids in equilibrium with water, presumably by formation of a cupric phosphate scale (Edwards, M., Hidmi, L. & Gladwell, D. 2002).

The inhibition of copper corrosion in aqueous media by inorganic phosphates has been studied using a chemiometric approach. The optimum experimental conditions are: inhibitor:

$[\text{Na}_5\text{P}_3\text{O}_{10}] = 0.017 \text{ mol/L}$  and passivation time  $t_p = 2.17 \text{ h}$ . Under these conditions an inhibition efficiency of 98% was reached (Souissi, N. & Triki, E. 2007).

### *Lead*

To solve copper corrosion problems while maintaining lead control, pilot tests were carried out by USEPA and Indian Hill Water Works (IHWW) in Cincinnati in 1998. Results of the pilot tests suggested an increased orthophosphate residual of 3 mg/L as  $\text{PO}_4$ . The recommended treatment was implemented beginning in 1999. Lead levels were below 0.005 mg/l for the 90th percentile, and the 90th percentile copper levels were reduced to 1.04 mg/L for the fall 1999 and Spring 2000 sampling rounds. Copper levels remain consistently below the 1.3 mg/L Action Level, and IHWW has now successfully met simultaneous lead and copper control requirements of the regulations (Schock, M.R. & Fox, J.C. 2001).

In an effort to further optimize their corrosion control strategy, a Lake Michigan water utility tested several phosphate inhibitors for their effectiveness to control lead. Overall results from the testing showed orthophosphate was more effective than polyphosphate for controlling lead levels (Amrou Atassi, et al 2004).

### **Possible detrimental effects**

Evidences have been founded that phosphate based inhibitors may have an unfavorable effect from a corrosion control point of view when used at low flow or in stagnant waters. McNeill completed a four-year study exam long-term phosphate inhibitors performance in a variety of water qualities under stagnant conditions. (McNeill, L.S. & Edwards, M. 2000). Study

parameters included pH and alkalinity of the water, age of the pipe, water stagnation time, and inhibitor type. For iron release, addition of phosphate inhibitors had no statistically significant effect (at 95% confidence) in two-thirds of the experiments. In the remaining experiments, addition of orthophosphate or zinc orthophosphate always increased iron concentrations. Polyphosphate addition decreased iron release at only one water quality and increased it at other conditions.

Maddison and Gagnon also reported that phosphate inhibitors had no positive impacts under such conditions. (Maddison, L.A. & Gagnon, G.A. 1999). Katsanis found phosphate inhibitors were more efficient at high velocities, rather than stagnant or low velocities (Katsanis. E P & Esmonde. W B 1985).

Dosing of polyphosphates, which are invariably a blend of orthophosphate and polyphosphates due to reversion, does not provide the same magnitude of reduction in copper release as orthophosphate. Copper complexation by polyphosphate tends to increase soluble copper release, whereas higher doses of orthophosphate tend to decrease copper solubility. The net effect of polyphosphate dosing will depend on the relative concentration of each species and the pH (Edwards, M., Hidmi, L. & Gladwell, D. 2002).

Lead concentrations in drinking water can be minimized by adjusting the pH and alkalinity. Holm found that such lead solubility controls, however, may be offset by other water treatment measures that inadvertently increase lead solubility, e.g., the adding of polyphosphate. Therefore, the application of polyphosphates for the specific purpose of lead corrosion control entails considerable uncertainty and risk (Holm, T.R. & Schock, M.R. 1991). Although this



hypothesis is controversial and has been debated for at least a decade (Boffardi, B.P., Holm, T.R. & Schock, M.R. 1991), recent monitoring data supported these concerns.

According to Dodrill's survey, it was observed that without phosphate inhibitors, higher alkalinity resulted in lower lead release. At low alkalinity, using inhibitors reduced lead release compared to no inhibitors. The utilities with the low alkalinity and pH below 7.4 benefited from using orthophosphate but not polyphosphate. Polyphosphate increased lead release at higher alkalinity (Dodrill, D.M. & Edwards, M. 1995).

A study to investigate the effect of polyphosphate inhibitors on lead release indicated that orthophosphate dosing often led to > 70% decreases in lead release except in some exceptional cases in new pipes. Polyphosphate tends to increase release of both particulate and soluble lead to drinking water. These adverse effects should be considered whenever polyphosphate is used to prevent scaling or iron precipitation (Edwards, M. & McNeill, L.S. 2002). Cantor also found when polyphosphate blends were added to water systems under certain conditions, leaching of pipe metal into the water may be significantly increased rather than decreased (Cantor, A.F., et al 2000).

Since lead leaching accelerated in the water distribution system, Washington Aqueduct (WA) decided to add phosphoric acid to the system. The initial target residual was 3.2mg/L phosphate, which Water and Sewer Authority (WASA) intended to maintain until the corrosion control treatment optimized. The 90<sup>th</sup> percentile lead levels declined from 59 to 15 ppb within eight months of phosphate addition. WASA began to receive customer complaints of white cloudy water after a year of continuous phosphate treatment. Investigation results indicate high

levels of phosphate in the presence of metal ions formed flocs in the distribution system which produces the white cloudy appearance (Tesfai, F., Constant, P. & Reibier, S. 2006).

In search of a less labor intensive and costly solution to the problem of losing disinfectant residual, the Southern California Water Company – Southwest District implemented a pilot study to investigate the effect of polyphosphate based corrosion inhibitors on disinfection residuals, hydraulics, and water quality. Results of the pilot study suggested polyphosphate addition can soften and remove existing biofilm layers and corrosion tubercles. Short-term episodes of low disinfectant residuals and high R2A-HPC levels should be expected shortly after the implementation of polyphosphate. (Arweiler, S. & Cohen, K. 2003)

### **Zinc Orthophosphate Inhibitor**

#### **Introduction and application history**

Zinc orthophosphate (ZOP) has been widely used for many years as a reliable, known and safe corrosion inhibitor to eliminate or minimize drinking water problems associated with corrosion.

The introduction of sodium hexametaphosphate in 1938 helped considerably for scale prevention by keeping transmission mains free of calcium carbonate scale (Hoover, C.P. & Rice, O. 1939). It was soon found that the sodium hexametaphosphate offered simultaneous control of calcite precipitation and corrosion which made it a popular inhibitor at that age. Although sodium hexametaphosphate was one of the greatest advances in corrosion control, it has its limitations. Most of these limitations result from the fairly long time required to build up a

protective film on metal surfaces, particularly under some difficult conditions such as very high temperatures or very low rates of flow (Kleber, J.P. 1965).

It was also found that iron corrosion product may actually be removed and dispersed in the water during the initial glassy phosphates treatment period, causing the water to be temporarily worse than it was before treatment (White, J.H. 1949).

Zinc orthophosphate was then developed and first used as corrosion inhibitors in the 1950's (Kleber, J.P. 1965). The developed sodium-zinc glassy phosphate containing 8-9 percent zinc proved to be three to five times as effective as sodium hexametaphosphate. The zinc not only acts as an accelerator to speed up the formation of the protective metaphosphate film, but it also seems to form a more complete, more protective film.

In the 1960s, manufacturers started to blend orthophosphates with 5%-25% zinc to form bimetallic phosphates. In 1973, Kelly found that Zinc to phosphate weight ratio of 1.13:1 was found to be the most effective zinc phosphate ratio to reduce corrosion. In certain concentration, a precipitation of zinc phosphate forms and a pH adjustment was necessary to keep the salt in solution (Kelly, T.E., Kise, M.A. & Steketee, F.B. 1973).

In the corrosion testing experiments conducted at the Danvers Massachusetts Water Treatment Plant, Bancroft found that 0.5 mg/L zinc orthophosphate addition could significantly reduce corrosion (Bancroft, D. 1988).

Today, zinc orthophosphate products with zinc to phosphate ratios vary from 2:1 to 1:15, depending on specific requirements defined by the end-user, engineering firm, and/or vendor. These corrosion inhibitors are typically formulated from the zinc salt, for example zinc chloride or zinc sulfate and blended with phosphoric acid.

According to Powers, zinc orthophosphate corrosion inhibitor has following advantages (Powers, J.T., Cahalan, E.M. & Zalfa, A.J. 1966):

- Film formation is rapid. With the greater efficiency of film formation, ZOP will cause a film to deposit over tuberculated pipe where mechanical cleaning is either undesirable or unnecessary.
- A lower feed rate is required when ZOP is applied compared with other phosphate inhibitors and the resulting film is more stable.
- Protection in dead end or low flow areas is greater than with sodium glassy phosphates, although still not complete.
- ZOP has less of a dispersing effect on iron corrosion product than other complex sodium phosphates therefore have a lesser tendency to upset a water system.
- Safe and approved for use in potable water.
- Cost is usually equal or less when ZOP is used.

### **Proposed ZOP inhibition mechanism**

It is generally believed that zinc orthophosphates produces a microscopic film on metal surfaces that acts as a barrier to corrosive environments that would normally cause corrosion. As a result, undesirable corrosion products such as iron, lead, and copper are not produced and system protection is enhanced.

Murray found when zinc phosphate added to near neutral water (pH 6.5 - 8.3) in small quantities (3 ppm), zinc and phosphate ions immediately precipitate as zinc phosphate. The precipitate was finely divided and adheres to these surfaces in a thin layer (Murray, W.B. 1970).

It is also believed that zinc orthophosphate offer control of corrosion at both the cathodic and anodic sites. Zinc has been proposed to form a film on the cathodic site, whereas the orthophosphates have been proposed to form films on the bare metals.

Different  $\text{PO}_4/\text{Zn}$  ratios were evaluated when Volk try to investigate the impact of various corrosion control strategies. The reduction of zinc did not affect the effectiveness of corrosion inhibitor. Zinc may help to form protective films on the interior of pipe. Zinc molecules are supposed to react with carbonates at the cathode and form deposits, while phosphates block the anodic sites. The presence of zinc in orthophosphate solutions usually reduces the preconditioning period to establish a film within pipes. (Volk, C., et al 2000).

### **Performance studies**

Numerous studies and cases histories indicated similar results: the presence of zinc either accelerated film formation or helped to form a film which was superior to regular phosphate films. According to Reese, zinc bearing phosphate could provide excellent protection for interior corrosion. It was superior to straight sodium hexametaphosphate by accelerating the formation of a protective film on metal surfaces. The more rapid film formation is believed to result from the accelerating action of zinc (Reese, W.J. 1962).

Kleber also proved that zinc phosphate was three to five times as effective as sodium phosphate in preventing corrosion in water systems. The zinc not only acts as an accelerator to speed up tremendously the formation of the protective meta-phosphate film, but it also seems to form a more complete, more protective film (Kleber, J.P. 1965).

The City of Methuen, Massachusetts decided to clean their distribution system mechanically in July 1959 due to the reduced flow rate. The cleaning was announced in advance so that residents could expect a “few days” of red water. Up until December, there were still lots of red water complaints. A milk processing plant only one mile distant from the pumping station had to shut down because it could no longer clean milk bottles with the chocolate colored water. Bi-metallic glassy phosphate was fed to the affected system one morning in December and the plant was back in operation that same day. Consumer complaints have been virtually non-existent since December 1959 (Powers, J.T., Cahalan, E.M. & Zalfa, A.J. 1966).

The Town of Lexington, Massachusetts began feeding bi-metallic glassy phosphate in 1963. There has been only one red water complaint in the next year which was a significant reduction. The City of Haverhill, Massachusetts was also unable to eliminate red water complaints or to maintain adequate flow rates with sodium hexametaphosphate feeds as high as 10 ppm. After feeding 2 ppm bi-metallic glassy phosphate, the city successfully achieved considerable reductions in red water complaints for 5 years (Powers, J.T., Cahalan, E.M. & Zalfa, A.J. 1966).

In June of 1967, the city of Long Beach, California began using zinc phosphate in an attempt to stop a serious problem of pitting type corrosion in one section of the water system and a plugging type corrosion in the remainder of the system. Pitting has been stopped and tests indicate a 95% reduction in corrosion (Murray, W.B. 1970).

When a change in the source water generated discolored water complaints, a laboratory coupon testing program was established to evaluate selected inhibitors. The zinc orthophosphate

inhibitor treatment was found to be a more effective corrosion inhibitor than caustic soda (Mullen, E.D. & Ritter, J.A. 1974). The same authors also found that in addition to the improvement of water quality, applying zinc orthophosphate inhibitor could yield considerable economic benefits. The savings in chemical treatment costs, the effectiveness in protecting utilities' major investment - the drinking water distribution system and the elimination of the operational and administrative costs of responding to consumer complaints were significant (Mullen, E.D. & Ritter, J.A. 1980).

In 1976 the city of Carbondale, Illinois began using a commercial zinc phosphate compound for corrosion control rather than caustic soda as sodium hydroxide for pH control. Compared with caustic soda, the phosphate compound proved to be less expensive and safer to use (Swayze, J. 1983).

Use of zinc orthophosphate and sodium silicate has shown promising results in the control of copper corrosion (MacQuarrie, D., Mavinic, D. & Neden, D. 1997). A study was initiated to evaluate, in Greater Vancouver Water District water, the effectiveness of zinc orthophosphate, type N sodium silicate, and a commercial blend of the two as corrosion inhibitors. The results of the weight loss determinations from the pipe inserts indicated that all of the inhibitors, particularly the zinc orthophosphate, worked very favorably with copper, but they offered no additional benefit over that obtained from the pH and alkalinity adjustments alone, in the case of the cast iron coupons.

A 12-month pilot plant study was conducted to evaluate a number of corrosion control treatments to reduce metal leaching from typical household plumbing materials in Greater Vancouver District, Canada (Churchill, D.M., et al 2000). A pipe loop system was used to test

six treatment options, with a control loop of the characteristically soft, acidic water. Four pH–alkalinity combinations and two concentrations of zinc orthophosphate (0.37 mg/L and 1.0 mg/L as Zn) were studied. Results of this study showed when compared to the control loop, the pH–alkalinity treatments appeared to exacerbate metal leaching in standing samples. The zinc orthophosphate treated loops were both effective at reducing lead and copper leaching to below control levels.

Indian Hill Water Works (IHWW) (Ohio) supplies water to several suburban communities to the east of Cincinnati. In the late 1980's and early 1990's, various coupon and field tests were carried out using zinc orthophosphate chemicals of different Zn:PO<sub>4</sub> ratios and dosages. The zinc orthophosphate treatment was mostly successful for lead and inconsistently successful for copper throughout the early and mid-1990's, yet the 90th percentile was still at 1.54 mg/L for copper in 1997. This prompted withdrawal of the zinc orthophosphate treatment from IHWW. (Schock, M.R. & Fox, J.C. 2001).

Phosphonates and different kinds of phosphonic acids have been widely used as corrosion inhibitors (Rajendran, S., Apparao, B.V. & Palaniswamy, N. 1999). Phosphonates have shown synergistic effects in combination with Zn<sup>2+</sup> ions in corrosion control. The role of phosphonates in the presence of Zn<sup>2+</sup> ions has been investigated (Rajendran, S. 2002). Phosphonates function as transporters of Zn<sup>2+</sup> from the bulk of the solution towards the metal surface. The molecular size of the Fe<sup>2+</sup>-phosphonate complex and Zn<sup>2+</sup> transporting ability of the phosphonates influence the overall efficiency of corrosion inhibition.

Zinc species were shown to be primarily responsible for the observed scale reduction effects (Coetzee, P.P., Yacoby, M. & Howell, S. 1996). A minimum Zn/Ca mass ratio of  $0.06 \times$



$10^{-3}$  was reported to be required for zinc to cause measurable effect. The trace amount of zinc in particular, can slow down the nucleation rate of  $\text{CaCO}_3$  (Coetzee, P.P., et al 1998). Another study also suggested the most effective inhibitor of  $\text{CaCO}_3$  precipitation was zinc and the effect was linked to dose levels and temperature (Macadam, J. & Parsons, S.A. 2004).

However, some scholars believe that although many utilities use a combination of zinc sulfate and phosphoric acid in their lead and copper programs, the mechanism of zinc action on lead and copper surfaces has never been quantified. Most rigorous corrosion control pilot programs that have compared zinc orthophosphate compounds versus simple orthophosphates have shown no significant benefit from zinc additives at operational dosage levels. They also think the zinc used in the bimetallic corrosion inhibitors is an environmental concern because it contributes to the overall zinc load on wastewater treatment facilities, therefore may affect aerobic biological processes of secondary wastewater treatment plants. Zinc is also believed will concentrate in the wastewater sludge and may limit land disposal application (HDR Engineering Inc 2001).

A screening analysis was conducted to identify potential negative impacts of zinc orthophosphate addition to operation of wastewater treatment facilities and to the quality of receiving waters. It was believed that zinc addition to drinking water could increase the total zinc loading thus could inhibit nitrification and activated sludge processes at WPCP (The Cadmus Group Inc. 2004).

## **Identification and Modeling of Corrosion Scales**

### **General film studies**

#### *Iron*

The use of phosphate inhibitors forms a layer on the surface of pipes, which protect them against corrosion (Benjamin, M.M., et al 1990). The surface structure of iron corrosion scales plays a significant role in iron release. Iron corrosion byproducts tend to accumulate in large mounded tubercles which, often merge to cover the entire pipe surface (Sarin, P., et al 2004). Scales in iron pipes are often characterized by a corroded floor, a porous core, a dense shell-like layer, and a surface layer loosely attached to the shell-like layer (Sarin, P., et al 2001).

Key parameters that influence the films in the interior of pipes and thereby iron corrosion include chlorides, sulfates, alkalinity, calcium, pH, buffer intensity and dissolved organic carbon. Presence of chlorides and sulfates in water leads to iron diffusion from scales, which can cause increased iron concentration in water (F. Kumpera, et al 1987).

Surface corrosion was examined when blended orthophosphate was used as an inhibitor. Two types of protective film were formed on the pipe surface: an inner thin monolayer film formed from adsorption of orthophosphate and an outer thicker layer composed of a weakly soluble compound, generally porous, which was formed by the polyphosphate. The inner layer reduces iron dissolution while the outer, protective layer serves as a physical barrier to diffusion and electron transfer (Moriarty, B.E. 1990).

The calcium phosphate deposition on iron in oxygen-containing neutral aqueous solutions has been studied with respect to the corrosion inhibition properties of the deposited layer. Results

of this study show that calcium phosphate deposition on iron results from super saturation (pH increase). Calcium carbonate co-deposition via heterogeneous nucleation accounts for up to 15% of inhibition. The apparent thickness of the calcium phosphate layer increases linearly with temperature and bulk solution pH (Jovancicevic, V. & Bauer, B. 1989).

Six phosphate and silicate based inhibitors including zinc orthophosphate were used to determine the sequestration capacity for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . No significant difference was found in sequestration capacities for either metal ion (Harwood, J.J., Temkar, P.M. & Scholtze, R.J. 1995).

Klueh and Robinson also investigated effectiveness of sequestering iron in groundwater by polyphosphate addition. Polyphosphate dosing proved beneficial in sequestering iron, compared to no polyphosphate addition, but the presence of calcium adversely limited iron sequestration by polyphosphate (Klueh, K.G. & Robinson, R.B. 1988).

The surface speciation of orthophosphate ions on goethite has been studied as a function of pH, time, total phosphate concentration, and ionic medium. Phosphate anions have a high affinity for corroded surface metals which leads to the formation of a stable phosphate metal complex on the pipe surface and limits further corrosion (Persson, P., Nilsson, N. & Sjoberg, S. 1996).

Boffardi has noted that overdosing polyphosphates can cause old loose deposits, especially iron oxide deposits, to dislodge from pipe surface and disperse, increasing red water problems (Boffardi, B.P. 1993).

### *Copper*

Electrochemical kinetic parameters on copper plumbing surfaces were investigated under hydraulic and water quality conditions typical of distribution systems. Orthophosphates were found to significantly reduce corrosion rates on copper surfaces, however, the film formed due to phosphate addition can dissolve at a pH below 6, which can lead to higher corrosion rates comparable to new copper surfaces (Reiber, S.H. 1989).

The benefits of orthophosphate vs. polyphosphate were compared 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. It was believed that orthophosphate reduced copper solubility by forming a cupric phosphate scale. While in the absence of any phosphate inhibitors, an insoluble malachite scale formed over a period of years. Polyphosphate, however, increased copper release in comparison to orthophosphate because it complexed copper, increasing soluble copper release (Edwards, M., et al 2001).

### *Lead*

The study conducted by Sheiham concludes that lead concentrations in water from lead pipes were limited to a high degree by the solubility of lead in water, and that water treatment can reduce lead levels effectively by ensuring that this solubility was as low as possible. In low alkalinity water, low pH was the predominant cause of high lead concentrations, and pH elevation to about pH 8.5 is required but not generally necessary to increase alkalinity. Addition of orthophosphate is a secondary approach to the treatment of this type of water. For water of

high alkalinity addition of orthophosphate is the favored method of treatment, as simple pH adjustment is unlikely to produce a significant decrease in lead concentration (Sheiham, I. & Jackson, P.J. 1981).

### **Effects of divalent metal ions**

Addition of divalent metal ions such as calcium or zinc was found to provide corrosion protection through cathodic inhibition. Under appropriate solution and pH conditions, insoluble calcium or zinc compounds can form barrier-type films on the surface.

The corrosion behavior of pure iron in polyphosphate solutions has been investigated by means of x-ray photoelectron spectroscopy (XPS). The enhanced efficiency of polyphosphate in reducing the corrosion rate obtained by the conjoint use of the divalent  $\text{Ca}^{2+}$  or  $\text{Zn}^{2+}$  ions, has been connected with the formation on the cathodic areas of a diffusion barrier layer impeding access of oxygen to the iron surface. Analysis results suggested the reversion of polyphosphates to orthophosphates as being an essential step in the formation of the protective film. The results of XPS analysis confirmed that the protective film contains a substantial amount of ferric phosphate ( $\text{FePO}_4$ ) (Koudelka, M., Sanchez, J. & Augustynski, J. 1982).

Similar results were found in another analysis using Auger electron spectroscopy (AES) in which corrosion inhibiting films formed on iron in phosphate-containing solutions were depth profiled. In calcium free solutions, orthophosphate was not incorporated into the film in significant amounts. The composition of these films was essentially iron oxide with inclusions of solution anions. When divalent calcium ion was added to the solution, the resulting film contains significant amounts of phosphate, and the film composition depends on the applied potential.

Cathodic polarization leads to essentially calcium phosphate phases whereas anodic polarization produces films consisting of a mixture of iron oxide and iron phosphate. Under open circuit conditions the film was much thinner and was composed mostly of iron oxide with small amounts of calcium phosphate. (Kamrath, M., Mrozek, P. & Wieckowski, A. 1993).

### **Surface characterization and thermodynamic modeling**

#### *Iron*

It is generally believed that in the absence of corrosion inhibitor, red water was caused by reduction and dissolution of formed corrosion products (Kuch, A. 1988).

Tubercle deposits collected from pipelines in the Columbus, Ohio, distribution system were analyzed by surface characterization techniques. Results revealed that the tubercles consisted largely of iron oxides, although minor and trace elements were present in varying quantities (Tuovinen, O.H., et al 1980).

Interior scales on PVC, lined ductile iron, unlined cast iron and galvanized steel were analyzed by XRD, RMS, and XPS after contact with varying water quality for 1 year.  $\text{FeCO}_3$ , a- $\text{FeOOH}$ , b- $\text{FeOOH}$ , c- $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  were identified. Soluble Fe and  $\text{FeCO}_3$  transformation indicated  $\text{FeCO}_3$  solid was controlling Fe release.  $\text{FeCO}_3$  model and pilot data showed Fe increased as alkalinity and pH decreased (Tang, Z., et al 2006). (Tang, Z., et al 2006).

Another study also showed the dominant iron corrosion product accumulated on the inner wall of a mild steel "water pipe" was composed predominantly of goethite (alpha- $\text{FeOOH}$  - 75.6%), with magnetite ( $\text{Fe}_3\text{O}_4$  - 21.5%) and lepidocrocite (gamma- $\text{FeOOH}$  - 2.9%) also being present (Lin, J., Ellaway, M. & Adrien, R. 2001).

According to Sontheimer, the formation of  $\text{FeCO}_3$  is critical for the development of highly protective, corrosion-resistant scales in water distribution pipes. Conditions that tend to hinder siderite formation lead to higher corrosion rates and non-uniform, thick scales (Sontheimer, H., Kollé, W. & Snoeyink, V.L. 1981).

XPS was used to investigate the corrosion behavior of iron in polyphosphate solutions. The enhanced efficiency of polyphosphate in reducing the corrosion rate obtained by the conjoint use of the divalent  $\text{Ca}^{2+}$  or  $\text{Zn}^{2+}$  ions, has been connected with the formation on the cathodic areas of a diffusion barrier layer impeding access of oxygen to the iron surface. The results of XPS analysis confirmed that the protective film contains a substantial amount of ferric phosphate ( $\text{FePO}_4$ ) (Koudelka, M., Sanchez, J. & Augustynski, J. 1982).

The behavior of iron electrodes immersed in pH 8.9-11.0  $\text{Na}_2\text{HPO}_4$  solutions was studied by scanning electron microscopy (SEM). Initially,  $\text{Fe}_3(\text{PO}_4)_2$  and  $\text{Fe}(\text{OH})_2$  were formed. Subsequently, these ferrous species were further oxidized to  $\gamma\text{-FeOOH}$ , the latter being transformed into  $\text{Fe}_2\text{O}_3$  in the passive region.  $\text{Fe}_3\text{O}_4$  was clearly present as an intermediate oxide structure between the ferrous and ferric species mentioned earlier (Giacomelli, C.D. 2004).

### *Copper and lead*

Feng et al. conducted very thorough experiments in order to understand the rate limiting processes of copper corrosion. X-ray Photon Spectroscopy (XPS) was utilized for the film characterization to gain insight into the important elementary processes controlling copper corrosion. The study found that under their experimental conditions, the rate limiting process

(which controls the overall corrosion rate) was the diffusion of copper ions through the oxide film. (Feng, Y., et al 1996a; Feng, Y., et al 1996b)

A study was conducted to evaluate the performance and stability of an artificially synthesized  $\text{Cu}_2\text{O}$  film and naturally formed heterogeneous corrosion scales under the influence of a number of synthetic and real waters, using Electrochemical Impedance Spectroscopy (EIS) (Palit, A. & Pehkonenb, S.O. 2000). According to Palit, the quantitative prediction of copper levels in drinking water was found to rely on the solubility and physical properties of cupric oxide, hydroxide and basic carbonate solids, which comprise most scales in drinking water supplies. Due to considerable uncertainty in the solubility constants of all these minerals, the tendency for prolonged existence of thermodynamically metastable phases like  $\text{Cu}(\text{OH})_2(\text{s})$  and the possible slow rate of formation of  $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$  (malachite), quantification becomes difficult.

The effect on copper corrosion of adding six different mixtures of orthophosphate and polyphosphate (sodium hexmetaphosphate) to the drinking water was investigated. It was found that in all cases orthophosphate reduced copper corrosion and ortho/polyphosphate blends tended to increase copper corrosion. For all pipes fed phosphate inhibitors, their surfaces appeared brown and shiny and no phosphates were found on the surfaces.  $\text{CuO}$  or/and  $\text{Cu}_2\text{O}$  existed on the surfaces (Junling Qiu & Dvorak, B.I. 2004).

To compare the efficacy of various phosphate inhibitors on forming films on Pb and Cu test coupons, low voltage field emission scanning electron microscopy (FESEM) was used to image topographical features on films formed on Pb and Cu coupons after two months of exposure to various treated water supplies. On the coupon from zinc phosphate treatment, a



complete coverage of the coupons surface by a film containing a uniform distribution of P, Zn and Al to a depth of more than 5  $\mu\text{m}$  was found (Vesecky, S.M., et al 1997).

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  $[\text{Pb}_5(\text{PO}_4)_3\text{OH}]$ . The study indicated that solubility modeling did not accurately predict copper and lead release because of the lack of accuracy of constants in the model, misunderstanding of scale types and the influence of other mechanisms such as colloid detachment from the surface (Edwards, M., Jacobs, S. & Dodrill, D. 1999)

Holm and Schock studied the effects of polyphosphate products on lead solubility in plumbing systems. Results showed elevated soluble lead concentrations compared to no inhibitors use at a wide range of alkalinity values. It is believed 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. This explains the elevated Pb concentrations found when polyphosphates are used (Holm, T.R. & Schock, M.R. 1991)

Corrosion products, obtained from lead service pipes carrying the public drinking water supply to the Glasgow area, have been characterized by surface analysis techniques. As expected, the products which formed in the presence of pH adjusted-water were mainly lead carbonate or basic lead carbonate. Products from areas where the water supply had been treated with orthophosphoric acid and pH adjustment for up to eight years also contained a variable

proportion (up to ~30% w/w) of a phosphate species. This has been identified as an apatite, most probably lead hydroxyapatite,  $Pb_5(PO_4)_3OH$  (Peters, N.J., et al 1999).

In another similar study, Modern analytical techniques have been applied to investigate the nature of lead pipe corrosion products formed in pH adjusted, orthophosphate-treated, low alkalinity water, under supply conditions. Depth profiling and surface analysis have been carried out on pipe samples obtained from the water distribution system in Glasgow, Scotland, UK. XRD identified basic lead carbonate, lead oxide and lead phosphate as the principal components. SEM revealed the crystalline structure within the corrosion product and also showed spatial correlations existed between calcium, iron, lead, oxygen and phosphorus (Davidson, C.M., et al 2004)

#### *Thermodynamic modeling*

The thermodynamic models for dissolved iron, copper and lead were developed to predict the metal release from pipe surface (Taylor, J.S., et al 2005).

Siderite ( $FeCO_3$ ) was assumed to be the solid phase controlling iron ion concentration in water, based on surface characteristics of cast iron pipes, determined by XRD and XPS analyses. The developed dissolved iron thermodynamic model is shown below.

$$[Fe]_T = [Fe^{+2}] + [FeOH^+] + [Fe(OH)_2] + [Fe(OH)_3] + [FeHCO_3^+] + [FeCO_3] + [FeSO_4] \quad (\text{Equation 2.9})$$

Similarly, assuming the controlling solid phase is  $CuO$  or  $Cu(OH)_2$ , the developed dissolved copper model is:

$$\begin{aligned}
[Cu]_T = & [Cu^{2+}] + [CuOH^+] + [Cu(OH)_2^0] + [Cu(OH)_3^-] + \\
& [CuHCO_3^-] + [CuCO_3^0] + [Cu(CO_3)_2^{2-}] + \\
& [Cu(OH)_2CO_3^{2-}]
\end{aligned}
\tag{Equation 2.10}$$

Assuming  $Pb_3(OH)_2(CO_3)_2$  was the solid phase controlling lead release, the developed dissolved lead model is :

$$\begin{aligned}
[Pb]_T = & [Pb^{2+}] + 4[Pb_4(OH)_4^{4+}] + 2[Pb_2OH^{3+}] + [PbOH^+] + 3\{Pb_3(OH)_4^{2+}\} \\
& + 6\{Pb_6(OH)_8^{4+}\} + [Pb(OH)_2^0] + [Pb(OH)_3^-] + [Pb(OH)_4^{2-}] + [PbCO_3^0] \\
& + 3[Pb_3CO_3^{4+}] + 2[Pb_2CO_3^{2+}] + [Pb(CO_3)_2^{2-}] + [PbHCO_3^+] + [PbSO_4^0] \\
& + [Pb(SO_4)_2^{2-}] + [PbCl^+] + [Pb(Cl)_2^0] + [Pb(Cl)_3^-] + [Pb(Cl)_4^{2-}]
\end{aligned}
\tag{Equation 2.11}$$

### **Metal release empirical modeling**

A study sponsored by the AWWA Research Foundation and TBW was conducted to evaluate the effect of blending water supplies on the deterioration of water quality within the distribution systems (Taylor, J.S., et al 2005). Data obtained from two years of continuous operation were used to develop statistical linear and nonlinear relationships that described the metal release in terms of source water quality. Copper, lead, and iron release models have been developed (shown below) to analyze different blends of source waters and identify a feasible range of blends that satisfy the water quality required for control of copper, lead, and color release. (Imran, S.A., et al 2006).

#### *Iron release empirical model*

It was determined that effluent values for apparent color were well correlated with total iron concentrations (Shown in equation 2.12). Because of the high coefficient of correlation (R

Square = 0.82) between apparent color and total iron concentrations, effluent values for apparent color was used in this study as a substitute measurement for total iron.

$$Fe = 0.0132 \times \text{Apparent Color} \quad (\text{Equation 2.12})$$

As shown in Equation 2.12, in the nonlinear regression color (iron) release model, Cl, sodium, sulfate, DO, temperature, HRT and alkalinity are statistically significant. (Imran, S.A., et al 2005a).

$$\Delta C = \frac{(Cl^-)^{0.485} (Na^+)^{0.561} (SO_4^{2-})^{0.118} (DO)^{0.967} (T)^{0.813} (HRT)^{0.836}}{10^{1.321} (Alkalinity)^{0.912}} \quad (\text{Equation 2.13})$$

Where

$\Delta C$  = increase in effluent values for apparent color in cpu  
 $Na, Cl, SO_4^{2-}$  = sodium, sulfates and chlorides respectively in mg/L  
 $Alk$  = alkalinity in mg/L as  $CaCO_3$   
 $DO$  = dissolved oxygen content in mg/L  
 $T$  = temperature in  $^{\circ}C$   
 $HRT$  = hydraulic retention time in days

#### Copper release empirical model

As shown in Equation 2.14, the nonlinear copper release model indicates alkalinity, temperature, sulfate, silica and pH will significantly affect total copper release.

$$Cu = 0.28 + Temp^{0.72} \times Alk^{0.73} \times pH^{-2.86} \times (SO_4^{2-})^{0.10} \times SiO_2^{-0.22} \quad (\text{Equation 2.14})$$

Where

$Cu$  = total copper release in mg/L  
 $Temp$  = temperature in  $^{\circ}C$   
 $Alk$  = alkalinity in mg/L as  $CaCO_3$   
 $SO_4^{2-}$  = sulfate in mg/L  
 $SiO_2$  = silica in mg/L as  $SiO_2$

Both experimental data and empirical model showed increasing alkalinity will produce more total copper release than any other water quality parameters. Copper concentration increased with increasing temperature and sulfate. Increasing pH and silica were observed to decrease copper concentration for the conditions of this investigation (Xiao, W. 2004).

#### *Lead release empirical model*

Ten major parameters were chosen for multiple regressions to develop lead release model, e.g. alkalinity, pH, chloride, sulfate, DO, temperature, calcium, SiO<sub>2</sub>, conductivity, UV-254, and chloramine. A variety of regression functions were examined and evaluated. Temperature, alkalinity, pH, Cl and sulfate are statistically significant in lead release model, as shown in Equation 2.15.

$$Pb = 1.027^{(T-25)} (Alk)^{0.677} (pH)^{-2.726} (Cl)^{1.462} (SO_4^{2-})^{-0.228} \quad (\text{Equation 2.15})$$

*Where*

*Pb* = total lead release in mg/L  
*Alk* = alkalinity in mg/L as CaCO<sub>3</sub>  
*T* = temperature in °C  
*Cl* = chloride in mg/L  
*SO<sub>4</sub><sup>2-</sup>* = sulfate in mg/L

The statistical models indicate that increasing pH and sulfate will decrease lead release, while high alkalinity and chloride content will increase lead release. It is believed that confounding effect between pH and alkalinity is present since both of them varied with addition of acid or base: increasing pH came with increasing alkalinity, while low pH corresponded with low alkalinity.

### **Water Blending Effects**

Increasing demand of drinking water requires the exploration of additional water resources. Numerous studies founded that changeover to new source water or blending different source waters might alter the equilibrium conditions in pipelines, thereby causing sloughing of calcium carbonate and rust deposits that are stable and compatible to the existing source water. According to Kumpera, mixing water of different qualities can lead to a disintegration of the pipe-internal protective layers. If the distribution system and plumbing are not made of corrosion-resistant material, corrosion will take place and give rise to complaints about the deterioration in water quality. Subsequently the presence of corrosion products will form a refuge for the growth of microorganisms. Such organisms suspended in water together with corrosion products may cause taste and odor problems and make the water unpalatable for the consumer. (F. Kumpera, et al 1987)

In 1992, the city of Tucson, Arizona changed its source water from historical groundwater to surface water. This introduction of new source water changed the water quality in contact with the steady-state corrosion scale on the inner surface of the pipes. These changes led to the removal of the aerobic deposits on the interior of the pipes and led the anaerobic corrosion deposits exposed, which resulted in excessive taste, odor and color complaints (Malcom Pirnie Inc. 1997).

Imran (Imran, S.A., et al 2006) found that varying water quality to minimize iron release can lead to increased copper and lead release within the distribution system . For example, corrosion of copper and lead pipes was increased by increasing alkalinity, whereas increasing

alkalinity was beneficial in reducing the release of iron products from pipes. Increasing sulfates was found to reduce the release of lead but increased the release of iron. These conflicting water quality requirements for lead, copper, and iron release require evaluation of the tradeoffs between water quality and the corrosion response of all metals subject to corrosion in the distribution system.

The Paris Water Utility needed to blend nanofiltered water (37 MGD), with conventionally treated hard surface water (53 MGD). A 1-year research project has been conducted to select model to calculate the suitable dosage of soda ash (sodium carbonate) and contact time. The study found that blending of nanofiltered and surface finished waters resulted in carbonate imbalance in the water, which resulted in excessive lead and copper release. Experiments have shown that to obtain a stable pH, the necessary contact time before release to the distribution system can be as high as 7 min in cold-water conditions. The Hallopeau-Dubin model, which uses flow rate, temperature, conductivity, calcium hardness, alkalinity and pH as input parameters, led to very satisfactory results and could be generalized to other water mixtures. (Plottu-Pecheux, A., et al 2001)

## CHAPTER 3 METHODS AND MATERIALS

### Experimental Design

#### **Pilot distribution systems**

UCF has constructed an extensive research facility for investigation of distribution system water quality at the Cypress Creek Water Treatment Facility. This facility consists of seven pilot water treatment facilities, eighteen pilot distribution systems (PDSs) with individual sampling ports and cradles for individual coupon analyses, corrosion facility with eighteen copper and lead corrosion loops, a stainless steel food grade trailer for hauling water and laboratory trailers for field analyses and equipment storage. These facilities were unique and afford a highly capable research environment for evaluating and possibly anticipating water quality problems in distribution systems. Pictures of these facilities are shown in Figure 3.1, Figure 3.2, Figure 3.3 and Figure 3.4.



Figure 3.1 Tanker truck for surface water hauling and surface water storage tanks





Figure 3.2 Water production area and laboratory, storage and pilot trailers



Figure 3.3 Influent standpipes, feed pumps and coupon cradles



Figure 3.4 Corrosion shed and copper loops

As shown in Figure 3.1, a truck and a stainless steel food grade trailer was used to haul surface water to the pilot site. The surface water was obtained from the TBW regional surface water treatment plant and was stored in two 7000 gallon ( $26.5 \text{ m}^3$ ) storage tanks before being transferred to the finished water tank. The large process area used to prepare the finished waters is shown in Figure 3.2 and was covered by  $4400 \text{ ft}^2$  ( $409 \text{ m}^2$ ) of 6 inches (0.15 m) cement pad and hurricane rated roof. The trailers showed contained a reverse osmosis pilot plant, an electro-noise monitoring facility, a storage facility, and a field laboratory.

Figure 3.3 shows the influent standpipes which allowed direct input from the finished storage and inhibitor tanks. Peristaltic pumps were used to control the flow of water and inhibitors to the PDS as well as the flow to the cradles which were four inch (0.1 m) PVC pipes and used for housing coupons for surface characterization and microbiological studies. The majority of the PDS effluent was eventually directed to a corrosion shed, shown in Figure 3.4, which contained eighteen loops of copper pipes and lead coupons for the copper and lead corrosion study.

The pipes used in the PDSs traditionally received conventionally treated groundwater. Both the physical systems and pipe geometries selected represent typical scenarios experienced in a real distribution system. These PDSs were identical and consist of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series. The principal characteristics of the 14 PDSs used in this study are presented in Table 3.1. Each hybrid line was composed for: 20 feet of 6-inch PVC, 20 feet of 6-inch lined-ductile iron, 12 feet of 6-inch unlined cast iron, and, 40-feet of 2-inch galvanized steel.

Table 3.1  
Characteristics of PDSs 1-14

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

In the fourteen PDSs, PDS 1-12 received four different corrosion inhibitors at three different doses. The remaining two PDSs (PDS 13 and PDS14) received only pH adjustment. PDS 13 influent was adjusted to  $\text{pH}_s$  and PDS 14 influent was adjusted to  $\text{pH}_s + 0.3$ . PDS 13 and 14 served as controls or references for the project. All PDSs were provided with a sampling port after each pipe reach to allow an assessment of water quality changes associated with each pipe reach. A picture of the PDSs is shown in Figure 3.5.



Figure 3.5 Pilot Distribution System

The pilot distribution systems were operated to maintain a two-day hydraulic residence time (HRT). Standpipes were located at the beginning and end of each PDS to ensure the presence of water inside of the lines at all times. The standpipes were made from translucent plastic pipe that were 60 inches (1.5 m) long and had a diameter of 4 inches (0.1 m). The retention time in the PDS feed standpipe was 3.1 hours because of the low velocities associated with the two-day HRT. The standpipes as well as the peristaltic pumps were used to control the flow rate as shown in Figure 3.6.



Figure 3.6 Pilot distribution system headwork

### **Source and blend water quality**

Conventionally treated groundwater (GW), enhanced treated surface water (SW) and desalinated water by reverse osmosis (RO) were blended and fed to the PDSs. The surface water

was actual finished surface water from the Regional Surface Water Treatment Facility that was transported to the project site and the groundwater and desalinated water were obtained from the pilot water treatment systems at the project site. The description of the three finished source waters is presented in Table 3.2.

Table 3.2  
Finished source water descriptions

Source Water	Source	System Description
GW	Groundwater	Ground water source. Treatment by aeration, disinfection by free chlorine with a residual of 5 mg/L after a 5 minute contact time. 5.0 mg/L chloramine residual.
SW	Surface water	TBW treatment plant: Treatment by ferric sulfate coagulation, flocculation, settling, filtration, disinfection by ozonation and chloramination. Project site: adjustment of chloramine residual to 5.0 chloramine residual.
RO	Groundwater	Treatment by membrane reverse osmosis, aeration, disinfection by free chlorine with a residual of 5 mg/L after a 5 minute contact time. 5.0 mg/L chloramine residual.

#### *Groundwater (GW)*

The groundwater (GW) pilot unit was designed to simulate the finished water of member governments that utilize conventional treatment of ground water. The GW unit used the Cypress Creek well field as a raw water source. The main unit processes were aeration, disinfection, and pH stabilization. Before disinfection, GW was aerated to reduce hydrogen sulfide, produce an

aerobic water supply, and stabilize the water with respect to calcium carbonate. Aeration was achieved in GW by pumping the raw water to the top of the finished water tank through a nozzle that sprayed the water inside the tank.

#### *Surface water (SW)*

Surface water (SW) was treated at the TBW Regional Surface Water Treatment Facility by enhanced coagulation, ozonation, biologically activated carbon (BAC) filtration, aeration, and chloramination. The SW was hauled weekly to the field facility for use and temporarily stored in two 7000 gallon (26.5 m<sup>3</sup>) storage tanks, before being transferred to the SW finished water tank.

#### *Reverse osmosis water (RO)*

Reverse osmosis (RO) treatment pilot system produced finished water that was described as RO. The RO pilot plant utilized raw groundwater for the feed stream and required the addition of TDS, calcium, and alkalinity to the RO permeate to represent the finished water produced by the TBW Regional Desalination Facility.

#### *Blend finished water*

The project was divided into 4 phases; each of three months duration. Three different blends of GW, SW, and RO were investigated during the project. All PDSs received the same blend composition for a three month period or phase. At the end of each three month period the blend composition was changed as shown in Table 3.3.

Table 3.3  
Blend ratios of GW, SW, and RO waters used during project

Phase	Time Period	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

The blends had different water quality due to the variation of the ratios of the main water sources used in the blends. But the blend ratios during phases I and III were identical. The reason for repeating the blend was to evaluate seasonal effects. The timing of the phases with the repeated blend was designed to capture the largest temperature variation during the year.

Water quality was monitored after each batch was produced to ensure they met target water quality objectives designed to mimic the actual and expected TBW blended water quality as shown in Table 3.4. The treated source water quality and resulting blend water quality is shown in Table 3.5

Table 3.4  
Water quality objectives for finished process waters

Parameters	GW	SW	RO	Blend
pH	pH <sub>s</sub> + 0.3	>pH <sub>s</sub>	>pH <sub>s</sub>	>pH <sub>s</sub>
Total Hardness (mg/L as CaCO <sub>3</sub> )	240	60 min	60 min	60 min
Alkalinity (meq/L)	4	1 min	1 min	1 min
Total Cl <sub>2</sub> (mg/L as Cl <sub>2</sub> )	4.0	4.0	4.0	4.0
Na (mg/L)	80 max	80 max	80 max	80 max
SO <sub>4</sub> & Cl <sup>-</sup> (meq/L)	3.8 max	3.8 max	3.8 max	3.8 max
TDS (mg/L)	500 max	500 max	500 max	500 max
Color (CPU)	15 max	15 max	15 max	15 max
TOC (mg/L)	3.6 max	3.6 max	3.6 max	3.6 max

Table 3.5  
Source and blend water quality

Parameter	Units	GW	RO	SW	WQ1	WQ2	WQ3
pH		7	8.3	7.8	7.3	7.6	7.5
TDS	mg/L	420	310	305	377	337	352
HCO <sub>3</sub>	mg/L as	215	50	80	160	113	128
Ca	mg/L as	225	50	75	165	113	130
Mg	mg/L as	15	30	20	18	20	20
Na	mg/L	5	71	50	24	40	36
Cl	mg/L	15	95	10	22	21	29
SO <sub>4</sub>	mg/L	15	30	100	40	69	52
Si	mg/l as SiO <sub>2</sub>	20	20	5	16	11	14
TOC	mg/L C	3	0.3	2	2.4	2.1	2.1
NH <sub>2</sub> Cl	mg/L Cl <sub>2</sub>	4	4	4	4	4	4

### **Zinc orthophosphate inhibitor**

Zinc orthophosphate inhibitor was dosed in PDS 7-9. The dose rate of ZOP for a given PDS, was held constant for one year of investigation. The target doses of the inhibitors were defined as: 0.5, 1.0, and 2.0 mg/L as P. The stock solutions of the corrosion inhibitors were diluted in a 40 gallon (151 m<sup>3</sup>) tank prepared twice a week, and the feed rates of the diluted inhibitor solution were calibrated to deliver the low, medium, and high inhibitor target concentration.

The zinc orthophosphate inhibitor used in this study is CP630 (Sweetwater Technologies, Temecula, CA). It was made by dissolving zinc sulfate into phosphoric acid solution. The product has a ratio of 1 part Zinc to five parts PO<sub>4</sub> with a target of 6% as Zinc and 30% as PO<sub>4</sub>. It was a clear acidic liquid with slight odor. The bulk density of the liquid was 10.81 lbs/gal and the specific gravity was 1.41. The pH of the product was less than 1. Table 3.6 shows a summary



of the properties of the ZOP inhibitor along with manufacture recommendations for use and storage.

Table 3.6  
ZOP inhibitor properties

Property	Value
Manufacturer	Sweetwater Technologies
Product	CP 630
Percent Orthophosphate	30%
Percent Zinc	6%
Bulk Density	10.8 lbs/gal
Specific Gravity	1.41
pH	< 1
Recommended dose (range)	2-3 ppm
Used dose (low-med-high)	0.5-1.0-2.0 mg/L as P
Recommended pH range	around 7, < 8
Storage limitation	No reversion, very cold weather cause precipitation. Good for <6 months, best at 3 month

### **Data Collecting and Analysis**

Samples were collected and analyzed in the field and at the UCF laboratory. Monitoring and analyses of many physical, chemical and biological water quality parameters was carried out on the influent and effluent to each of the fourteen PDS, cradles and corrosion lines. The data collection was done for one year of operation. Data collection for one year is critical to understanding the seasonal variation of the blends, microbial activity and water quality parameters.

Weekly analyses were completed in the field laboratory and samples were also brought back to UCF laboratory for analysis. 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 determine whether the results were acceptable.

### **PDS chemical and physical water quality characterization**

The fourteen PDSs and stored source waters were monitored for physical and chemical water quality as shown in Table 3.7. The general water quality varied in sets of four, as there were four phases to the project. Parameters such as free and total chlorine, free ammonia, ortho-phosphorus and silica were monitored at least 3 times a week, and more if necessary.

Table 3.7  
Chemical and physical water quality parameters

General	N & P Forms	Anions-Metals- regulatory/aesthetic
Flow	TKN	Silica
Alkalinity	NH3 N	Calcium
pH Color	Org N	Magnesium Sodium
Apparent Color	NO3	Chlorides
Temperature	NO2	Sulfates
Turbidity	TP	TDS
Total and Free Chlorine	OP	NPDOC
Dissolved Oxygen		Iron
		Total Lead
		Total Copper

Weekly to quarterly samples were taken as needed and analyzed in the laboratory and on-site as needed. Free and total chlorine, temperature, turbidity, UV254 (organic content), apparent color, DO, conductivity and pH were analyzed on site. Analytical procedures as stated in the 19th Edition of Standard Methods were utilized, as shown in Table 3.8.

Table 3.8  
Analytical procedures utilized and ranges/reporting limits

Parameter	Method	Method Reference	Approximate Range
Chlorine, free	DPD colorimetric	SM 4500-Cl G or Hach 8021	0.1 - 2 ppm
Chlorine, total	DPD colorimetric	SM 4500-Cl-G or Hach 8167	0.1 - 2 ppm
UV-254	UV spectrometry	SM 5910 A	0-0.5200 cm-1
Temperature	Direct reading		0 - 100 deg C
Oxygen, Dissolved (DO)	Membrane probe	SM 4500-O G	0.1 - 20 mg/L
Turbidity	Nephelometric	SM 2130 B	0.02 - 200 ntu
Color, apparent	Visual Comparison (by spectrometer)	SM 2120 B	1 - 50 cpu
pH	Electrometric Method	SM 4500-H+ B	0.1 pH units
Total Iron	Electrothermal Atomic Absorption	SM 3113	Reporting limit: 0.01 mg/L
	Direct Air/Acetylene Flame AAS	SM 3111B	Reporting limit: 0.3 mg/L

\*All techniques designated with “SM” referenced in Standard Methods are from the 19th Edition (1995).

### Corrosion loops

A corrosion shed was built that housed eighteen corrosion loops. A portion of the flow from each PDS discharged to a designated corrosion loop to simulate a consumer environment and tap monitoring for LCR (lead and copper rule) compliance. The corrosion loop consisted of 30 feet (9.1 m) copper tubing with a diameter of 1.6 cm (5/8 inch), which could hold approximately 1.8 L of water. One lead-tin coupon was placed within the copper tubing between two standard copper tube fittings (brass) for each loop system. All other fittings and materials

were PVC or other plastic polymers. The coupons had a surface area of 3.38 square inches (21.8 cm<sup>2</sup>). Assuming that 1/8th inch (3.2 mm) bead on the inside of each 0.5 inch (1.27 cm) diameter joint was the surface area exposed to water using solder, the coupon surface area was equivalent to 17 joint-ends or 7 to 8 fittings and was reasonable for a kitchen sink.

To simulate the water that is delivered to customers, the corrosion loop units received water after passing through the associated pipe distribution system. The corrosion loops were flushed with 2 gallons (7.6 L) of water every morning. The effluent of the copper loops was monitored regularly for copper and lead release. Samples were usually taken weekly with extra samples taken when needed for specific purposes. To sample the copper loops, a 1 liter sample was collected after six hours of water stagnation, shaken to mix completely, and then 125 ml of it was used for metal measurements. Various water quality parameters such as pH, alkalinity, chloride, sulfate, silicate, calcium, sodium, DO etc. were also monitored.

### **Surface characterization**

Surface characterization is a critical part of documenting the effects of zinc phosphate corrosion inhibitors on distribution system water quality. Surface characterization investigations were conducted using coupons made from the same pipes that were used to construct the PDSs. The galvanized steel coupons for surface characterization were rectangular and were housed in cradles which were developed following every PDS for surface characterization study. The length of the cradles was approximately 3m. Each cradle was connected in series to a pilot distribution system so that equivalent coupon, PDS water quality and flow velocity were maintained. The pipe coupon holders were easily removed from the cradles and replaced. The

holders were transported in a large plastic bin with the coupons still in place. The humidity in the bin was elevated by placing a wet sponge inside. The iron, copper and lead coupons for surface characterization study were also rectangular and were housed in the electrochemical trailer which received PDS effluent.

Changes in the coupons were documented through coupon incubation and surface characterization. The amounts of coupons of four pipe materials for four phases (i.e. Cast Iron, Galvanized Steel, Copper and Lead) are shown in Table 3.9.

Table 3.9 Number of pipe coupons for surface characterization

Material	Total Number of Coupons
Cast Iron	56
Galvanized Steel	56
Copper	56
Lead	56

For ZOP PDSs (PDS7, PDS 8 and PDS 9), a total of 48 coupons were prepared, installed, collected for all four phases. 16 coupons in the medium dose PDS (PDS8) were analyzed by surface characterization tests.

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.

#### *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.

### *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 thermionically 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 on the identification of chemical components, thus verifying indirectly the results of other detection techniques as 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, with adequate standards, 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.



## **CHAPTER 4**

### **EFFECTS OF ZINC ORTHOPHOSPHATE (ZOP) CORROSION INHIBITOR ON SURFACE CHARACTERISTICS OF IRON CORROSION PRODUCTS IN A CHANGING WATER QUALITY ENVIRONMENT**

#### **Abstract**

A study was conducted to determine the impact of ZOP inhibitor on iron release in a changing water quality environment and the role of zinc in ZOP inhibition. Three different doses of zinc orthophosphate (ZOP) inhibitor were added to blends of finished ground, surface and desalinated waters, which were input to existing pilot distribution systems (PDSs) over a one year period.

Surface composition of iron surface scales for iron and galvanized steel coupons incubated in different blended waters in the presence of ZOP inhibitor was analyzed by X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS). The associated and predictive equilibrium models were developed to gain insight into the controlling solid phase and the mechanism of ZOP inhibition and the role of zinc for iron release.

#### **Introduction and Literature Review**

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. In order to meet increasing consumer demand and more stringent environmental and drinking water regulations, Tampa Bay Water (TBW) has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use and provide for future growth in the region. To seek understanding of the issues

involved when multiple-source waters were blended, TBW and UCF has conducted research since 2000. The work had demonstrated that control of the scale or film in the existing distribution systems was essential 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 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. The film or barrier separates the bulk water from the metal surface and can be renewed by continuous addition of the corrosion inhibitor to the distributed finished water.

Numerous studies have been conducted to investigate iron corrosion products with or without impact of phosphate based inhibitors to elucidate mechanisms of iron release. It is generally believed that in the absence of corrosion inhibitor, red water was caused by reduction and dissolution of formed corrosion products (Kuch, A. 1988). Typical iron corrosion products formed on aged iron pipe surfaces can be described using three different layers: (a) a macroporous layer of black rust (magnetite,  $\text{Fe}_3\text{O}_4$ ) in contact with the metal, (b) a microporous film of mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species that covers the macrolayer, and (c) a top layer of red rust. In a large field scale project (Taylor, J.S., et al 2005), interior scales on PVC, lined ductile iron, unlined cast iron and galvanized steel were analyzed by X-Ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) after contact with varying water quality for 1 year.  $\text{FeCO}_3$ ,  $\alpha\text{-FeOOH}$ ,  $\beta\text{-FeOOH}$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  were identified. Soluble iron and  $\text{FeCO}_3$  transformation indicated  $\text{FeCO}_3$  solid was controlling iron release (Tang, Z., et al 2006). The

formation of  $\text{FeCO}_3$  is critical for the development of highly protective, corrosion-resistant scales in water distribution pipes (Sontheimer, H., Kolle, W. & Snoeyink, V.L. 1981).

When phosphate corrosion inhibitor was used, two portions of the protective film were formed on the pipe surface. The outer layer was composed of iron and calcium phosphate and provided a barrier to oxygen diffusion and electron conduction. This inner portion of the film may help to improve the adhesion of the phosphate film to the pipe surface and reduce the dissolution of iron (Moriarty, B.E. 1990). Another study also found that formation of a diffusion barrier layer impeding access of oxygen to the iron surface. The results of XPS analysis confirmed that the protective film contains a substantial amount of ferric phosphate ( $\text{FePO}_4$ ). (Koudelka, M., Sanchez, J. & Augustynski, J. 1982). Corrosion inhibiting films formed on iron in phosphate-containing solutions were depth profiled using Auger electron spectroscopy (AES). When divalent calcium ion was added to the solution, orthophosphate was incorporated into the film in significant amounts (Kamrath, M., Mrozek, P. & Wieckowski, A. 1993). The behavior of iron electrodes immersed in phosphate-containing solution was studied by scanning electron microscopy (SEM). Initially,  $\text{Fe}_3(\text{PO}_4)_2$  and  $\text{Fe}(\text{OH})_2$  were formed. Subsequently, these ferrous species were further oxidized to  $\gamma\text{-FeOOH}$ , the latter being transformed into  $\text{Fe}_2\text{O}_3$  in the passive region.  $\text{Fe}_3\text{O}_4$  was clearly present as an intermediate oxide structure between the ferrous and ferric species mentioned earlier (Giacomelli, C.D. 2004).

Zinc orthophosphate (ZOP) has been widely used for many years as a reliable, known and safe corrosion inhibitor. Some scholars believed that ZOP inhibitor passivated the surface of the pipe material by depositing a zinc phosphate film over the surface of the metal (Murray, W.B. 1970). Additional studies suggested that the presence of zinc in the inhibitor either

accelerated film formation or helped to form a better-quality film than regular phosphate films for inhibiting corrosion (Reese, W.J. 1962; Kleber, J.P. 1965; Powers, J.T., Cahalan, E.M. & Zalfa, A.J. 1966; Murray, W.B. 1970; Mullen, E.D. & Ritter, J.A. 1974; Mullen, E.D. & Ritter, J.A. 1980; Swayze, J. 1983; Bancroft, D. 1988).

However, several scholars held different opinions with respect to ZOP inhibitor passivation. Although Volk considered the presence of zinc in orthophosphate solutions reduced the preconditioning period to establish a film within pipes, he found that the reduction of zinc did not affect the effectiveness of the corrosion inhibitor (Volk, C., et al 2000). Several other studies that have compared zinc orthophosphate compounds versus simple orthophosphates have shown no significant benefit from zinc additives at operational dosage (HDR Engineering Inc 2001).

Zinc is an environmental concern because of the adverse effects of zinc on wastewater treatment facilities and its limits on the land disposal of sludge. Hence, it is important to understand the role of zinc, if any, in corrosion inhibition and especially in iron release in a variable water quality environment. The work described in this article summarize the characterization of iron surface scales for iron and galvanized coupons incubated in different blended waters in the presence of ZOP inhibitor. In addition, the development of associated and predictive equilibrium models provides insight into the mechanism of ZOP inhibition and the role of zinc regarding metal release in drinking water distribution systems.

## **Experimental Methods**

### **The pilot distribution systems (PDSs)**

An extensive research facility was constructed for this study, which consisted of seven pilot water treatment facilities, eighteen pilot distribution systems (PDSs) with individual sampling ports and cradles for individual coupon analyses, a corrosion facility with eighteen copper and lead corrosion loops, a stainless steel food grade trailer for hauling water and five trailers for housing of pilot facilities, chemical analyses and equipment storage.

The PDSs were designed to represent typical scenarios for changing water quality that were experienced in a real distribution system. Fourteen of the 18 PDSs were used in this work and were identical. Each PDS consisted of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series as shown in Figure 4.1. The PDSs were operated to maintain a two-day hydraulic residence time (HRT). Standpipes were located at the beginning and end of each PDS to maintain the presence of water inside of the lines at all times.



Figure 4.1 Pilot Distribution System

A corrosion shed was built that housed a corrosion loop that was paired with each PDS. A portion of the PDS effluent was discharged to the corrosion loop to simulate a consumer environment and tap monitoring for LCR (lead and copper rule) compliance.

### **The use of zinc orthophosphate (ZOP) inhibitor**

In the fourteen PDSs, PDS 1-12 received four different corrosion inhibitors at three different doses, while the influent to the remaining two PDSs was adjusted for pH treatment. PDS 13 was adjusted to  $\text{pH}_s$  and the PDS 14 was adjusted to  $\text{pH}_s + 0.3$ . Both of them served as controls or references for the investigation.

ZOP inhibitor was dosed in PDSs 7, 8 and 9. The dose rate of ZOP for a given PDS was held constant for one year of investigation. The target doses of the inhibitor were 0.5, 1.0, and 2.0 mg/L as P. The ZOP inhibitor used in this study was made by dissolving zinc sulfate into a

phosphoric acid solution at a ratio of 1 part Zinc to five parts PO<sub>4</sub> with a target of 6% as Zinc and 30% as PO<sub>4</sub>.

Orthophosphate (OP) inhibitor was dosed in PDS 4, 5 and 6. The target doses of the OP inhibitors were also 0.5, 1.0, and 2.0 mg/L as P. Since the presence of zinc is the major difference between ZOP inhibitor and OP inhibitor, comparison of the effects of OP inhibitor and ZOP inhibitor on iron release provided insight into the role of zinc in ZOP inhibition of iron release.

### Source and blend water quality

Conventionally treated groundwater (GW), enhanced treated surface water (SW) and desalinated water produced by reverse osmosis (RO) were blended and fed to the PDSs. The blends of GW, SW and RO were changed quarterly over one year as shown in Table 4.1. All PDSs received the same blend during each phase. The blend of phases I and III were identical in order to evaluate seasonal effects, which were predictable by water quality.

Table 4.1  
Blend ratios of GW, SW, and RO waters used during this project

Phase	Time Period	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

### **Data collecting and analysis**

Monitoring and analyses of several physical and chemical water quality parameters were carried out on the influent and effluent to each of the fourteen PDS, cradles and corrosion lines. The data collection was performed for one year of operation.

Surface characterization is a critical part of documenting the effects of ZOP corrosion inhibitor on iron release. Surface characterization investigations were conducted using coupons made from the same pipes that were used to construct the PDSs. The galvanized steel coupons for surface characterization study were rectangular and were housed in coupon holders which were placed following every PDS as shown in Figure 4.2. Iron coupons were purchased and housed in another cradle in a trailer which received PDS effluent.



Figure 4.2 Cradles for housing cast iron coupons for surface characterization



Surface characterization of 48 coupons were performed using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The XPS spectra patterns identify chemical components in the 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.

## **Results and Discussions**

### **Surface characterization by XPS**

The coupons exposed to ZOP, OP and pH inhibition were analyzed by XPS for comparison. The XPS scanning consists of a two-step process: the initial “survey” scan conducted over a broad range of energy levels to identify all possible elements present on the coupon and the high resolution scan, over a narrow range of energy levels, for establishing the chemical states present for a given element.

#### *Elemental analysis*

A representative XPS survey scan for an iron coupon exposed to a medium dose of ZOP inhibitor (1mg/L) is shown in Figure 4.3. O, Ca, C, Fe, P, Zn and Si are indicated on the survey by pronounced peaks. Specific compounds for each of these elements were identified using high resolution XPS scans.

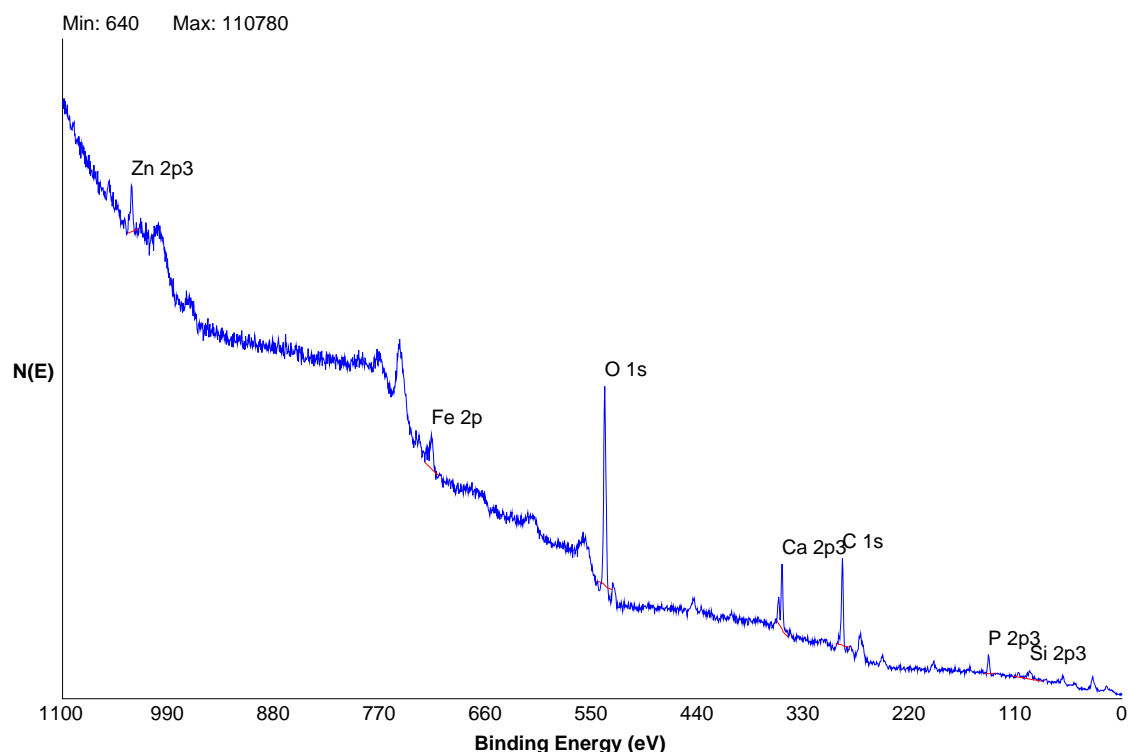


Figure 4.3 Representative XPS survey scan for an iron coupon exposed to ZOP inhibitor in Phase I

The number of coupons where each element was detected out of the total number of coupons exposed to ZOP inhibitor, OP inhibitor and pH control treatment are presented in Table 4.2. Carbon, calcium and oxygen were detected on most of the coupons, this is reasonable since carbonate alkalinity (carbon), calcium hardness and dissolved oxygen contained in the raw water may form calcium carbonate on iron scale. The fact that calcium was missing on seven of thirty two samples suggests that  $\text{CaCO}_3$  was not uniformly distributed throughout the iron scale. Given the nature of corrosion in distribution systems, it is not unusual to find non-uniform scales. Iron and oxygen were found in all scale samples. This was due to the initial presence of iron in all of

the coupons, which accounted for the uniform distribution of iron oxides throughout the iron coupon scales.

Table 4.2  
Number of coupons containing detected elements from XPS scan

Detected element	No. of coupons where indicated element was detected					
	Iron coupons			Galvanized steel coupons		
	ZOP (4 total)	OP (4 total)	pH (8 total)	ZOP (4 total)	OP (4 total)	pH (8 total)
Carbon (C)	4	4	8	4	4	8
Calcium (Ca)	3	3	6	4	2	7
Iron (Fe)	4	4	8	4	4	8
Oxygen (O)	4	4	8	4	4	8
Phosphorous (P)	3	3	0	3	3	0
Silicon (Si)	2	3	6	2	3	6
Zinc (Zn)	3	4	5	4	4	7

The presence of silicon in the scales of twenty two out of thirty two coupons indicates that the raw water silicon was at a high enough level to form scale on the iron and galvanized steel coupons. The detection of zinc on most of the galvanized steel coupons is not surprising due to the presence of zinc coating outside of the galvanized steel. However, contrary to iron, it would be possible to eventually leach all of the zinc out of a galvanized steel coating on an iron based pipe. The iron coupons were housed in a position after the unlined cast iron pipes and galvanized steel pipes of the PDSs, therefore zinc was identified on twelve out of sixteen iron coupons.

Phosphorus was detected in twelve of sixteen coupons exposed to phosphate based inhibitors and none of the sixteen coupons without inhibitor addition. This indicates that solid

forms of compounds containing solid phosphorus might exist and could be a barrier to iron release from iron and galvanized steel pipe.

#### *Identification of iron corrosion products*

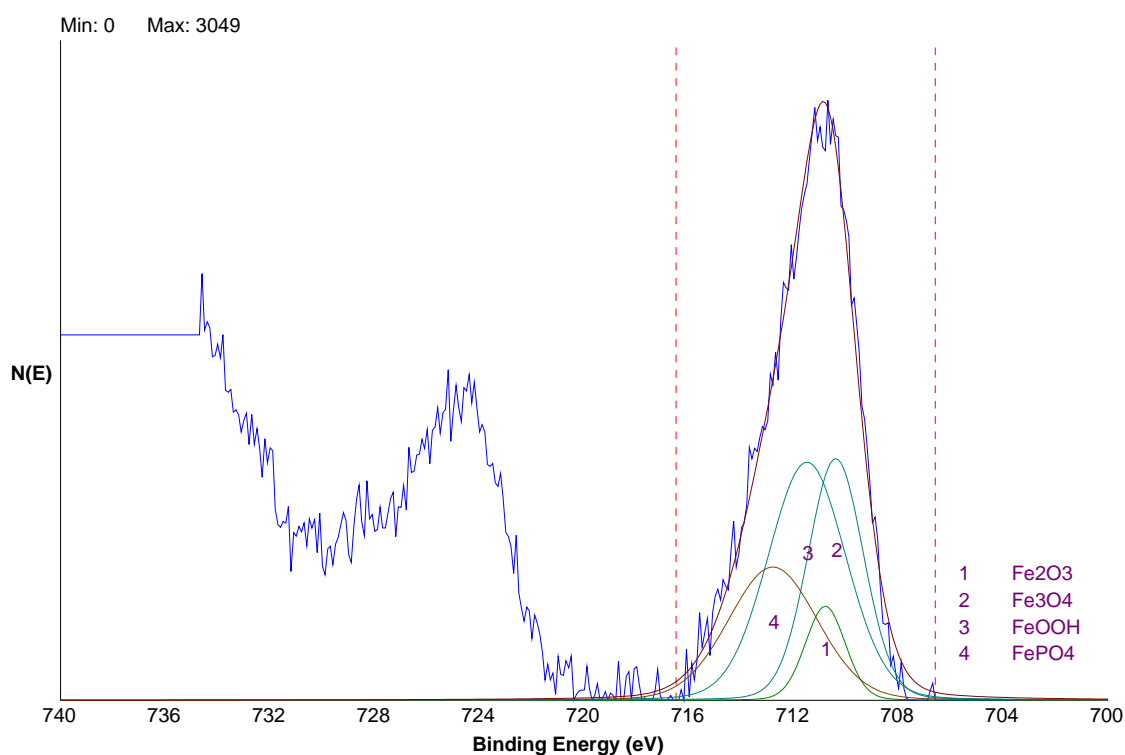


Figure 4.4 High-resolution XPS scan and deconvolution of Fe peak for a galvanized steel coupon exposed to ZOP inhibitor in Phase IV

High resolution spectra for iron components were deconvoluted to identify the specific corrosion products of iron on the surface and to determine their relative abundance as shown in Figure 4.4. 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 detected in the scale of the iron and galvanized steel coupons exposed

to the phosphate based inhibitors, while only ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), hydrated ferric oxide ( $\text{FeOOH}$ ) were found when no inhibitor was added. Ferric phosphate ( $\text{FePO}_4$ ) was only found on coupons exposed to phosphate inhibitors. Binding energies for ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and hydrated ferric oxide ( $\text{FeOOH}$ ) were 710.8, 710.4 and 711.5 eV respectively.

Relative distribution of identified iron corrosion products in the scale of the iron and galvanized steel coupons are illustrated in Figure 4.5 and Figure 4.6 respectively for each inhibitor using a bar and whiskers format. The bars represent the average while the whiskers represent the minimum and maximum of the four phases. The percentages represent the average relative fraction of each corrosion product in the scale for all 4 phases. Three treatments are compared in the graphs: OP inhibitor, ZOP inhibitor and pH adjustment treatment.

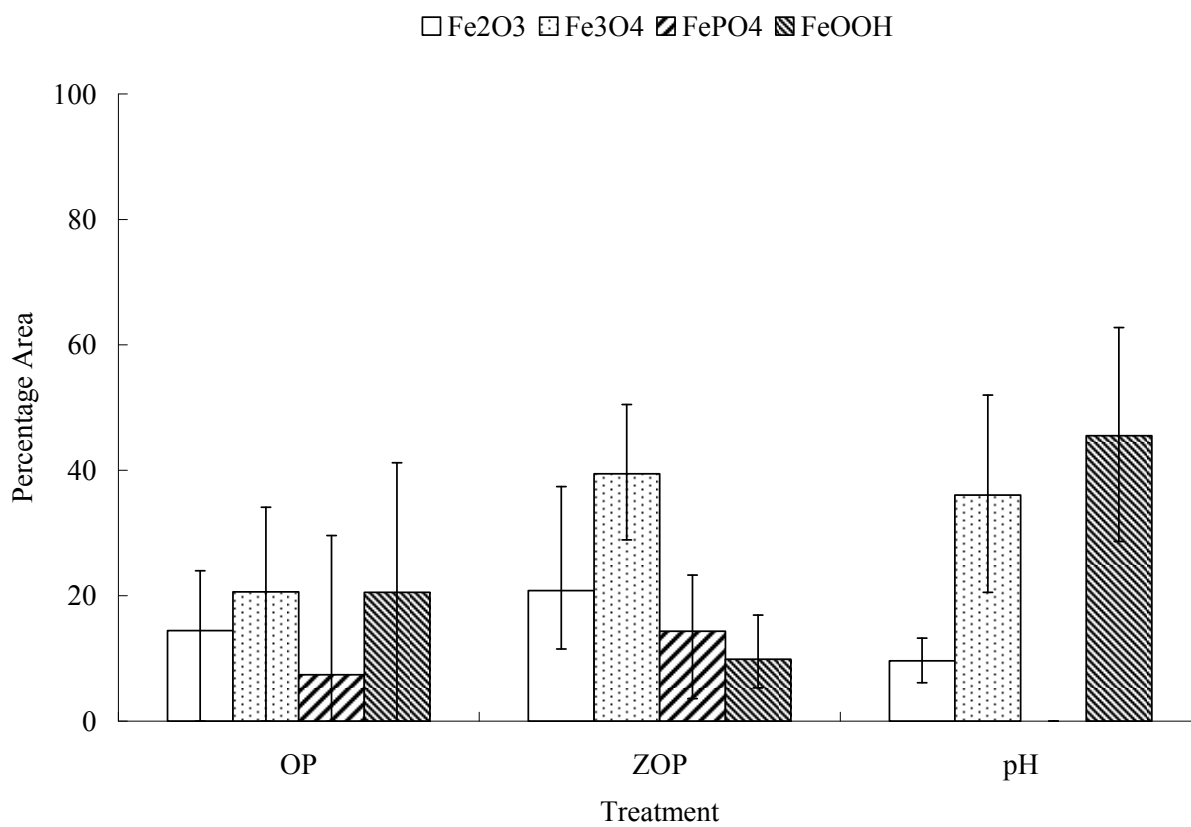


Figure 4.5 Average distribution of iron compounds for iron coupons

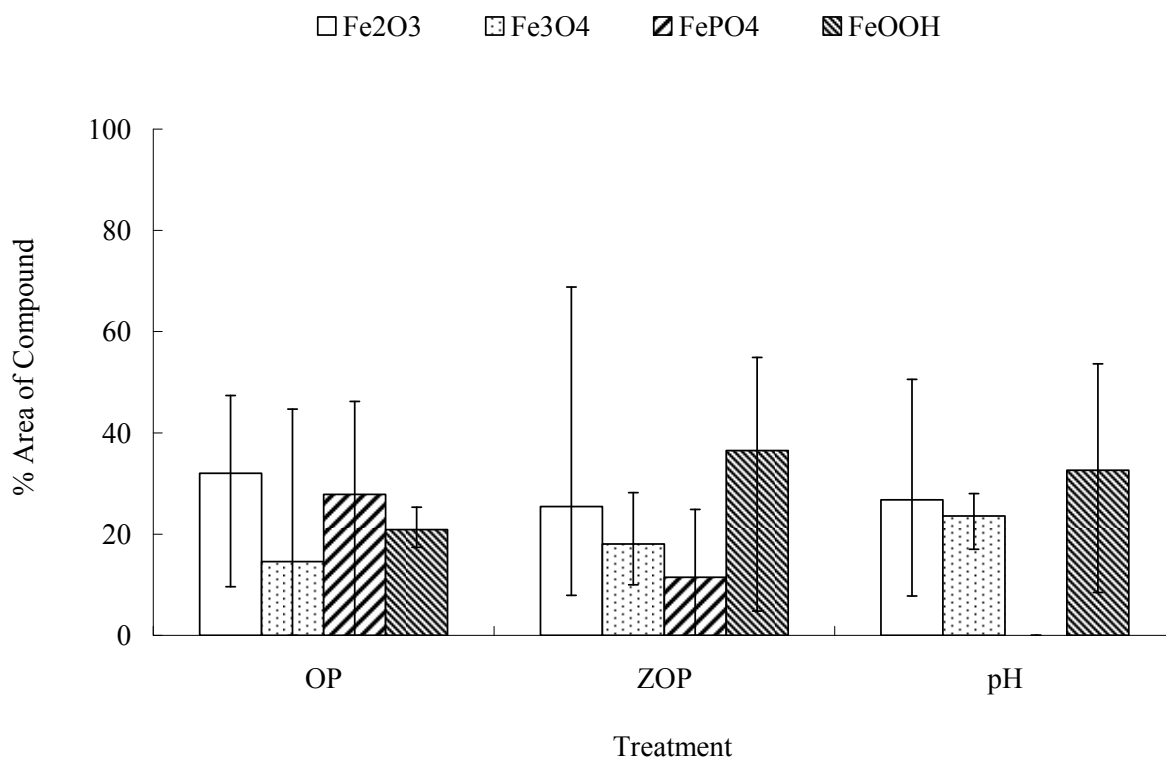


Figure 4.6 Average distribution of iron compounds for galvanized steel coupons

The data collected in this investigation indicate that the surfaces of iron and galvanized steel coupons contained a mixture of several different iron corrosion products, with no dominant iron compound being present. Such results are consistent with a corrosion mechanism that consists of the oxidation of zero valent iron to ferrous and ferric iron respectively. Ferrous carbonate has been shown to form in anaerobic conditions (Taylor, J.S., et al 2005); however ferrous carbonate tends to degrade to  $\text{Fe}_2\text{O}_3$  upon exposure to air before the XPS analysis. Although there was no evidence of correlation between ferric oxide ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and hydrated ferric oxide ( $\text{FeOOH}$ ) surface compounds and iron release in this work; iron oxides

were by far the greatest solid form of iron in the films and must be involved in the release of iron from iron and galvanized steel pipe.

As shown in Figure 4.5 and Figure 4.6, corrosion inhibitors like ZOP and OP do not appear to influence the proportion of each iron oxide present. However, ferric phosphate ( $\text{FePO}_4$ ) was only present among those samples where phosphate inhibition was present which suggests phosphate based inhibitors may produce a solid phosphate film which could inhibit iron release.

Comparison of the impacts of OP inhibitor and ZOP inhibitor on the average composition of the surface scale on both iron coupons and galvanized steel coupons doesn't reveal any significant difference. The percentage of ferric phosphate on iron coupon incubated in ZOP inhibitor was higher than in the OP inhibitor while the percentage on galvanized steel coupon in ZOP inhibitor was lower than in the OP inhibitor. Such results indicates that the mechanisms of inhibition of iron release for these two phosphate based inhibitors are quite similar and zinc doesn't participate in the formation of the phosphate film directly. However, zinc might still play an important role in ZOP inhibition and may accelerate and/or improve the phosphorus film formation process.

#### *Identification of zinc corrosion products*

Zinc deposits were present in the iron and galvanized steel scales for most samples. A majority of the zinc existed as zinc oxide ( $\text{ZnO}$ ) and zinc hydroxide ( $\text{Zn(OH)}_2$ ). The lack of zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) scale in the presence of ZOP indicates that zinc phosphate precipitation was not a factor in inhibiting iron release.



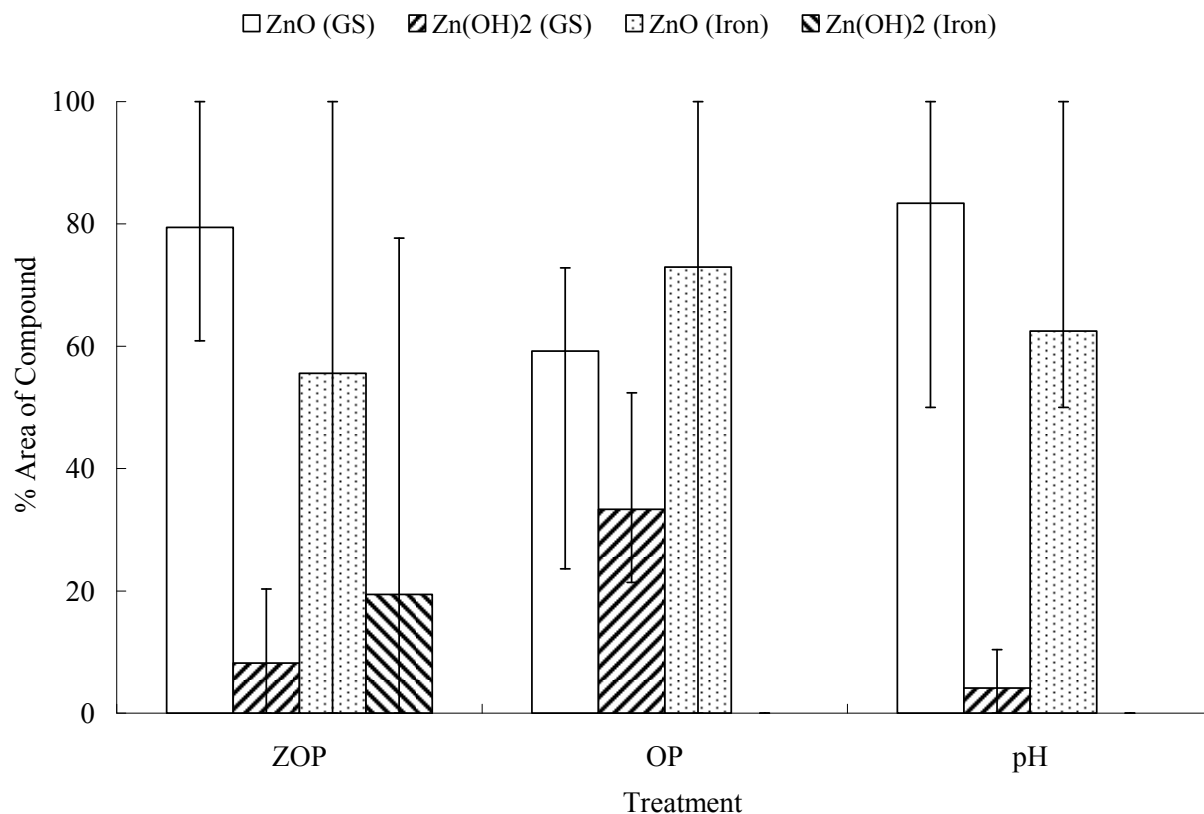


Figure 4.7 Average distribution of zinc compounds for iron and galvanized steel coupons

Relative distribution of identified zinc corrosion products in the scale of the iron and galvanized steel coupons is illustrated in Figure 4.7. Similarly, no evidence was found that corrosion inhibitors influence the proportion of each zinc compound significantly and no consistent trend can be found comparing the influences of ZOP inhibitor and OP inhibitor. Therefore, the zinc present in the scales was mostly released from galvanized steel pipe as mentioned previously but not from zinc in the ZOP inhibitor. The contribution from zinc in ZOP inhibitor for iron release inhibition is not clear in terms of zinc corrosion products distribution.

### *Effects of varying water quality*

The relationship of phase water quality and the relative composition of the iron compounds in the scale on the iron and galvanized steel coupons was evaluated for each identified iron compound. No significant relationship was found between phase water quality and the percentage of the three iron compounds found in the surface scale. Hence variation in phase water quality (84 mg/L-175 mg/L as  $\text{CaCO}_3$  alkalinity, 35.4 mg/L to 122.9 mg/L Cl and 136 mg/L-252 mg/L as  $\text{CaCO}_3$  total hardness) did not affect the relative distribution of the solid iron compounds found in the scale of the iron and galvanized steel coupons.

### **Surface characterization by SEM/EDS**

Iron and galvanized steel coupons exposed to ZOP inhibitor was also analyzed by SEM/EDS. SEM is capable of producing high magnification images of solid materials with a high depth of field. Theoretically, under certain circumstances, the crystalline structure could be observed clearly resulting in the identification of chemical components present. However, the corrosion layer formed in water solution may not exhibit the legible crystalline structures, but only the amorphous state within a short-term incubation. In this case, SEM can still provide information to determine if the corrosion scale is homogeneous or a result of pitting and whether the corrosion layer formed is compact or porous. EDS can provide rapid qualitative or quantitative analysis, with adequate standards, of elemental composition with a sampling depth of 1-2 microns. Representative images obtained from SEM/EDS analysis on different locations of iron and galvanized steel coupons incubated in ZOP inhibitor are presented in Figure 4.8, Figure 4.9 and Figure 4.10.

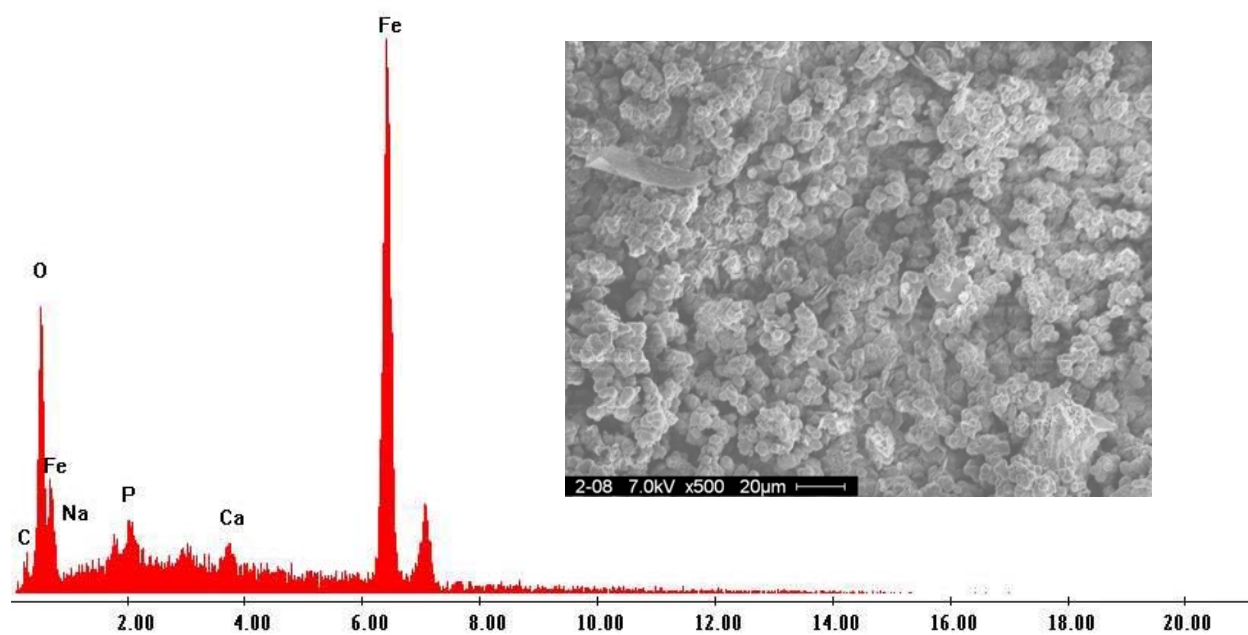


Figure 4.8 7.0kV x500 SEM image of location A for a galvanized steel coupon in Phase II and corresponding EDS analysis results

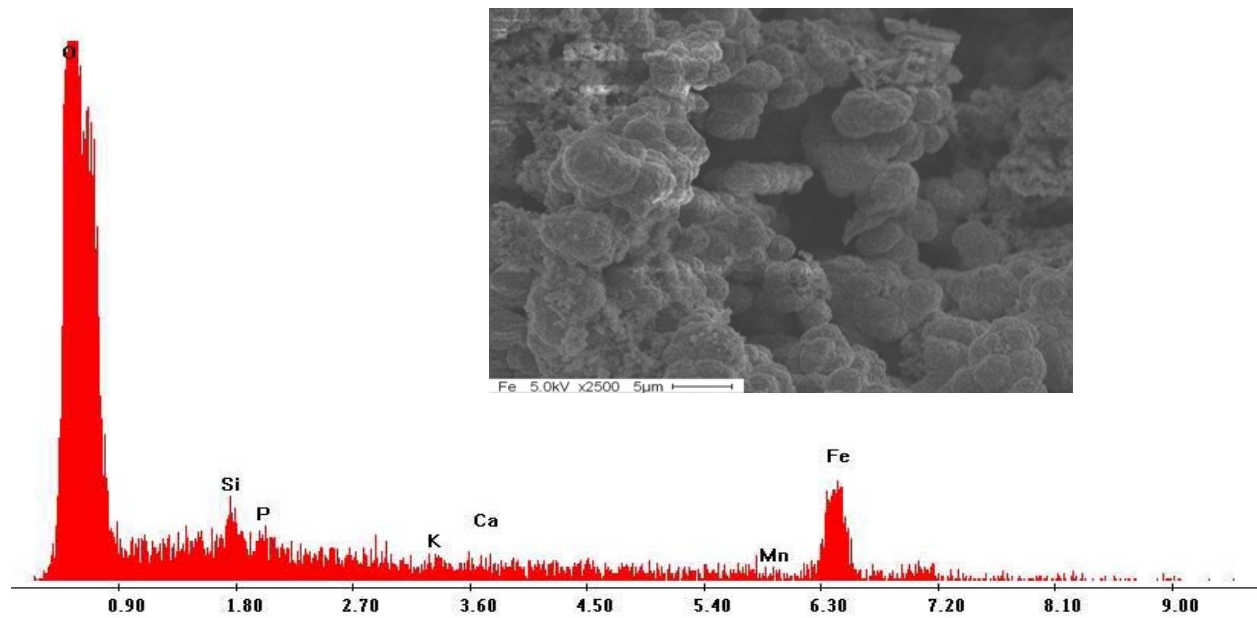


Figure 4.9 5.0kV x2500 SEM image of location **B** for an iron coupon in Phase II and corresponding EDS analysis results

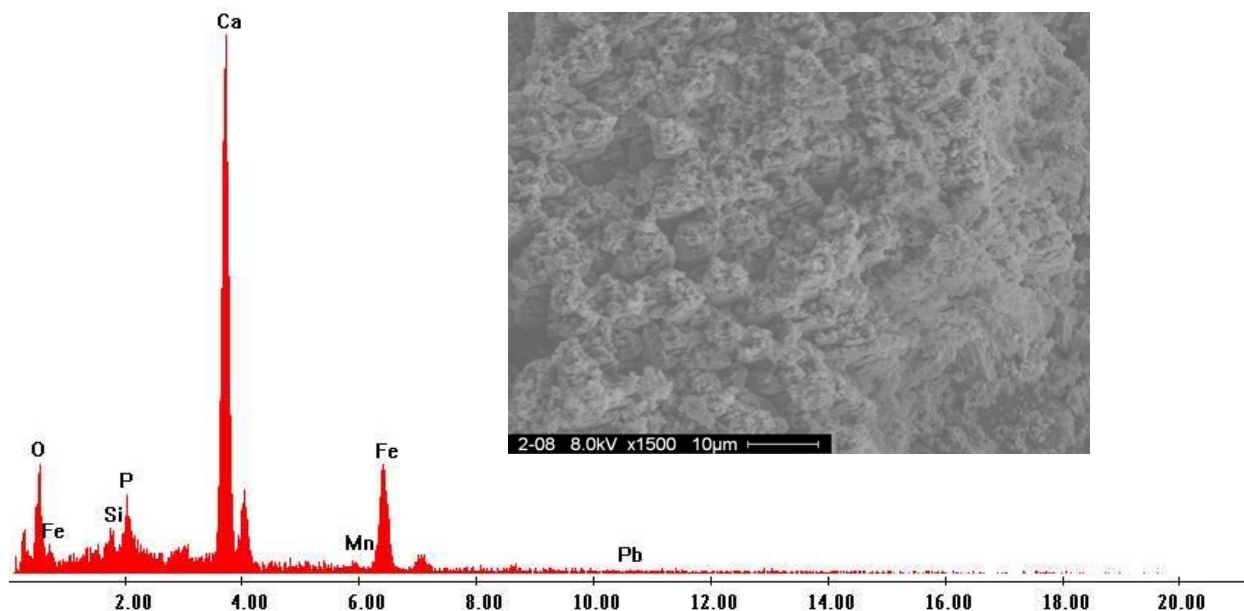


Figure 4.10 8.0kV x1500 SEM image of location B for an iron coupon in Phase I and corresponding EDS analysis results

As shown in these images, corrosion scales formed on iron and galvanized steel coupons were not uniform. That is, a different location may have different scale structures and differing elemental composition. Figure 4.7 exhibits location A of a galvanized steel coupon exposed to medium dose of ZOP inhibitor for Phase II, the scales appear to be porous and EDS revealed the composition was predominantly Fe with lesser amounts of O, P and Ca. While Figure 4.10 indicated that most of the scale structures at the analyzed location were composed of Ca, with small amounts of Fe, O and P, and sometimes with traces of Si and Mn.

Although the dominant element varies with the analyzed location, phosphorus was detected on most coupons incubated in ZOP inhibitor. This result was consistent with previous

conclusions: solid phosphate films are present and are likely a primary means of corrosion inhibition for phosphate based inhibitors. Zinc was seldom identified by SEM analysis. This may be limited by the surface characterization technique.

### **Thermodynamic modeling**

Iron release from pipe surfaces may be predicted by the solubility of solid phases formed within the corrosion scales. The XPS analysis of iron and galvanized steel coupons revealed the possible controlling solid forms that may be responsible for iron release. Thermodynamic models were constructed by assuming different iron solid was the controlling solid phase. Dissolved iron concentrations were calculated by assuming free dissolved iron is in equilibrium with the controlling solid phase. Concentrations of other dissolved iron complexes were determined using the appropriate equilibrium constants. This thermodynamic approach is limited to a prediction of dissolved iron, and will under predict total iron release because most of the iron was present in a particulate form.

The XPS analysis of iron coupons exposed to phosphate-based inhibitors revealed the presence of ferric phosphate ( $\text{FePO}_4$ ) as a solid compound on the surface. Investigation of ferric phosphate as the possible controlling solid phase of dissolved iron showed that the calculated iron concentrations by the ferric phosphate model ( $\text{FePO}_4$ ) were much lower (10,000 times) than the actual dissolved iron concentrations and those calculated by the siderite ( $\text{FeCO}_3$ ) model which was proposed in the previous TBW project (Taylor, J.S., et al 2005). Hence, still assuming siderite was the controlling solid phase, the developed thermodynamic model for dissolved iron release in the presence of ZOP inhibitor is shown in Equation 4.1 and calculated iron

concentrations by both  $\text{FePO}_4$  and  $\text{FeCO}_3$  models were compared to actual dissolved iron in Table 4.3.

$$\begin{aligned} Fe = & [\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{Fe}(\text{OH})_2^0] + [\text{Fe}(\text{OH})_3^-] + [\text{FeHCO}_3^+] + [\text{FeCO}_3^0] \\ & + [\text{FeSO}_4^0] + [\text{FeCl}^+] + [\text{FeH}_2\text{PO}_4^+] + [\text{FeHPO}_4^0] \end{aligned} \quad (\text{Equation 4.1})$$

The model development was based on the assumption that the ORP was 0.43V (the average of all the phases of water quality) and at a temperature of 25°C. Under these conditions, ferric species were ignored in model development since  $\text{Fe}^{2+}$  concentrations were much more abundant than  $\text{Fe}^{3+}$ .

Table 4.3  
Iron thermodynamic modeling for ZOP inhibitor

Inhibitor	Phase	Actual Iron Release (mg/L)		Modeled Iron Release (mg/L)	
		Dissolved Fe	Total Fe	$\text{FePO}_4$	$\text{FeCO}_3$
ZOP	1	0.04	0.14	1.1E-05	0.12
	2	0.01	0.23	1.7E-05	0.27
	3	0.01	0.22	7.6E-07	0.13
	4	0.00	0.24	3.0E-07	0.21

Predicted dissolved concentrations by the siderite model slightly over predicted actual release. This suggests that dissolved iron release was not solely dependent on  $\text{FeCO}_3$  but rather may depend on  $\text{FePO}_4$  or other iron phosphate solids which form and reduce iron release with ZOP inhibitor addition. 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 which reduce the rate of iron release, while the equilibrium iron concentration remains unchanged.

### **Conclusions**

Surface composition of scales on cast iron and galvanized steel coupons was analyzed by XPS and SEM to gain insight into the controlling solid phase and mechanism of iron release with ZOP 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 phosphate based inhibitors and were found to be uniformly distributed throughout the iron 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 in this work, however iron oxides were by far 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 iron coupons. This suggested phosphate based inhibitors may produce a solid phosphate film which could be a barrier to iron release from pipe materials and consequently inhibit iron release.

A majority of the zinc identified in the surface scale on iron and galvanized steel coupons existed as zinc oxide ( $\text{ZnO}$ ) and zinc hydroxide ( $\text{Zn}(\text{OH})_2$ ). The lack of zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) scale in the presence of ZOP indicates that zinc phosphate precipitation was not a factor in inhibiting iron release by ZOP inhibition. It was found that the zinc present in the scales was mostly released from galvanized steel pipe rather than from zinc in the ZOP inhibitor.



Comparison of the impacts of OP inhibitor and ZOP inhibitor indicated zinc doesn't participate in the formation of the phosphate film directly.

Variation of phase water quality did not significantly affect the distribution of solid iron forms in the films, which suggests that variations in water quality in this work would not adversely affect iron release.

Thermodynamic equilibrium models for iron release were developed and evaluated relative to the actual and predicted iron release. The model confirmed that the presence of a phosphate-based solid contributes to the reduction of iron release and is likely a primary means of corrosion inhibition for phosphate based inhibitors.

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## **CHAPTER 5**

### **EFFECTS OF ZINC ORTHOPHOSPHATE (ZOP) CORROSION INHIBITOR ON TOTAL IRON RELEASE IN A CHANGING WATER QUALITY ENVIRONMENT**

#### **Abstract**

A study was conducted to determine the impact of ZOP inhibitor on iron release in a changing water quality environment and the role of zinc in ZOP inhibition. Three different doses of zinc orthophosphate (ZOP) inhibitor were added to blends of finished ground, surface and desalinated waters, which were input to existing pilot distribution systems (PDSs) over a one year period.

Development of empirical models for total iron release and mass balances for zinc and phosphorus provided insight into the mechanism of ZOP inhibition and the role of zinc regarding iron release in drinking water distribution systems.

#### **Introduction**

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. In order to meet increasing consumer demand and more stringent environmental and drinking water regulations, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use and provide for future growth in the region. TBW and UCF have conducted research to seek understanding of the issues involved when multiple-source waters were blended since 2000. The work had demonstrated that control of the scale or film in the existing distribution systems was essential 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 using corrosion inhibitors. Corrosion inhibitors offer an opportunity for scale control because they bond directly with the elemental metal or scale and form a barrier on the pipe surface. The film or barrier separates the bulk water from the metal surface and can be renewed by continuous addition of the corrosion inhibitor to finished water.

Phosphate inhibitors have been used for more than 60 years to prevent scale buildup and to control pipe corrosion. A nationwide utility survey conducted in 2001 (McNeill, L.S. & Edwards, M. 2002) reported that 56% of all responding utilities add phosphate inhibitors in 2001, 50% of utilities currently dose inhibitors for iron corrosion or red water.

Numerous studies found that phosphate based inhibitors could prevent iron corrosion related problems (McNeill, L.S. & Edwards, M. 2001). The specific mechanisms of inhibition were not clear. However, formation of a solid phosphate film or scale that inhibited iron release following addition of phosphate based inhibitors was suggested by the same group in another article.

A total iron release empirical model was developed in a large field scale project funded by Tampa Bay Water (TBW) and AwwaRF, (Taylor, J.S., et al 2005), which related water quality to iron release. Analysis of variance (ANOVA) methods were employed to identify those water quality variables that were significant in the empirical models at a confidence level of 95 % ( $\alpha = 0.05$ ). Independent variables that did not meet this level of significance were omitted from the models. Apparent color was correlated with total iron release as shown in Equation 5.1 (Imran, S.A., et al 2005a). The water quality model for total iron release is shown in Equation 2.

Increasing alkalinity has a beneficial effect on iron release control. Sulfate, chloride, sodium, DO, temperature, and HRT were all found to have a positive correlation with iron release. pH did not have a significant effect on iron release due to the water being stabilized with respect to  $\text{CaCO}_3$  solubility.

$$Fe = 0.0132 \times \text{Apparent Color} \quad (\text{Equation 5.1})$$

$$\Delta C = \frac{(Cl^-)^{0.485} (Na^+)^{0.561} (SO_4^{2-})^{0.118} (DO)^{0.967} (T)^{0.813} (HRT)^{0.836}}{10^{1.321} (\text{Alkalinity})^{0.912}} \quad (\text{Equation 5.2})$$

where:  $\Delta C$  = CPU  
 Alkalinity = mg/L as  $\text{CaCO}_3$   
 $SO_4^{2-}$  = mg/L  
 $Cl^-$  = mg/L  
 $Na^+$  = mg/L  
 DO = dissolved oxygen, mg/L  
 T =  $^{\circ}\text{C}$   
 HRT = hydraulic residence time, days

Zinc orthophosphate (ZOP) has been widely used for many years as a reliable, known and safe corrosion inhibitor. ZOP is generally believed to produce a microscopic film on metal surfaces that acts as a barrier to corrosive environments. Some studies suggested that the presence of zinc in the inhibitor either accelerated film formation or helped to form a better-quality film than regular phosphate films for inhibiting corrosion (Reese, W.J. 1962; Kleber, J.P. 1965; Powers, J.T., Cahalan, E.M. & Zalfa, A.J. 1966; Murray, W.B. 1970; Mullen, E.D. & Ritter, J.A. 1974; Mullen, E.D. & Ritter, J.A. 1980; Swayze, J. 1983; Bancroft, D. 1988).

There are, however, several scholars held different opinion for the effectiveness of ZOP inhibitor especially for the role of zinc. Although Volk considered the presence of zinc in

orthophosphate solutions reduced the preconditioning period to establish a film within pipes, he found that the reduction of zinc did not affect the effectiveness of corrosion inhibitor (Volk, C., et al 2000). Several other studies that have compared zinc orthophosphate compounds versus simple orthophosphates have shown no significant benefit from zinc additives at operational dosage (HDR Engineering Inc 2001).

Zinc is an environmental concern because of the adverse effects of zinc on wastewater treatment facilities and its limits on the land disposal of sludge. Hence, it is important to understand the role of zinc, if any, in corrosion inhibition and especially in iron release in a variable water quality environment.

### **Experimental Methods**

#### **The pilot distribution systems (PDSs)**

An extensive research facility constructed for this study consisted of seven pilot water treatment facilities, eighteen pilot distribution systems (PDSs) with individual sampling ports and cradles for individual coupon analyses, a corrosion facility with eighteen copper and lead corrosion loops, a stainless steel food grade trailer for hauling water and five trailers for field, housing of pilot facilities, chemical analyses and equipment storage.

The PDSs were designed to represent typical scenarios experienced in a real distribution system. These PDSs were identical and consist of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series. A picture of the PDSs is shown in Figure 5.1. The PDSs were operated to maintain a two-day hydraulic residence time (HRT). Standpipes were located at the beginning and end of each PDS to ensure the presence of water inside of the

lines at all times. All PDSs were provided with sampling ports after each pipe material to allow an assessment of water quality changes associated with each pipe material.



Figure 5.1 Pilot Distribution System

A corrosion shed was built that housed eighteen corrosion loops. Only fourteen of the PDSs and corrosion loops were used in this work. A portion of the flow from each PDS was discharged to the corrosion loop to simulate a consumer environment and tap monitoring for LCR (lead and copper rule) compliance. Only fourteen of the eighteen PDSs and corrosion loops were utilized in this work.

### **The use of zinc orthophosphate (ZOP) inhibitor**

In the fourteen PDSs, PDSs 1-12 received four different corrosion inhibitors at three different doses, while the remaining two PDSs were adjusted for pH treatment. PDS 13 was



adjusted to  $pH_s$  (The pH at which a water is saturated with  $CaCO_3$ ) and the PDS 14 was adjusted to  $pH_s + 0.3$ . Both of them served as controls or references for the investigation.

ZOP inhibitor was dosed in PDSs 7, 8 and 9. The dose rate of ZOP for a given PDS was held constant for one year of investigation. The target doses of the inhibitor were 0.5, 1.0, and 2.0 mg/L as P. The ZOP inhibitor used in this study was made by dissolving zinc sulfate into a phosphoric acid solution. The product had a ratio of 1 part Zinc to five parts  $PO_4$  with a target of 6% as Zinc and 30% as  $PO_4$  on a weight basis.

### **Source and blend water quality**

Conventionally treated groundwater (GW), enhanced treated surface water (SW) and desalinated water produced by reverse osmosis (RO) were blended and fed to the PDSs. The blends of GW, SW and RO was changed quarterly over one year as shown in Table 5.1. All PDSs received the same blend during each phase. The phases I and III were identical in order to evaluate seasonal effects, which were predictable by water quality.

Table 5.1  
Blend ratios of GW, SW, and RO waters used during this project

Phase	Time Period	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

### **Data collecting and analysis**

Influent and effluent water quality was monitored for each of the fourteen PDSs over the year of operation. Quality assurance and quality control of both the laboratory and field determinations of water quality parameters was accomplished by taking duplicate samples and repeating at least 10% of the analyses in the laboratory and field. Blind duplicates and spikes were also used to determine the accuracy of measurements. Dynamic control charts were used to monitor precision and accuracy of laboratory and field analysis.

PDS influent water quality was typically identical except for pH, inhibitor type and inhibitor concentration. Monitored influent and effluent water quality parameters are presented in Table 5.2. Items in the table were usually measured weekly or biweekly. Parameters such as ortho-phosphorus were monitored at least 3 times a week to maintain dose control.

Table 5.2  
Related influent and effluent chemical monitoring for each of 14 PDSs and cradles

Parameter	Method
Alkalinity	Titration
Ammonia	NH <sub>3</sub> probe
Chlorine, Free	Spectrophotometer
Chlorine, Total	Spectrophotometer
Color, Apparent	Spectrophotometer
Conductivity	Conduct probe
Nitrite-N	Spectrophotometer
ORP	Redox probe
Oxygen, Dissolved	DO probe
pH	pH probe
Phosphorus, Ortho	Spectrophotometer
Silica	Spectrophotometer
TDS	TDS probe
Temperature	Probe
Turbidity	Turbidimeter
UV-254	Spectrophotometer
Aluminum	ICP
Calcium	ICP
Chloride	IC
Copper, Dissolved	ICP
Copper, Total	ICP
Iron, Dissolved	ICP
Iron, Total	ICP
Lead, Dissolved	ICP
Lead, Total	ICP
Magnesium	ICP
NPDOC	TOC Instrument
Phosphorus, Total	ICP
Silica	ICP
Sodium	ICP
Sulfate	IC
TKN	Digestion
Zinc, Dissolved	ICP
Zinc, Total	ICP

## Results and Discussions

### Mass balance analysis

#### *Total phosphorus analysis*

The target doses of the ZOP inhibitors were set as: 0.5, 1.0, and 2.0 mg/L as P. The measured average influent concentrations for the reporting period are noted to be 0.54, 0.91, and 1.73 mg P/L for the low, medium, and high inhibitor doses. Figure 5.2 shows the average values as well as the minimum and maximum observed for each of the PDSs using a bar and whiskers format. The bars represent the average while the whiskers represent the minimum and maximum of the four phases.

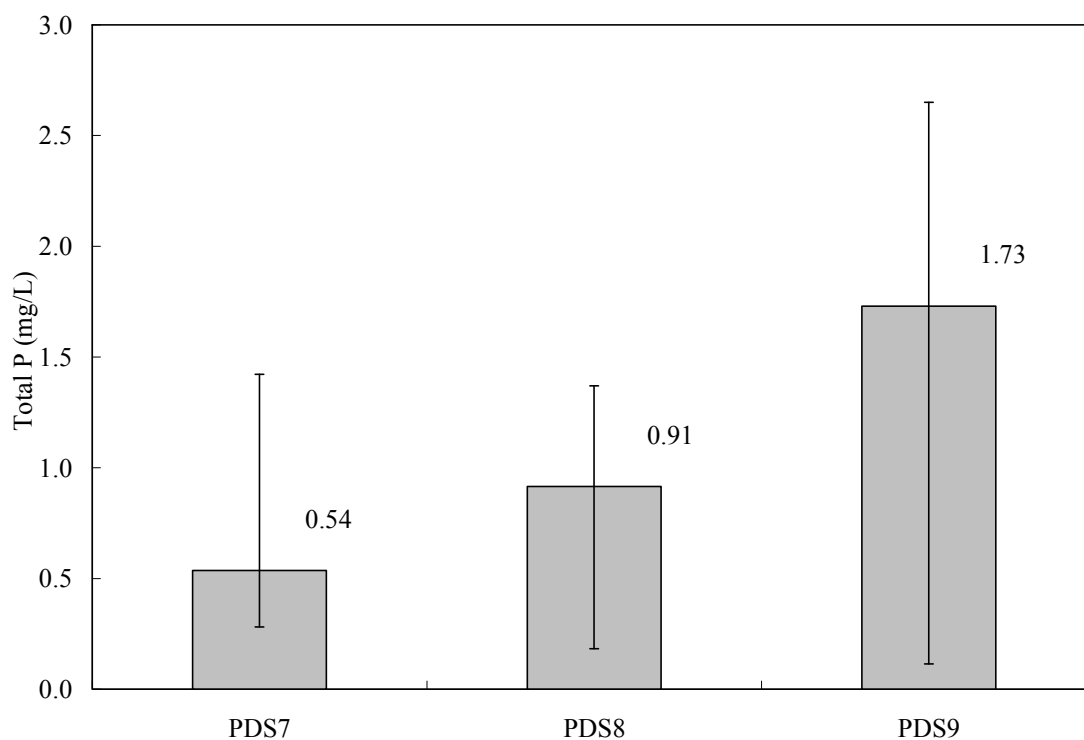


Figure 5.2 Average measured total phosphorus concentration

Figure 5.3 shows the percent recovery of total phosphorus in the low, medium and high dose PDSs for the 12-month study duration. The percent recovery in this case was based on a weekly mass balance and represents the fraction of total influent total phosphorus recovered in the PDS effluent. A percent recovery greater than 100% indicates release of the inhibitor while recovery below 100% indicates uptake of the inhibitor. There was phosphorus uptake on the pipe of 18% for the low concentration PDS (PDS 7) and 5% for the high concentration PDS (PDS 09). The average recovery was 82%, 91% and 95% for PDS 07, PDS 08 and PDS 09 respectively. Variation of phase water quality did not significantly affect the recovery of total phosphorus.

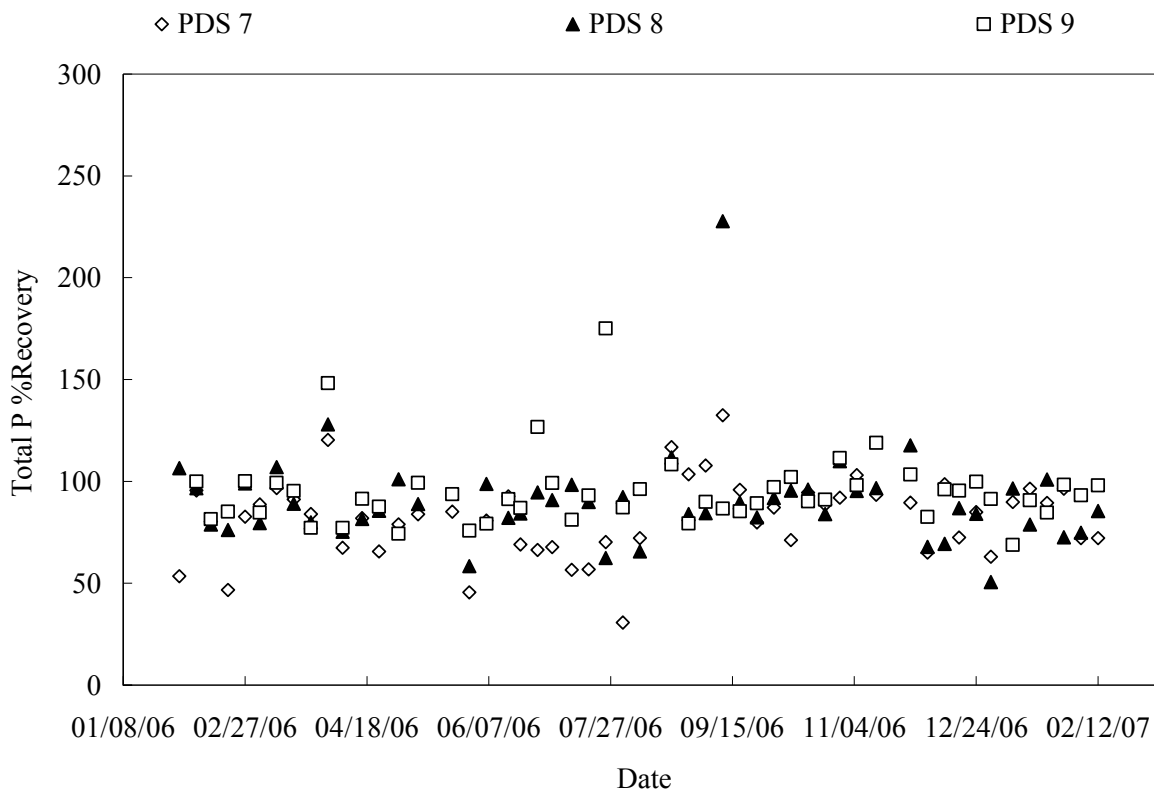


Figure 5.3 Percent recovery of total phosphorus for low, medium and high dose

The continuous uptake of phosphorus in all ZOP PDSs for all 4 phases indicated a phosphorus-containing film was probably produced on the pipe surface which functioned as a barrier for iron release. The lower total phosphorus uptake in the PDSs with higher ZOP dose indicates that increasing phosphorus dose was not beneficial for the film formation.

#### *Total zinc analysis*

Total zinc data from ZOP PDSs was analyzed using a similar approach. The measured average values for all 4 phases were noted to be 0.05, 0.13, and 0.25 mg P/L for the low,

medium, and high inhibitor doses. The average values as well as the minimum and maximum zinc concentrations observed in each PDS effluent are presented in Figure 5.4 using a bar and whiskers format.

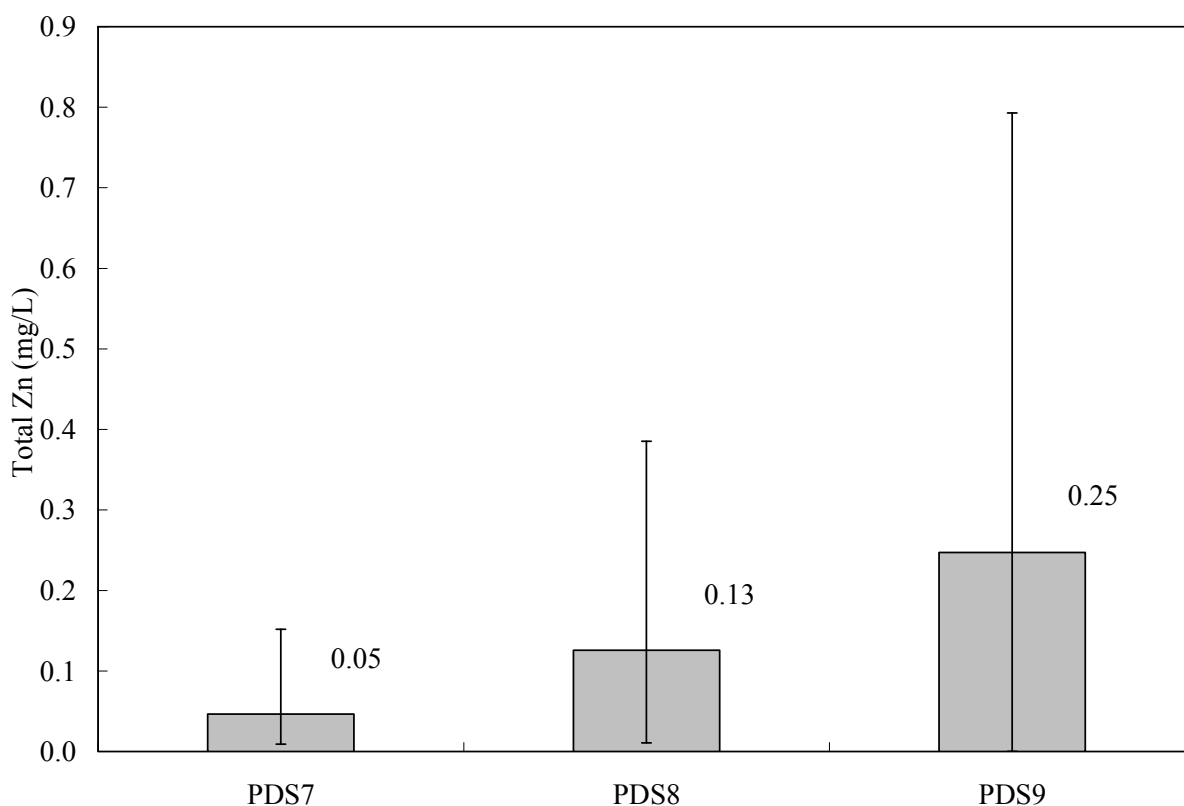


Figure 5.4 Average measured total zinc concentration

According to inhibitor manufacturer's specification, the product has a ratio of 1 part Zinc to five parts  $\text{PO}_4$  with a target of 6% as Zinc and 30% as  $\text{PO}_4$ . However, theoretical zinc concentration calculated base on measured total phosphorus value was much higher than measured zinc concentration as shown in Table 5.3. This was most likely due to the precipitation

of zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) in the inhibitor feed tank, which could be an operational or cost problem for utilities using ZOP.

The stock solutions of the ZOP inhibitor product were diluted in a 40 gallon ( $151 \text{ m}^3$ ) feed tank. During field operation, white precipitate was observed in this ZOP feed tank. Majority of this white precipitate was identified as zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) solid by X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS) (as shown in Figure 5.5) and Ion Coupled Plasma (ICP) Spectrophotometer.

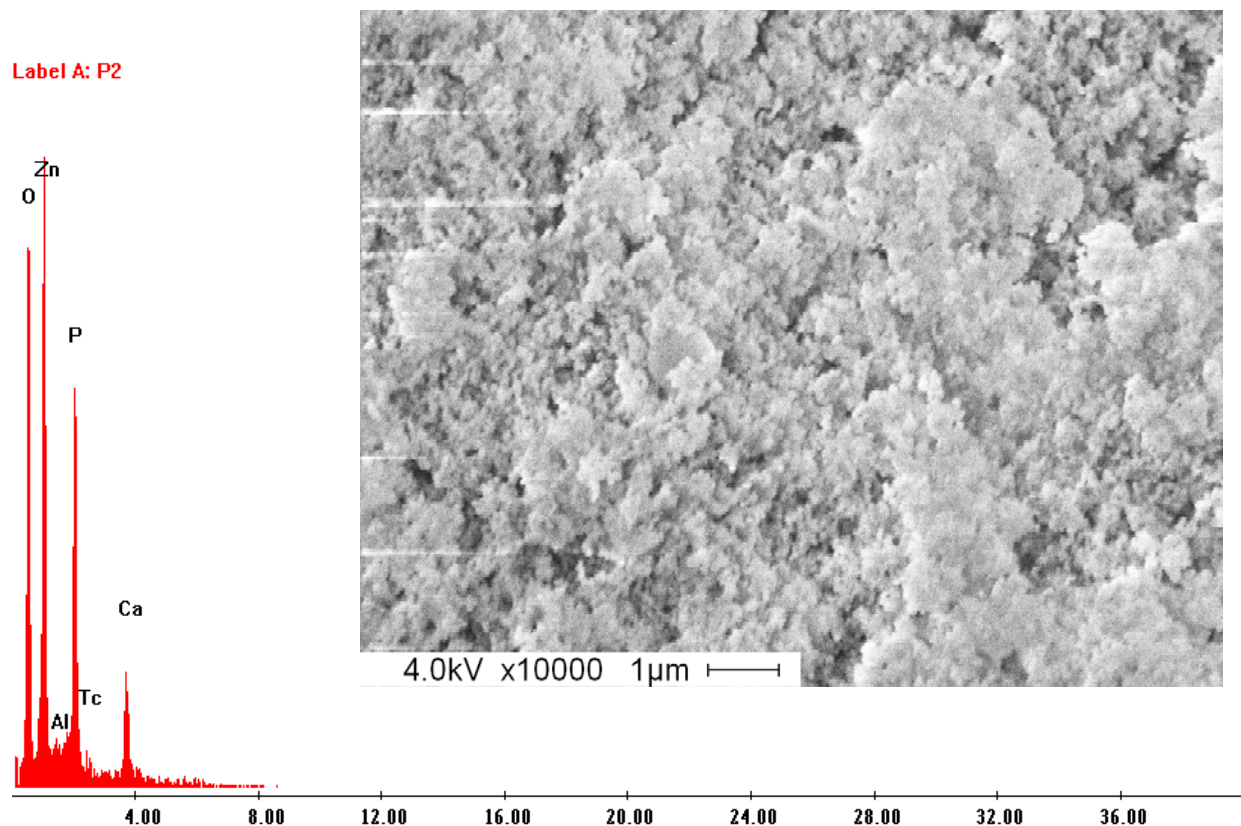


Figure 5.5 EDS analysis results and SEM image (4.0kV×10000)



The solubility modeling for zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was undertaken to simulate the situation ZOP inhibitor was dosed directly into the PDSs. The modeling results are shown in Table 5.3. Taking into account the effects of ionic strength, the solubility calculation confirmed the presence of  $\text{Zn}_3(\text{PO}_4)_2$  precipitation in the feed tank. The results also suggested that  $\text{Zn}_3(\text{PO}_4)_2$  would not precipitate if the inhibitor feed tank was bypassed and ZOP inhibitor was added directly to the PDSs. Hence, the precipitation of zinc phosphate precipitation was not a factor in inhibiting iron release by ZOP inhibition.

Table 5.3  
ZOP solubility modeling

	Stock	Feed Tank	PDS 7	PDS 8	PDS 9
pH	1	6.7	7.9	7.8	7.7
P (mg/L)	123974	19.30	0.55	0.92	1.65
PO4(mg/L)	379920	59.15	1.69	2.82	5.06
Calculated Zn (mg/L)	75984	11.829	0.337	0.564	1.011
$\text{Zn}_3(\text{PO}_4)_2$ Precipitation	No	Yes	No	No	No

Calculated percent recoveries of total zinc in the low, medium and high dose PDSs were presented in Figure 5.6. Since effluent zinc concentration contains zinc release from galvanized steel pipe, calculated percent recoveries were expected to greater than 100%. The average percent recovery of total zinc for all 4 phases was 260%, 191% and 227% for low dose PDS (PDS 7), medium dose PDS (PDS 8) and high dose PDS (PDS 9) respectively. Zinc concentrations at internal sampling points before galvanized steel pipe were also used for mass balance analysis to avoid the impact of zinc release from galvanized steel. Calculated total zinc percent recoveries were unsystematic and no significant correlation can be found between

inhibitor dose and zinc percent recovery. Hence zinc was not absorbed by the pipe surface, but was likely incorporated in the formed film intermittently during the field operation.

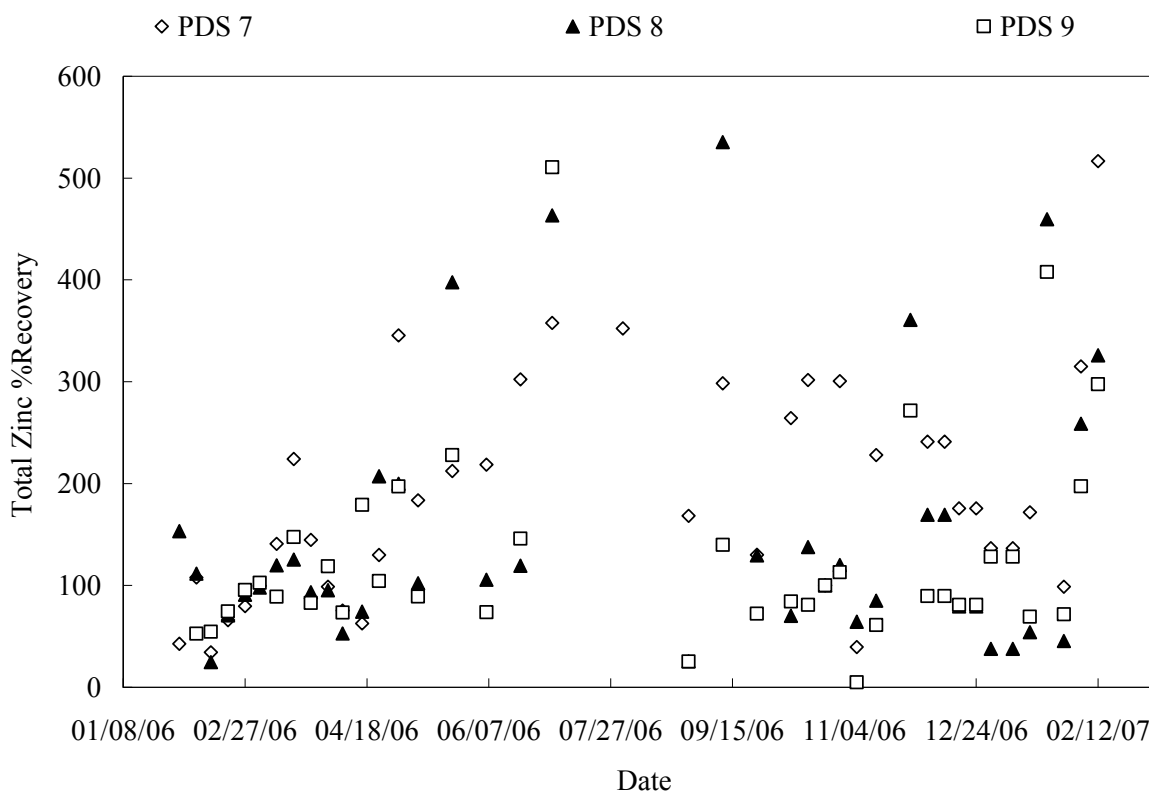


Figure 5.6 Percent recovery of total zinc for low, medium and high dose

## Empirical model development

### *Characterization of database*

Empirical model development was undertaken for prediction of total iron concentration in the PDSs. The regression for model development was done on the data for the 14 hybrid PDSs, including all four Phases. Dissolved iron and dissolved zinc concentrations below the detection limit were set at predetermined values (1  $\mu\text{g/L}$ ) so zero values would not cause

complications in convergence of the models. The ranges of variables used in model development for the current study are shown in Table 5.4.

Table 5.4  
Variable range for model development

Parameter	Minimum	Maximum
Total Phosphorus (mg/L as P)	0.01	3.36
Silica (mg/L)	4	65
pH	7.4	9.1
Alkalinity (mg/L as CaCO <sub>3</sub> )	84	175
Calcium (mg/L)	43	88
Zinc (mg/L)	0.001	0.793
Chloride (mg/L)	35	123
Sulfate (mg/L)	52	119
Sodium (mg/L)	5	92
Influent Iron (mg/L)	0.003	0.358
DO (mg/L)	6.6	10.9
UV-254 (cm <sup>-1</sup> )	0.007	0.105
Temperature (°C)	10.4	29.7

#### *Model development and evaluation*

A series of attempts were made to develop empirical models for prediction of total iron concentration as a function of water quality and inhibitor dose. The initial modeling effort incorporated all the monitored parameters from this study. A power form of the model was used and non-linear least squares regressions were completed on the entire data set to estimate all the parameter exponents. The water quality parameters monitored in the PDSs were evaluated using ANOVA procedures to identify statistically significant parameters. Those independent variables not shown to be significant at a 95% confidence level were eliminated from the models.

Confounding of independent water quality variables was investigated in order to develop a proper statistical model and was identified using linear correlation of all water quality parameters. The examination indicated that sodium was confounded with chloride. Calcium, sodium, and chloride were confounded with TDS. Color and turbidity were confounded. Temperature and dissolved oxygen were confounded. The existence of correlations between water quality parameters is unavoidable for blends of the three principal source waters. For example, the surface water contains high sulfate concentrations and low alkalinity. In contrast, the groundwater source has elevated alkalinity and reduced sulfate. Thus, blends that were enriched in groundwater will exhibit high alkalinity and low sulfate. For blends that were produced from GW and SW, alkalinity and sulfate will be negatively correlated. Therefore, selected independent variables were eliminated from model development and several modeling efforts were undertaken using different sets of water quality terms.

Eventually, alkalinity, pH, chloride, sulfate, temperature and influent iron concentration were selected as candidate independent variables for the final iron model. In addition, total phosphorus and zinc were included to account for the addition of ZOP inhibitor to the PDSs. This model specification significantly improved the accuracy of the empirical model, particularly with respect to the effect of inhibitor dose. The developed empirical models for total iron release in the presence of ZOP inhibitor were represented below:

$$Total\ Fe = 0.470 \times TP^{-0.073} \times Zn^{-0.180} \times Alk^{-0.457} \times Cl^{0.345} \times Fe_{inf}^{0.136} \quad (\text{Equation 5.3})$$

where

*Total Fe* = total iron, mg/L  
*TP* = total phosphorus, mg/L  
*Zn* = zinc, mg/L

$SiO_2$	= silica, mg/L as $SiO_2$
$Alk$	= alkalinity, mg/L as $CaCO_3$
$Cl$	= chloride, mg/L
$Fe_{inf}$	= influent iron, mg/L

The model suggests alkalinity will decrease iron release with increasing concentration, as shown by the negative exponent on the term while chloride and influent iron will contribute to iron release in the PDSs. pH did not exhibit a significant effect on iron release. This indicated that although the acidic characteristics of ZOP inhibitor caused the pH in ZOP PDSs decreased as inhibitor dose increased (7.9, 7.8 and 7.7 for low, medium and high dose PDS respectively), the impact of the pH change on iron release was insignificant. The impact of temperature in this work was also insignificant according to the ANOVA analysis. HRT also was not used in the iron models in this study because a constant two-day HRT was maintained in the hybrid PDSs for all phases. As shown previously, and thought here, the iron concentration would exhibit a linear dependence on time for HRT greater than 2 days (Imran, S.A., et al 2005b). The terms associated with total phosphorus were retained in the model in spite of the higher p-value ( $> 0.05$ ) in order to develop a model with some sensitivity to inhibitor dose.

The negative exponents on the total phosphorus term and zinc term in the empirical model indicate that both total phosphorus and zinc were beneficial for reducing iron release. Although the low values of the ZOP dose used and the near zero value of the exponent on the phosphorus term would not cause the model to display pronounced sensitivity to the phosphorus dose, the impact of zinc in the model enhances the effect of the inhibitor dose significantly. The end result of the dual impact of total phosphorus and zinc suggests that increasing the dose of ZOP should offer improved iron control.

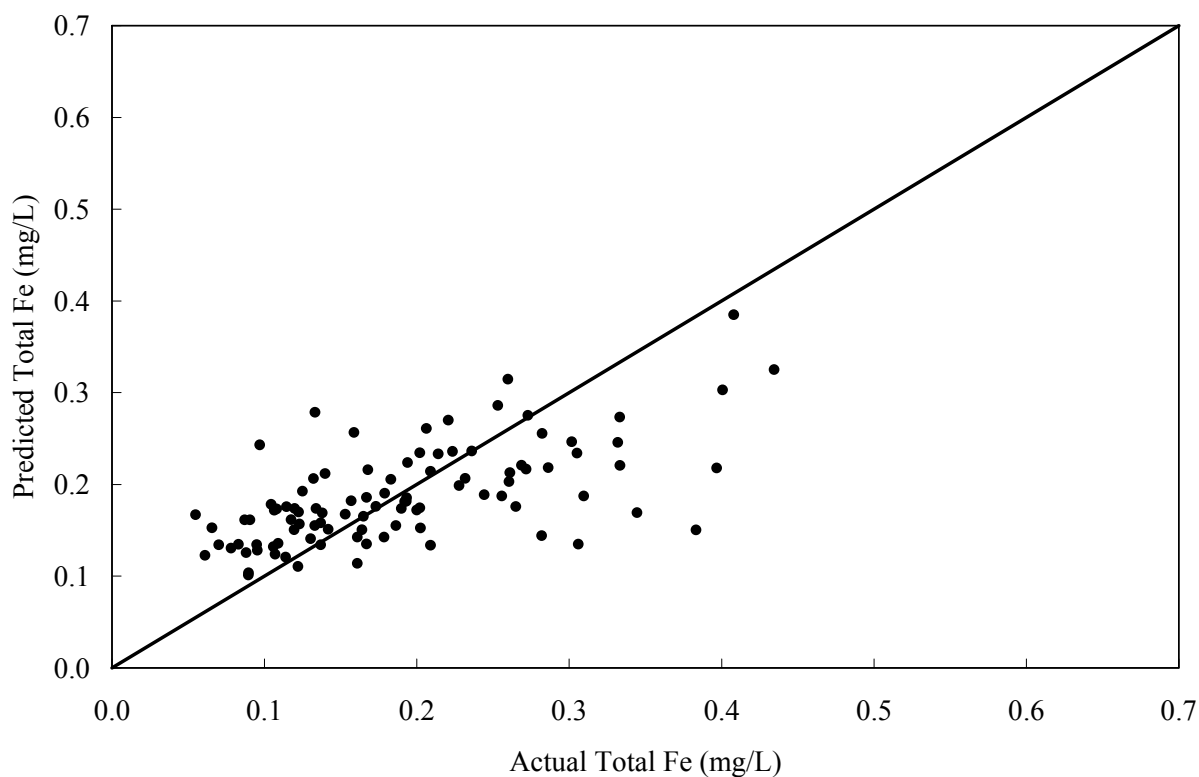


Figure 5.7 Model predicted versus actual total iron concentration

Figure 5.7 shows the fit of the total iron model predictions with the actual observations for all phases. A line is indicated on the plot that would represent perfect agreement between the model and the observed data. The coefficient of determination ( $R^2$ ) is not particularly impressive for the total iron model ( $R^2 = 0.45$ ). The low value is indicative of the absence of a monotonic response of the iron data to increases in inhibitor dose. The model tends to under-predict the higher concentrations of iron. It is noted that a number of observations that exceed the secondary iron standard of 0.3 mg/L were not always predicted to violate this standard.

### *ZOP inhibitor performance*

A summary of total and dissolved iron release data for each of the PDSs receiving ZOP inhibitor for the one year study duration is shown in Table 5.5. This data is segregated by phase and by PDS. PDSs 7, 8 and 9 were treated with the low, medium and high dose of ZOP inhibitor, respectively. As shown in the table, the majority of the iron in ZOP PDSs was present in a particulate form. The data showed that in most cases, the total iron release decreased as the inhibitor dose increased and iron release was lower in both Phase I and Phase III.

Table 5.5  
Iron release summary for ZOP PDSs

Phase	PDS	Dose	Dissolved Fe (mg/L)			Total Fe (mg/L)		
			Avg	Max	Min	Avg	Max	Min
I	7	0.64	0.04	0.19	0.00	0.18	0.27	0.13
	8	0.99	0.05	0.43	0.00	0.14	0.28	0.09
	9	1.78	0.02	0.09	0.00	0.16	0.41	0.06
II	7	0.54	0.01	0.10	0.00	0.34	0.64	0.12
	8	0.89	0.01	0.04	0.00	0.23	0.29	0.11
	9	1.77	0.01	0.04	0.00	0.16	0.24	0.07
III	7	0.49	0.01	0.03	0.00	0.22	0.30	0.10
	8	0.88	0.01	0.03	0.00	0.22	0.30	0.12
	9	1.82	0.01	0.03	0.00	0.11	0.13	0.08
IV	7	0.46	0.00	0.01	0.00	0.28	0.40	0.11
	8	0.88	0.00	0.00	0.00	0.24	0.37	0.01
	9	1.58	0.00	0.00	0.00	0.11	0.19	0.00
All	7	0.54	0.02	0.19	0.00	0.25	0.64	0.10
	8	0.91	0.02	0.43	0.00	0.21	0.37	0.01
	9	1.74	0.01	0.09	0.00	0.14	0.41	0.00

Figure 5.8 shows the average total iron release in each of the ZOP PDSs for each phase compared to the predicted iron release by the model. The maximum and minimum values are

also presented. As shown in the graph, the actual total iron release decreased as inhibitor dose increased in most cases, indicating improved performance with increasing inhibitor dose. The model suggests the same trend and does reasonably well at predicting iron release for the ZOP PDSs.

The water quality of Phase I and III was characterized by high alkalinity due to the reduced percentage of surface water. Phase II had the lowest percentage of groundwater and therefore the lowest alkalinity. The model suggests that a reduction of iron release can be achieved by increasing the alkalinity. This explained why Phase I and Phase III had lower iron release than Phase II.

The similar total iron release for phase I and phase III indicated that the impact of temperature on iron release was insignificant, which is consistent with the ANOVA analysis during model development.



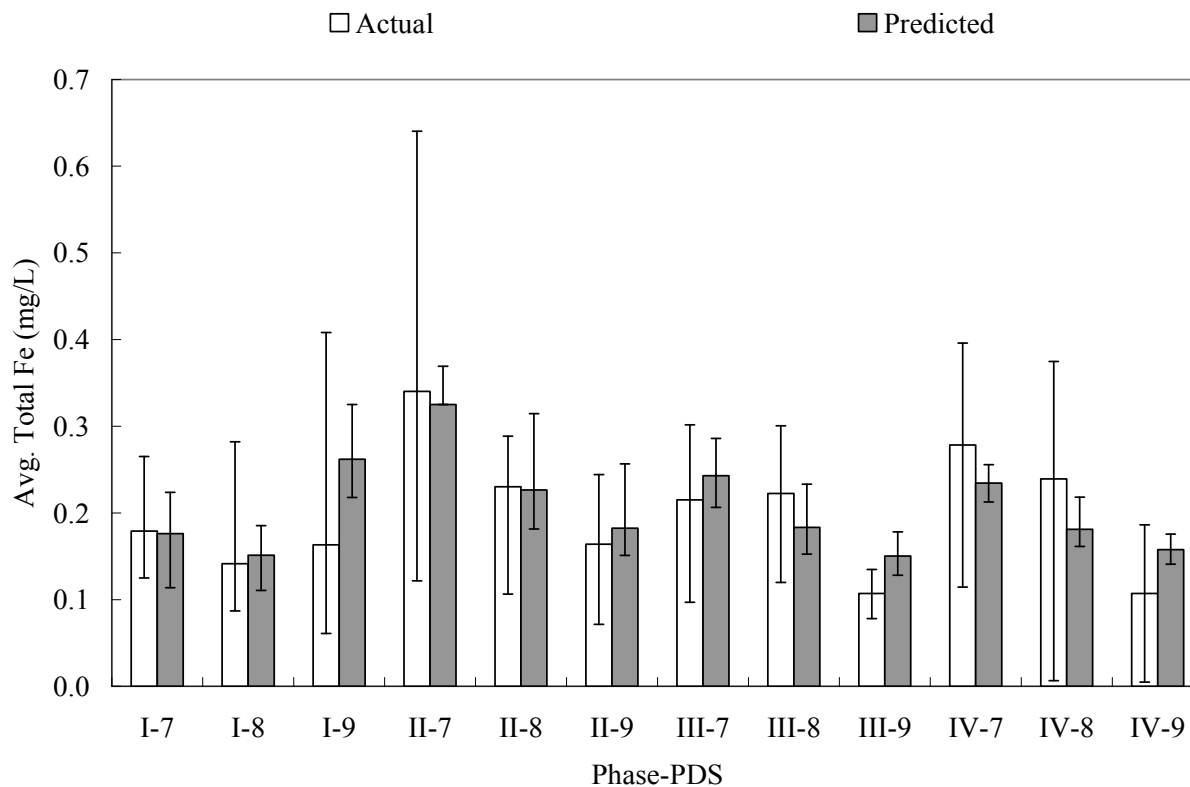


Figure 5.8 Total iron release model summary for ZOP PDSs by phase

Average output total iron concentrations of the entire study for PDSs treated with ZOP inhibitor and pH inhibition were compared in Figure 5.9 to analyze the performance of ZOP inhibitor for total iron release control. The intended comparison to be reviewed is between the pH<sub>s</sub> control (PDS13), pH elevation (PDS 14) and ZOP addition with low, medium, and high inhibitor dose.

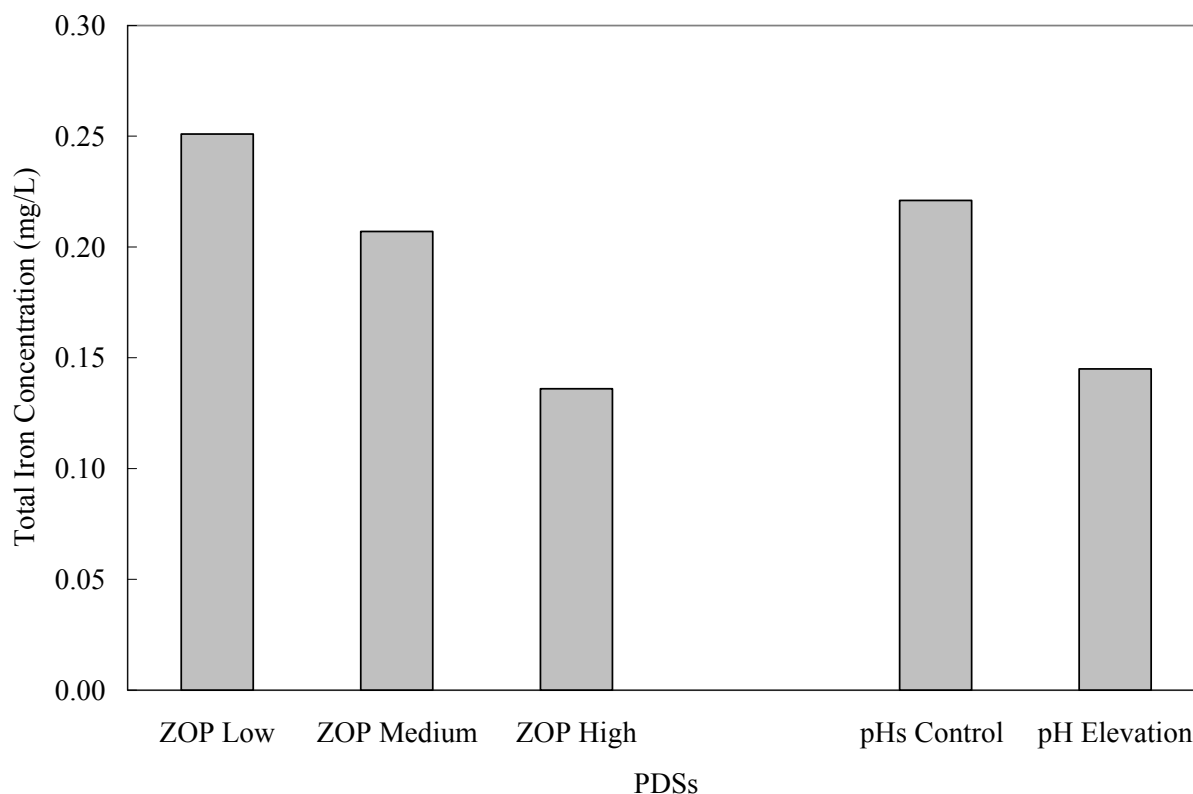


Figure 5.9 Data summary for total iron concentration

The graphical summary of the data supports the previous synopsis that was based on the empirical model. A significant improvement in performance was indicated by the graph with an increase in dose of ZOP inhibitor, within the range of values employed in this study. Since both mass balance analysis and empirical modeling confirmed that increasing phosphorus dose would not help to control iron release, elevated zinc concentration with increased inhibitor addition was the reason for the better iron inhibition performance.

Although it was unlikely to have a zinc-containing film on the pipe surface according to the mass balance results, zinc could act like a catalyst to accelerate and/or improve the

phosphorus film formation process. Since total phosphorus percent recovery decreased as inhibitor dose increased, zinc may have altered the structure and composition of the film and helped to produce a better film containing less amount of phosphorus during this process.

There appears to be a clear benefit associated with operation at an elevated pH. The average project total iron concentrations for PDS 13 and PDS 14 were 0.22 and 0.14 mg/L, respectively. ZOP Inhibitor addition does not appear to offer any clear advantage in comparison to pH elevation.

The average iron concentrations for ZOP PDSs displayed some improvement in comparison to the pH<sub>s</sub> control except for the low dose PDS. However, considering the chemical and operation cost, ZOP inhibitor is apparently not the top choice for iron release control even just compared to pH<sub>s</sub> inhibition. Utilities should consider other corrosion control strategies like orthophosphate corrosion inhibitor or silicate corrosion inhibitor for a better performance. If ZOP inhibitor is still selected (this may be reasonable when simultaneous control of copper and/or lead release is required), low dose (less than 1mg/L as P) should be avoided to meet the treatment objectives.

### **Conclusions**

Percent recovery for total phosphorus was calculated for all ZOP PDSs, the continuous uptake of phosphorus for the one year study duration indicated a phosphorus-containing film was produced on the pipe surface which was a barrier to iron release from pipe materials. Increasing phosphorus dose did not enhance film formation

Zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was found to precipitate in the inhibitor feed tank. Solubility modeling indicated  $\text{Zn}_3(\text{PO}_4)_2$  would not precipitate if ZOP inhibitor was added directly to the PDSs. Hence, the precipitation of zinc phosphate precipitation was not a factor in inhibiting iron release by ZOP inhibition.

Calculated total zinc percent recoveries were unsystematic and were not correlated to inhibitor dose. It is found that zinc was not absorbed by the pipe surface, but was likely incorporated in the formed film intermittently during the field operation.

Total iron release was described by a water quality empirical model, which showed iron release decreased as alkalinity increased and was independent of temperature in this work. The negative exponents on the total phosphorus term and zinc term in the empirical model indicate that both total phosphorus and zinc were beneficial for reducing iron release. The model didn't display pronounced sensitivity to the phosphorus dose but the impact of zinc enhances the effect of the inhibitor dose significantly.

Summaries of actual total and dissolved iron concentration data confirmed the significant improvement in performance with an increase in dose of ZOP inhibitor. Since increasing phosphorus dose was found to have no beneficial effects on iron release control, elevated zinc concentration should be the reason for the better performance. Although it was unlikely to have a zinc-containing film on the pipe, zinc could act like a catalyst to accelerate and/or improve the phosphorus film formation process. Since total phosphorus percent recovery decreased as inhibitor dose increased, zinc maybe altered the structure and composition of the film and helped to produce a better film containing less amount of phosphorus during this process.

Performance comparison between ZOP inhibitor and pH inhibition suggested ZOP inhibitor should not be the first choice for iron release control.

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## **CHAPTER 6**

### **EFFECTS OF ZINC ORTHOPHOSPHATE (ZOP) CORROSION INHIBITOR ON TOTAL COPPER RELEASE IN A CHANGING WATER QUALITY ENVIRONMENT**

#### **Abstract**

The role of zinc in ZOP inhibition was investigated in a large field study to determine the impact of ZOP inhibitor on copper release in a changing water quality environment. Water quality and copper scale formation was monitored in pilot distribution systems that received changing quarterly blends of finished ground, surface and desalinated waters with and without zinc orthophosphate (ZOP) inhibitor over a one year period.

Development of empirical models for total copper release and surface characterization of copper scale on coupons exposed to ZOP inhibitor by X-ray Photoelectron Spectroscopy (XPS) provided insight into the mechanism of ZOP inhibition and the role of zinc regarding copper release in drinking water distribution systems.

#### **Introduction**

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. In order to meet increasing consumer demand and more stringent environmental and drinking water regulations, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use and provide for future growth in the region. TBW and UCF have conducted research to seek understanding of the issues involved when multiple-source waters are blended since 2000. The work had demonstrated that control of the scale or film in the existing distribution systems was essential 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 using corrosion inhibitors. Corrosion inhibitors offer an opportunity for scale control because they bond directly with the elemental metal or scale and form a barrier on the pipe surface. The film or barrier separates the bulk water from the metal surface and can be renewed by continuous addition of the corrosion inhibitor to finished water.

Increasing awareness of the presence and potential health impacts of copper corrosion products in drinking water has led the US Environmental Protection Agency to mandate action levels of 1.3 mg/L for copper release. A nationwide utility survey conducted in 2001 (McNeill, L.S. & Edwards, M. 2002) reported that 56% of all responding utilities add phosphate inhibitors in 2001, 84% of utilities currently dose inhibitors to control lead and copper. Around 30% of water utilities reported using orthophosphate or zinc orthophosphate inhibitor.

Numerous studies found that orthophosphate based inhibitors could prevent copper corrosion related problems. It is believed that orthophosphate reduced copper solubility by forming a cupric phosphate scale (Reiber, S.H. 1989; Edwards, M., Jacobs, S. & Dodrill, D. 1999).

The thermodynamic models for dissolved copper have been developed to predict copper release from copper pipe (Taylor, J.S., et al 2005). Several different carbonate or oxide based solid phases were considered for model development. The most descriptive model assumed CuO or Cu(OH)<sub>2</sub> as the controlling solid phase and is shown in Equation 6.1. An empirical model as shown in Equation 6.2 was also developed for the prediction of total copper release during the same project, which indicates alkalinity, temperature, sulfate, silica and pH will significantly



affect total copper release (Xiao, W. 2004). Several investigators have reported formation of  $\text{Cu}_3(\text{PO}_4)_2$  following addition of phosphate inhibitors will likely to control copper (Schock, M.R., Lytle, D.A. & Clement, J.A. 1995; Edwards, M., Jacobs, S. & Dodrill, D. 1999).

$$\begin{aligned}
 [\text{Cu}]_T = & [\text{Cu}^{2+}] + [\text{CuOH}^+] + [\text{Cu}(\text{OH})_2^0] + [\text{Cu}(\text{OH})_3^-] + \\
 & [\text{CuHCO}_3^-] + [\text{CuCO}_3^0] + [\text{Cu}(\text{CO}_3)_2^{2-}] + \\
 & [\text{Cu}(\text{OH})_2\text{CO}_3^{2-}]
 \end{aligned}
 \tag{Equation 6.1}$$

$$\text{Cu} = 0.28 + \text{Temp}^{0.72} \times \text{Alk}^{0.73} \times \text{pH}^{-2.86} \times (\text{SO}_4^{2-})^{0.10} \times \text{SiO}_2^{-0.22}
 \tag{Equation 6.2}$$

Where

$\text{Cu}$  = total copper release in mg/L  
 $\text{Temp}$  = temperature in  $^\circ\text{C}$   
 $\text{Alk}$  = alkalinity in mg/L as  $\text{CaCO}_3$   
 $\text{SO}_4^{2-}$  = sulfate in mg/L  
 $\text{SiO}_2$  = silica in mg/L as  $\text{SiO}_2$

Zinc orthophosphate (ZOP) has been widely used for many years as a reliable, known and safe corrosion inhibitor. ZOP is generally believed to produce a microscopic film on metal surfaces that acts as a barrier to corrosive environments. It was also reported that zinc phosphates often performed better than orthophosphates for certain water types (Benjamin, M., Sontheimer, H. & Leroy, P. 1996). Some studies suggested that the presence of zinc in the inhibitor either accelerated film formation or helped to form a better-quality film than regular phosphate films for inhibiting corrosion (Reese, W.J. 1962; Kleber, J.P. 1965; Murray, W.B. 1970; Mullen, E.D. & Ritter, J.A. 1974; Mullen, E.D. & Ritter, J.A. 1980; Swayze, J. 1983).

However, several other studies that have compared zinc orthophosphate compounds versus simple orthophosphates have shown no significant benefit from zinc additives at

operational dosage (HDR Engineering Inc 2001). Zinc is an environmental concern because of the adverse effects of zinc on wastewater treatment facilities and its limits on the land disposal of sludge. Hence, it is important to understand the role of zinc, if any, in corrosion inhibition and especially in copper release in a variable water quality environment.

### **Experimental Methods**

#### **The pilot distribution systems (PDSs)**

An extensive research facility was constructed for this study and consisted of seven pilot water treatment facilities, eighteen pilot distribution systems (PDSs) with individual sampling ports and cradles for individual coupon analyses, a corrosion facility with eighteen copper and lead corrosion loops, a stainless steel food grade trailer for hauling water and five trailers for field, housing of pilot facilities, chemical analyses and equipment storage.

The PDSs were designed to represent typical scenarios for changing water quality that were experienced in a real distribution system. These PDSs were identical and consisted of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series. A picture of the PDSs is shown in Figure 6.1. The PDSs were operated to maintain a two-day hydraulic residence time (HRT). Standpipes were located at the beginning and end of each PDS to ensure the presence of water inside of the lines at all times.



Figure 6.1 Pilot Distribution System

A corrosion shed was built which contained eighteen loops of copper pipes, as shown in Figure 6.2, for the copper corrosion study. A portion of the flow from each PDS was discharged to the corrosion loop to simulate a consumer environment and tap monitoring for LCR (lead and copper rule) compliance. Only fourteen of the eighteen PDSs and corrosion loops were utilized in this work.



Figure 6.2 Corrosion shed and copper loops

### **The use of zinc orthophosphate (ZOP) inhibitor**

In the fourteen PDSs, PDS 1-12 received four different corrosion inhibitors at three different doses. The remaining two PDSs (PDS 13-14) received only pH adjustment. PDS 13 influent was adjusted to  $\text{pH}_s$  and PDS 14 influent was adjusted to  $\text{pH}_s + 0.3$ . PDS 13 and 14 served as controls or references for the project.

The ZOP dose was constant for the year of operation, and was 0.5, 1.0, and 2.0 mg/L as P in PDS 7, 8 and 9 respectively. Stock solutions of ZOP were diluted in a 40 gallon ( $151 \text{ m}^3$ ) tank and the feed rates of ZOP to the three PDSs were calibrated twice a week.

The ZOP inhibitor used in this study was made by dissolving zinc sulfate into a phosphoric acid solution. The product has a ratio of 1 part Zinc to five parts  $\text{PO}_4$  with a target of 6% as Zinc and 30% as  $\text{PO}_4$ .

### **Source and blend water quality**

Conventionally treated groundwater (GW), enhanced treated surface water (SW) and desalinated water treated by reverse osmosis (RO) were blended and fed to the PDSs. The blends of GW, SW and RO was changed quarterly over one year as shown in Table 6.1. All PDSs received the same blend during each phase. The phases I and III were identical in order to evaluate seasonal effects, which were predictable by water quality.

Table 6.1  
Blend ratios of GW, SW, and RO waters used during project

Phase	Time Period	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

### **Data collecting and analysis**

Influent and effluent water quality was monitored for each of the fourteen PDSs over the year of operation. Quality assurance and quality control of both the laboratory and field determinations of water quality parameters was accomplished by taking duplicate samples and repeating at least 10% of the analyses in the laboratory and field. Blind duplicates and spikes were also used to determine the accuracy of measurements. Dynamic control charts were used to monitor precision and accuracy of laboratory and field analysis.

PDS influent water quality was typically identical except for pH, inhibitor type and inhibitor concentration. Influent and effluent water quality parameters shown in Table 6.2 were typically monitored weekly or biweekly. Key parameters of investigation, ortho-phosphorus, pH, and flow were monitored at least 3 times a week for control.

Table 6.2  
Related influent and effluent chemical monitoring for each of 14 PDSs and cradles

Parameter	Method
Alkalinity	Titration
Ammonia	NH <sub>3</sub> probe
Chlorine, Free	Spectrophotometer
Chlorine, Total	Spectrophotometer
Color, Apparent	Spectrophotometer
Conductivity	Conduct probe
Nitrite-N	Spectrophotometer
ORP	Redox probe
Oxygen, Dissolved	DO probe
pH	pH probe
Phosphorus, Ortho	Spectrophotometer
Silica	Spectrophotometer
TDS	TDS probe
Temperature	Probe
Turbidity	Turbidimeter
UV-254	Spectrophotometer
Aluminum	ICP
Calcium	ICP
Chloride	IC
Copper, Dissolved	ICP
Copper, Total	ICP
Iron, Dissolved	ICP
Iron, Total	ICP
Lead, Dissolved	ICP
Lead, Total	ICP
Magnesium	ICP
NPDOC	TOC Instrument
Phosphorus, Total	ICP
Silica	ICP
Sodium	ICP
Sulfate	IC
TKN	Digestion
Zinc, Dissolved	ICP
Zinc, Total	ICP

Surface characterization was a critical part of documenting the effects of ZOP corrosion inhibitor on copper release. The copper coupons for surface characterization study were

rectangular and were housed in a cradle which received PDS effluent. Surface characterization was done on 24 coupons using X-ray Photoelectron Spectroscopy (XPS) to identify chemical components of the top surface of the corrosion layer.

## **Results and Discussions**

### **Filed operation**

#### *Total phosphorus*

Figure 6.3 shows the average, minimum and maximum total influent phosphorus concentrations for each of the PDSs using a bar and whiskers format over one year of operation. The measured average values for the reporting period were 0.54, 0.91, and 1.73 mg P/L for the low, medium, and high inhibitor doses.

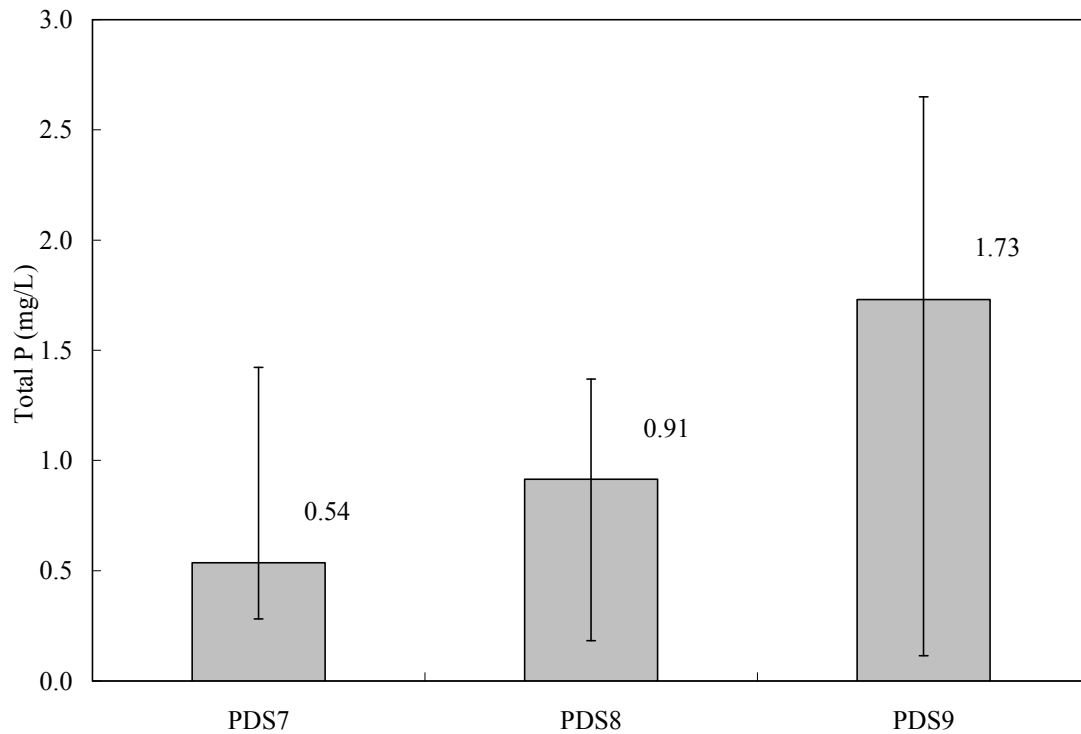


Figure 6.3 Average measured total phosphorus concentration

#### *Total zinc*

The measured average influent zinc concentrations for all 4 phases were noted to be 0.05, 0.13, and 0.25 mg P/L for the low, medium, and high inhibitor doses. The average values as well as the minimum and maximum zinc concentrations are presented in Figure 6.4 using a bar and whiskers format.



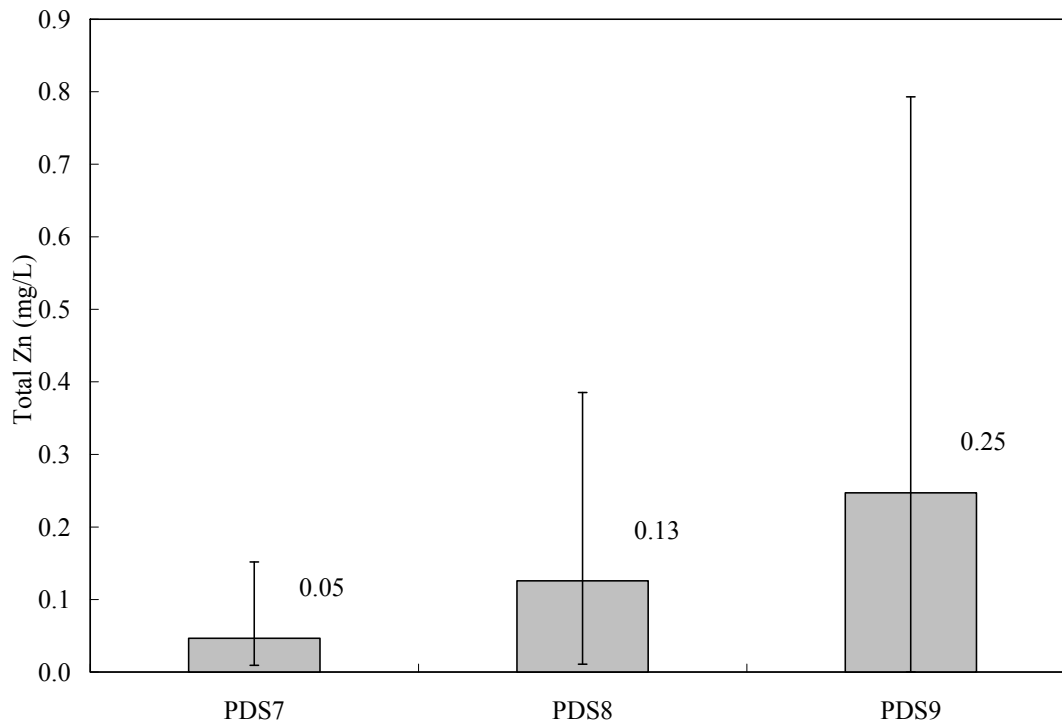


Figure 6.4 Average measured total zinc concentration

According to inhibitor manufacturer's specification, the product has a ratio of 1 part Zinc to five parts  $\text{PO}_4$  with a target of 6% as Zinc and 30% as  $\text{PO}_4$ . However, theoretical zinc concentration calculated base on measured total phosphorus value was much higher than measured zinc concentration as shown in Table 6.3. This is most likely due to the precipitation of zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) in the inhibitor feed tank, which could be an operational or cost problem for utilities using ZOP.

The stock solutions of the ZOP inhibitor product were diluted in a 40 gallon ( $151 \text{ m}^3$ ) feed tank. During field operation, a white precipitate was observed in the ZOP feed tank. Majority of this white precipitate was identified as zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) solid using X-ray

Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS) (as shown in Figure 6.5) and an Ion Coupled Plasma (ICP) Spectrophotometer.

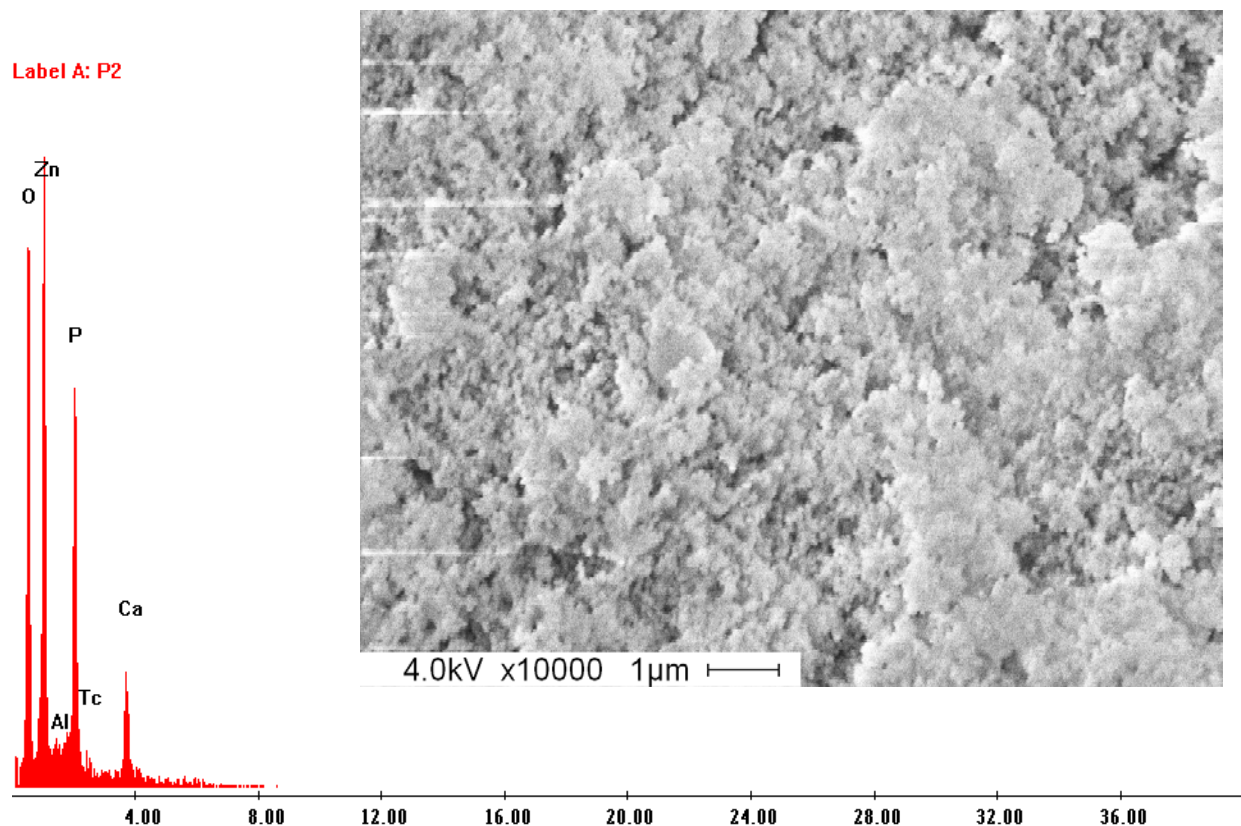


Figure 6.5 EDS analysis results and SEM image (4.0kV×10000) for the precipitation in ZOP feed tank

The solubility modeling for zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was undertaken to simulate addition of the ZOP inhibitor directly to the PDSs. The modeling results are shown in Table 6.3. Taking into account the effects of ionic strength, the solubility calculations were consistent with the precipitation of  $\text{Zn}_3(\text{PO}_4)_2$  in the feed tank. The results also suggested that  $\text{Zn}_3(\text{PO}_4)_2$  would not precipitate if the inhibitor feed tank was bypassed and ZOP inhibitor was added directly to

the PDSs. Since  $\text{Zn}_3(\text{PO}_4)_2$  would not be expected to precipitate in the PDSs or in actual use, the precipitation of zinc phosphate precipitation wasn't and would not be a factor in inhibiting copper release by ZOP inhibitor as indicated by equilibrium calculations.

Table 6.3  
ZOP solubility modeling

	Stock	Feed Tank	PDS 7	PDS 8	PDS 9
pH	1	6.7	7.9	7.8	7.7
P (mg/L)	123974	19.30	0.55	0.92	1.65
PO <sub>4</sub> (mg/L)	379920	59.15	1.69	2.82	5.06
Calculated Zn (mg/L)	75984	11.829	0.337	0.564	1.011
$\text{Zn}_3(\text{PO}_4)_2$ Precipitation	No	Yes	No	No	No

## Empirical model development

### *Characterization of database*

Empirical model development was undertaken for prediction of total copper concentration in the PDSs. The regression for model development was done on the data for the 14 hybrid PDSs, including all four Phases. The ranges of variables used in model development for the current study are shown in Table 6.4.

Table 6.4  
Variable range for model development

Parameter	Minimum	Maximum
Total Phosphorus (mg/L as P)	0.01	3.36
Silica (mg/L)	4	65
pH	7.4	9.1
Alkalinity (mg/L as CaCO <sub>3</sub> )	84	175
Calcium (mg/L)	43	88
Zinc (mg/L)	0.001	0.793
Chloride (mg/L)	35	123
Sulfate (mg/L)	52	119
Sodium (mg/L)	5	92
Influent Iron (mg/L)	0.003	0.358
DO (mg/L)	6.6	10.9
UV-254 (cm <sup>-1</sup> )	0.007	0.105
Temperature (°C)	10.4	29.7

#### *Model development and evaluation*

A series of attempts were made to develop empirical models for prediction of total copper concentration as a function of water quality and inhibitor dose. The initial modeling effort incorporated all the monitored parameters from this study. A power form of the model was used and non-linear least squares regressions were completed on the entire data set to estimate all the parameter exponents. The water quality parameters monitored in the PDSs were evaluated using ANOVA procedures to identify statistically significant parameters. Those independent variables not shown to be significant at a 95% confidence level were eliminated from the models.

Confounding of independent water quality variables was investigated in order to develop a proper statistical model and was identified using linear correlation of all water quality parameters. The examination indicated that sodium was confounded with chloride. Calcium,

sodium, and chloride were confounded with TDS. Color and turbidity were confounded. Temperature and dissolved oxygen were confounded. The existence of correlations between water quality parameters is unavoidable for blends of the three principal source waters. For example, the surface water contains high sulfate concentrations and low alkalinity. In contrast, the groundwater source has elevated alkalinity and reduced sulfate. Thus, blends that were enriched in groundwater will exhibit high alkalinity and low sulfate. For blends that were produced from GW and SW, alkalinity and sulfate will be negatively correlated. Therefore, selected independent variables were eliminated from model development and several modeling efforts were undertaken using different sets of water quality terms.

Eventually, alkalinity, pH, chloride, sulfate and temperature were selected as candidate independent variables for the final copper model. In addition, total phosphorus and zinc were included to account for the addition of ZOP inhibitor to the PDSs. This model specification significantly improved the accuracy of the empirical model, particularly with respect to the effect of inhibitor dose. The developed empirical models for total copper release in the presence of ZOP inhibitor were represented below:

$$Total\ Cu = 5.24 \times TP^{-0.205} \times Zn^{-0.069} \times pH^{-3.48} \times Alk^{0.569} \times Cl^{0.394} \quad (\text{Equation 6.3})$$

where

*Total Cu* = total copper, mg/L  
*TP* = total phosphorus, mg/L  
*Zn* = zinc, mg/L  
*pH* =  $-\text{Log } [H^+]$   
*Alk* = alkalinity, mg/L as  $CaCO_3$   
*Cl* = chloride, mg/L

Summary data for the corrosion loop total and dissolved copper concentrations for each of the PDSs receiving ZOP inhibitor are provided in Table 6.5. This data was segregated by Phase and by PDS.

PDS 7, 8 and 9 were treated with the low, medium and high dose of ZOP inhibitor, respectively as mentioned above. As shown in Table 6.5, on average, the majority of the copper in ZOP PDSs was present in a dissolved form. The data in the table indicated that the experienced copper concentration generally decreased as the ZOP inhibitor dose was increased.

Table 6.5  
Copper release summary for ZOP PDSs

Phase	PDS	Dose	Dissolved Cu			Total Cu		
			Avg	Max	Min	Avg	Max	Min
I	7	0.64	0.50	0.62	0.43	0.56	0.71	0.44
	8	0.99	0.34	0.44	0.23	0.36	0.44	0.23
	9	1.78	0.27	0.41	0.20	0.32	0.59	0.21
II	7	0.54	0.39	0.53	0.26	0.51	0.62	0.31
	8	0.89	0.32	0.52	0.19	0.39	0.58	0.25
	9	1.77	0.26	0.66	0.09	0.30	0.70	0.13
III	7	0.49	0.46	0.59	0.39	0.53	0.65	0.39
	8	0.88	0.30	0.41	0.24	0.34	0.45	0.28
	9	1.82	0.17	0.21	0.14	0.18	0.23	0.12
IV	7	0.46	0.40	0.73	0.27	0.49	0.84	0.34
	8	0.88	0.32	0.48	0.21	0.38	0.54	0.26
	9	1.58	0.29	0.61	0.15	0.32	0.67	0.18
All	7	0.54	0.44	0.73	0.26	0.52	0.84	0.31
	8	0.91	0.32	0.52	0.19	0.37	0.58	0.23
	9	1.74	0.25	0.66	0.09	0.28	0.70	0.12

The negative exponents on the total phosphorus and zinc terms in the model indicate that both total phosphorus and zinc were beneficial for reducing copper release. The small exponent on the zinc term (-0.069) generates a model that was not very sensitive to zinc for the ZOP PDSs. Nevertheless, the combined impact of total phosphorus and zinc in the empirical model indicate that addition of the ZOP inhibitor will reduce copper release.

The maximum, minimum and average predicted and actual total released copper concentrations are shown in Figure 6.6 for each ZOP PDS by phase. As shown in the graph, the actual total copper release decreased as inhibitor dose increased in all cases, confirming reduced release of total copper as ZOP dose increased. The model suggests the same trend in Figure 6.6, although the variation of predicted values was not as great as actual values.

All other terms in the model were related to the water quality of the blend. The blends in Phase I and III were characterized by high alkalinity. The positive exponent on the alkalinity term indicates that increased alkalinity will result in higher copper concentrations. This pattern was confirmed by the slightly higher average copper concentrations in Phase I and III in Figure 6.6.

The model is also sensitive to chloride. The positive exponent on the chloride term in the model suggests elevated chloride concentrations will aggravate copper release. The pH term in the model is shown with a negative exponent, which indicates better control of copper would occur at higher pH values. Since the acidic characteristics of ZOP inhibitor caused the pH in ZOP PDSs decreased as inhibitor dose increased (7.9, 7.8 and 7.7 for low, medium and high dose PDS respectively), the impact of the pH change may somehow offset the effect of ZOP inhibitor on copper release.

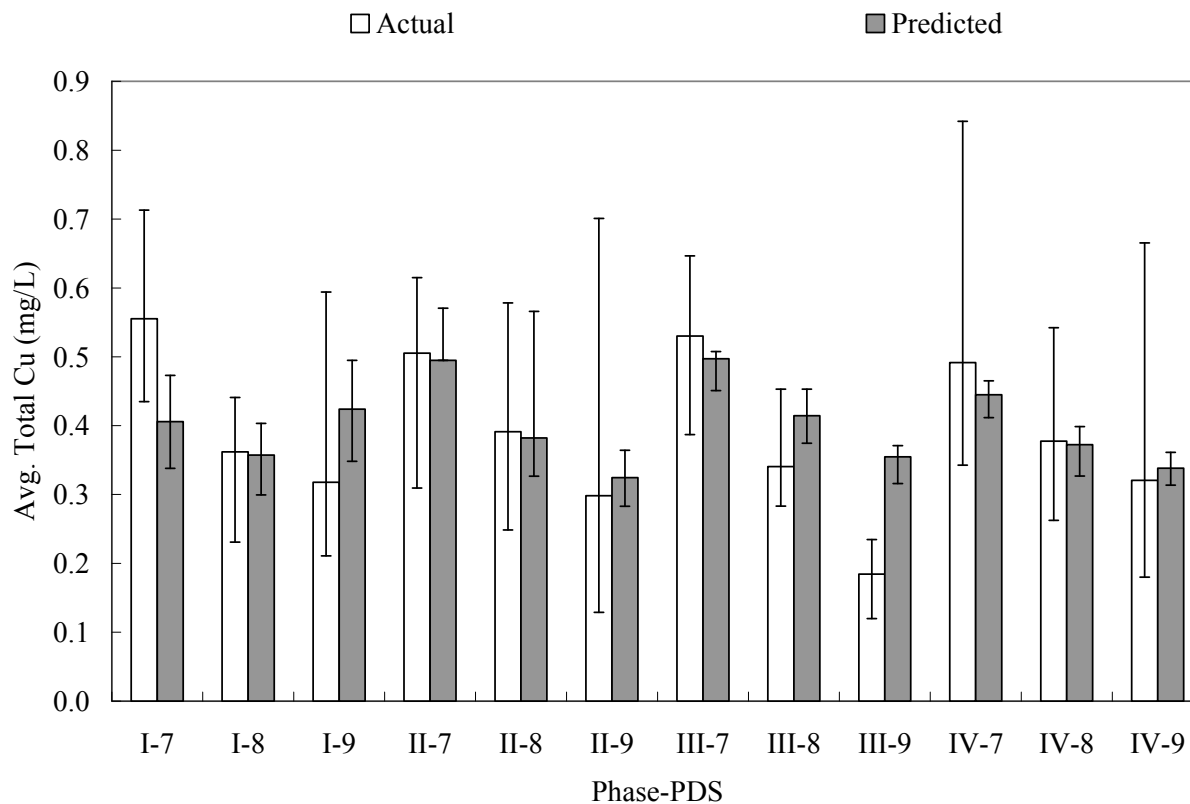


Figure 6.6 Total copper release model summary for ZOP PDSs by phase

Average output total copper concentrations of the entire study for PDSs treated with ZOP inhibitor and pH inhibition were compared in Figure 6.7 to analyze the performance of ZOP inhibitor. The graphical summary of the data supports the previous synopsis that was based on the empirical model. A significant improvement in performance (reduction of total released copper) was realized as ZOP dose increased in this work.



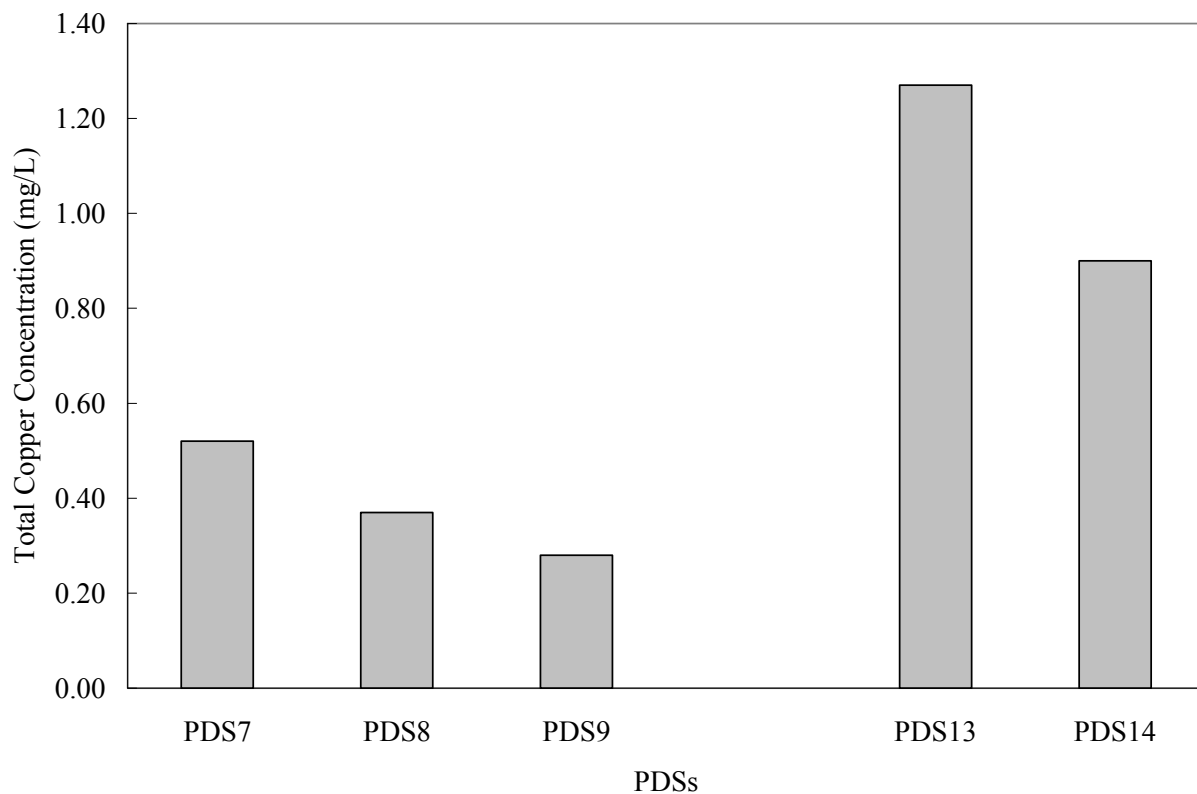


Figure 6.7 Data summary for total copper concentration

As shown in Figure 6.7, there was also a reduction in the release of total copper in PDS 14 compared to PDS 13. The annual average corrosion loop concentrations for PDS 13 ( $\text{pH}_s$ ) and PDS 14 ( $\text{pH}_s + 0.3$ ) were 1.27 and 0.90 mg/L, respectively. Hence increasing pH 0.3 units reduced total copper release by approximately one-fourth. In the absence of a control strategy (either pH elevation or inhibitor addition), compliance with the action level (90<sup>th</sup> percentile concentration) of 1.30 mg/L would be problematic for the expected water quality in the TBW MGs distribution systems. It is generally believed that pH adjustment treatment is an effective method to control copper release, however the average copper concentrations for ZOP PDSs

displayed a clear benefit in comparison to the pH<sub>s</sub> control and pH elevation. Relative to operation at pH<sub>s</sub>, the annual average corrosion loop concentrations were reduced by 60 to 80 %. This may be due to the relatively high concentration of alkalinity in the blended water (average: 140mg/L as CaCO<sub>3</sub> alkalinity). Obviously, ZOP inhibitor is a better choice for copper release control than pH inhibition for the expected water quality.

### **Surface characterization by XPS**

The coupons exposed to ZOP, OP and pH inhibition were analyzed by XPS for comparison. A representative XPS survey scan for copper coupon exposed to medium dose of ZOP inhibitor (1mg/L) is shown in Figure 6.8. O, Ca, C, Cu, P and Zn are indicated on the survey by pronounced peaks.

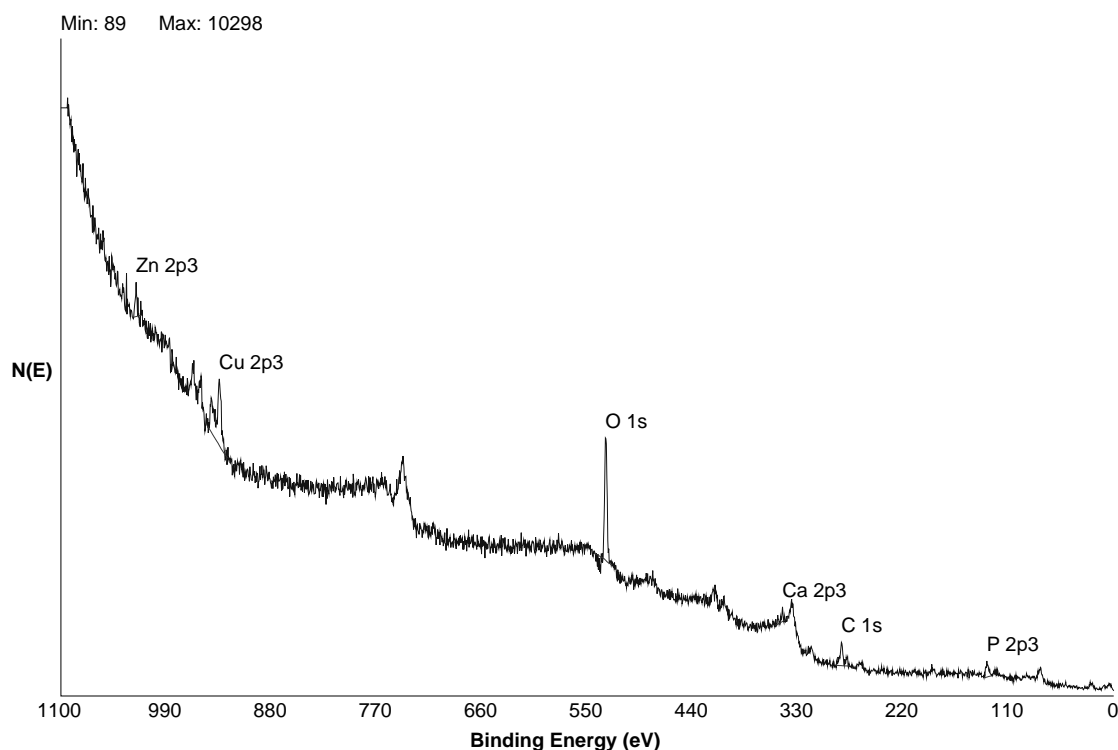


Figure 6.8 Representative XPS survey scan for a copper coupon exposed to ZOP inhibitor in Phase III

The number of coupons where each element was detected out of the total number of coupons exposed to ZOP inhibitor, OP inhibitor and pH control treatment are presented in Table 6.6. Carbon, oxygen and copper were detected in the copper scale on sixteen out of sixteen coupons. Phosphorus was found on six out of eight coupons incubated in phosphate based inhibitors. For coupon exposed to OP inhibitor and pH inhibition, zinc was detected only on one of the twelve coupons, but under ZOP inhibitor treatment, zinc was found in the copper scale on four out of four coupons. These suggested phosphorous and zinc were deposited on the pipe surface and a solid film containing phosphorous and zinc was produced which could be a barrier to copper release from pipe materials and consequently inhibit copper release.

Table 6.6  
Number of coupons containing detected elements from XPS scan

Detected element	No. of coupons where indicated element was detected		
	ZOP (4 total)	OP (4 total)	pH (8 total)
Carbon (C)	4	4	8
Calcium (Ca)	1	2	0
Copper (Cu)	4	4	8
Oxygen (O)	4	4	8
Phosphorous (P)	3	3	0
Zinc (Zn)	4	1	0

High resolution spectra for copper were deconvoluted to identify copper corrosion products and to determine their relative abundance. Copper compounds detected included:  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{Cu}(\text{OH})_2$  and cupric salts  $\text{Cu}(\text{II})$ . Copper orthophosphate solids like cupric phosphate dihydride ( $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ) and cupric phosphate ( $\text{Cu}_3(\text{PO}_4)_2$ ) were two possible forms of  $\text{Cu}(\text{II})$ .

Figure 6.9 depicts the percent area of the various compounds over all phases by inhibitor treatment. Cupric hydroxide was the most abundant copper surface compound. This implies that in the presence of ZOP inhibitor,  $\text{Cu}(\text{OH})_2$  was also the controlling solid phase for copper solubility instead of cupric phosphate.

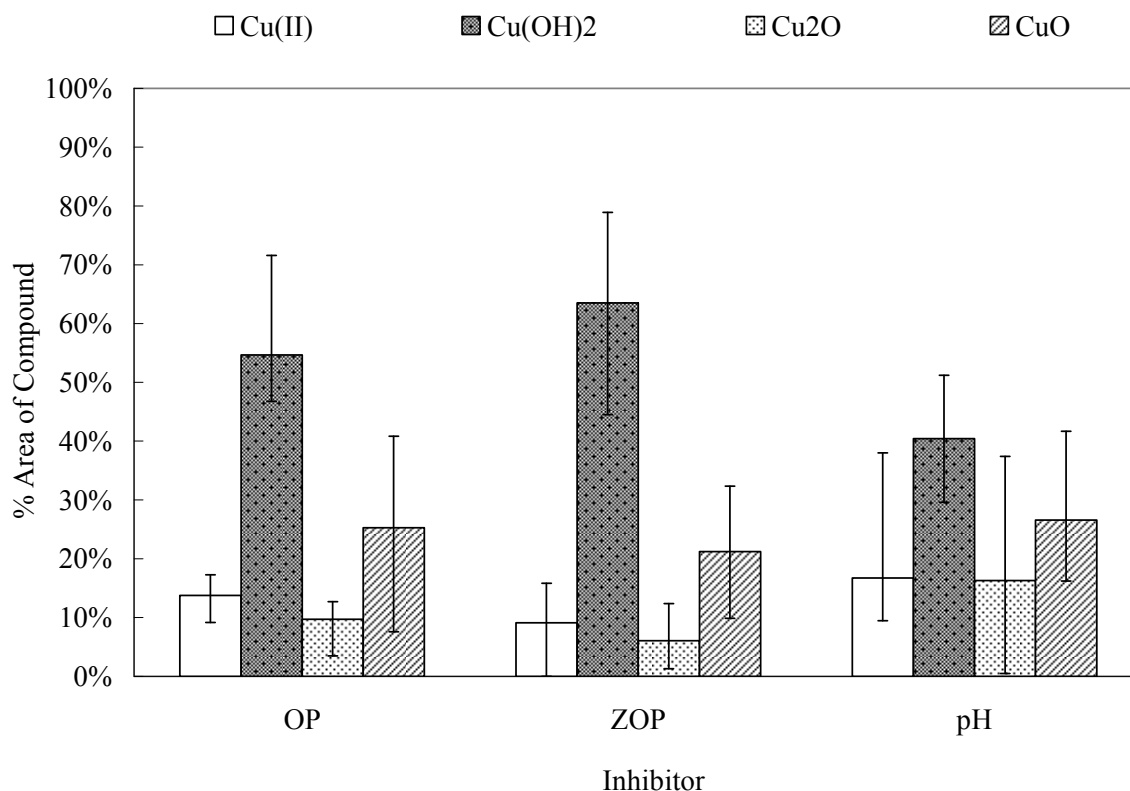


Figure 6.9 Distribution of copper compounds for all phases

Zinc deposits were present in the copper scales for all of the coupons exposed to ZOP inhibitor, being found mostly in the form of ZnO. No zinc compound was identified on most of coupons incubated in other treatments, which suggested ZOP inhibitor addition was the primary source of zinc on the copper scale and produced a zinc-containing film on the pipe surface. The lack of zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) scale in the presence of ZOP indicates that zinc phosphate precipitation was not a factor in inhibiting copper release, which was also indicated by equilibrium model presented previously.

## Thermodynamic model development

Thermodynamic modeling of the various blends was accomplished to evaluate the validity of a copper controlling solid phase. A thermodynamic model was constructed by assuming a copper solid was the controlling solid phase. Dissolved copper concentrations were calculated by assuming free dissolved copper was in equilibrium with the controlling solid phase. Concentrations of other dissolved copper complexes were determined using the appropriate equilibrium constants. This thermodynamic approach is limited to a prediction of dissolved copper, and will under predict total copper release.

The equilibrium model used to predict dissolved copper during previous TBW project was expanded to include phosphate, sulfate, chloride, and ammonia complexes. The developed thermodynamic model is shown below:

$$\begin{aligned} Cu_T = & [Cu^{2+}] + [CuOH^+] + [Cu(OH)_2^0] + [Cu(OH)_3^-] + [CuHCO_3^+] + [CuCO_3^0] \\ & + [Cu(CO_3)^{2-}] + [Cu(OH)CO_3^-] + [Cu(OH)_2CO_3^{2-}] + [CuH_2PO_4^+] \\ & + [CuHPO_4^0] + [CuSO_4^0] + [Cu(NH_3)^{2+}] + [Cu(NH_3)_2^{2+}] + [Cu(NH_3)_3^{2+}] \\ & + [Cu(NH_3)_4^{2+}] + [Cu(NH_3)_5^{2+}] + [CuCl^+] + [CuCl^0] \end{aligned} \quad (\text{Equation 6.4})$$

The primary ligands responsible for increases in total copper were all related to alkalinity, including  $CuHCO_3^-$ ,  $CuCO_3^0$ ,  $Cu(CO_3)_2^{2-}$ ,  $Cu(OH)CO_3^-$ , and  $Cu(OH)_2CO_3^{2-}$ . Equilibrium calculations demonstrated the profound effect of alkalinity on copper release: increased alkalinity will result in higher copper concentrations. This is consistent with the conclusion from empirical modeling.

Thermodynamic modeling results are provided in Table 6.7 assuming cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ), tenorite ( $\text{CuO}$ ), cupric phosphate dihydride ( $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ), and cupric phosphate ( $\text{Cu}_3(\text{PO}_4)_2$ ) each as the possible controlling solid phase. Although both cupric hydroxide and cupric phosphate dihydride solids over predict the observed dissolved copper release, these two models both provided reasonable predictions of dissolved copper release from copper loops receiving ZOP inhibitor. Considering the distribution of various compounds identified by XPS analysis (Figure 6.9),  $\text{Cu}(\text{OH})_2$  should be the corrosion product (solid phase) controlling copper release in the presence of ZOP inhibitor.

However, in contrast, the values predicted by cupric phosphate dihydride,  $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  were a closer match to the data compared to the predictions of the cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ) model, which confirmed the presence of a phosphate-based solid contributes to the reduction of copper release. This may imply that dissolved copper release was not solely dependent on  $\text{Cu}(\text{OH})_2$  but rather may depend on  $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  or other cupric phosphate solids which form and reduce copper release with ZOP inhibitor addition. Although inhibitor addition did not change the controlling solid for copper release, it promoted the formation of cupric phosphate solids which reduce the rate of copper release, while the equilibrium copper concentration remains unchanged.

Table 6.7  
Thermodynamic modeling

Inhibitor	Phase	Actual Copper Release (mg/L)		Modeled Copper Release (mg/L)			
		Diss Cu	Total Cu	$\text{Cu}(\text{OH})_2$	$\text{CuO}$	$\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{Cu}_3(\text{PO}_4)_2$

ZOP	1	0.34	0.36	0.64	0.08	0.63	2.70
	2	0.32	0.39	0.68	0.08	0.37	1.60
	3	0.30	0.34	0.63	0.08	0.59	2.52
	4	0.32	0.38	0.72	0.09	0.43	1.86
	All	0.32	0.37	0.72	0.09	0.52	2.24

### **Conclusion**

Zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was found to precipitate in the inhibitor feed tank. Solubility modeling indicated  $\text{Zn}_3(\text{PO}_4)_2$  would not precipitate if ZOP inhibitor was added directly to the PDSs. Since  $\text{Zn}_3(\text{PO}_4)_2$  would not be expected to precipitate in the PDSs or in actual use, the precipitation of zinc phosphate precipitation wasn't and would not be a factor in inhibiting copper release by ZOP inhibitor as indicated by equilibrium calculations.

Empirical model development was undertaken for prediction of total copper concentration in the PDSs. Several modeling efforts were undertaken using different sets of water quality terms to reduce the impacts of confounding. The negative exponents on the total phosphorus and zinc terms in the model indicate that both total phosphorus and zinc were beneficial for reducing copper release. The model was not very sensitive to zinc indicated that zinc from ZOP inhibitor doesn't play an important role in the inhibition process. The positive exponent on the alkalinity term suggested that increased alkalinity will result in higher copper concentrations. The model also indicated that elevated chloride concentrations will aggravate copper release. It was also found that better control of copper would occur at higher pH values. Actual average total copper concentrations confirmed above conclusions.

The actual average copper concentrations for ZOP PDSs displayed a clear benefit in comparison to the  $\text{pH}_s$  control and pH elevation. In the absence of a control strategy (either pH



elevation or inhibitor addition), compliance with the action level (90<sup>th</sup> percentile concentration) of 1.30 mg/L would be problematic for the expected water quality in the TBW MGs distribution systems. The actual total copper release decreased as inhibitor dose increased. The model suggested the same trend, confirming a better inhibitor performance at higher inhibitor doses.

The coupons exposed to ZOP, OP and pH inhibition were analyzed by XPS. Surface characterization results suggested that phosphorous and zinc were deposited on the pipe surface and a solid film containing phosphorous and zinc were produced which could be a barrier to copper release from pipe materials and consequently inhibit copper release. Copper compounds detected included:  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{Cu}(\text{OH})_2$  and cupric salts  $\text{Cu}(\text{II})$ . Copper orthophosphate solids were the possible forms of  $\text{Cu}(\text{II})$ . ZOP corrosion inhibitor addition was found to be the primary source of zinc on the copper scale and produced a zinc-containing film on the pipe surface. Zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was not found on the scale which was consistent with the solubility modeling result.

The distribution of various compounds identified by surface characterization indicated that  $\text{Cu}(\text{OH})_2$  was the possible controlling solid phase for copper release in the presence of ZOP inhibitor. Thermodynamic modeling for dissolved copper concentration found that the predictions of cupric phosphate dihydride,  $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  model was a closer match to the data which confirmed the presence of a phosphate-based solid contributes to the reduction of copper release.

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## **CHAPTER 7**

### **EFFECTS OF ZINC ORTHOPHOSPHATE (ZOP) CORROSION INHIBITOR ON TOTAL LEAD RELEASE IN A CHANGING WATER QUALITY ENVIRONMENT**

#### **Abstract**

A study was conducted to determine the impact of ZOP inhibitor on lead release in a changing water quality environment and the role of zinc in ZOP inhibition. Water quality and lead scale formation was monitored in pilot distribution systems that received changing quarterly blends of finished ground, surface and desalinated waters with and without zinc orthophosphate (ZOP) inhibitor over a one year period.

#### **Introduction**

Tampa Bay Water (TBW) manages drinking water resources for six member governments on the west coast of central Florida. To meet increasing consumer demand and more stringent environmental and drinking water regulations, TBW has developed regional surface water and desalinated supplies which will offset the reductions in groundwater use and provide for future growth in the region. TBW and UCF have conducted research to seek understanding of the issues involved when multiple-source waters are blended since 2000. The work had demonstrated that control of the scale or film in the existing distribution systems was essential 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 using corrosion inhibitors. Corrosion inhibitors offer an opportunity for scale control because they bond directly with the elemental metal or scale and form a barrier on the pipe surface. The film or barrier separates the bulk water from

the metal surface and can be renewed by continuous addition of the corrosion inhibitor to finished water.

Lead used to be the preferred material to connect customers to the water distribution system due to its flexibility, ease of installation and its longevity. However, increasing awareness of the presence and potential health related effects of lead in drinking water has led the US Environmental Protection Agency to mandate action levels of 0.015 mg/L. A nationwide utility survey conducted in 2001 (McNeill, L.S. & Edwards, M. 2002) reported that 56% of all responding utilities add phosphate inhibitors in 2001, 84% of utilities currently dose inhibitors to control lead and copper. Around 30% of water utilities reported using orthophosphate or zinc orthophosphate inhibitor.

The effectiveness of orthophosphate based inhibitors in preventing lead corrosion related problems has been proved by numerous studies. It is believed that dosing of orthophosphate might be predicted to decrease lead solubility through formation of relatively insoluble scales (Edwards, M. & McNeill, L.S. 2002). Evidence from lead pipe test rig studies suggested that a pyromorphite-like species, probably hydroxypyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ) formed when orthophosphate was added to the water supply system (Davidson, C.M., et al 2004). In Colling's study, although the deposit formed in phosphate-treated water could not be precisely identified, elemental analysis (Energy-Dispersive X-ray spectrometry (EDX) revealed it to contain lead, phosphorus and some calcium (Colling, J.H., Whincup, P.A.E. & Hayes, C.R. 1987). Grimes and Peters also found that in the presence of orthophosphate, lead corrosion products contained a variable proportion (up to ~30% w/w) of a phosphate species which is most probably ( $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ) (Grimes, S.M., Johnston, S.R. & Batchelder, D.N. 1995; Peters, N.J., et al 1999).

The thermodynamic models for dissolved lead was developed in a large field scale project funded by Tampa Bay Water (TBW) and AwwaRF to predict the lead release from pipe surface (Taylor, J.S., et al 2005). Assuming the controlling solid phase is  $Pb_3(OH)_2(CO_3)_2$ , the developed dissolved lead model is:

$$\begin{aligned}
 DIPb = & [Pb^{2+}] + 4[Pb_4(OH)_4^{4+}] + 2[Pb_2OH^{3+}] + [PbOH^+] + 3[Pb_3(OH)_4^{2+}] \\
 & + 6[Pb_6(OH)_8^{4+}] + [Pb(OH)_2^0] + [Pb(OH)_3^-] + [Pb(OH)_4^{2-}] + [PbCO_3^0] \\
 & + 3[Pb_3CO_3^{4+}] + 2[Pb_2CO_3^{2+}] + [Pb(CO_3)_2^{2-}] + [PbHCO_3^+] + [PbSO_4^0] \\
 & + [Pb(SO_4)_2^{2-}] + [PbCl^+] + [Pb(Cl)_2^0] + [Pb(Cl)_3^-] + [Pb(Cl)_4^{2-}]
 \end{aligned}
 \tag{Equation 7.1}$$

Zinc orthophosphate (ZOP) has been widely used for many years as a reliable, known and safe corrosion inhibitor. ZOP is generally believed to produce a microscopic film on metal surfaces that acts as a barrier to corrosive environments. It was also reported that zinc phosphates often performed better than orthophosphates for certain water types (Benjamin, M., Sontheimer, H. & Leroy, P. 1996). Some studies suggested that the presence of zinc in the inhibitor either accelerated film formation or helped to form a better-quality film than regular phosphate films for inhibiting corrosion (Reese, W.J. 1962; Kleber, J.P. 1965; Murray, W.B. 1970; Mullen, E.D. & Ritter, J.A. 1974; Mullen, E.D. & Ritter, J.A. 1980; Swayze, J. 1983; Bancroft, D. 1988; Horn, B.P. & McGiffney, G.J. 1999). However, several other studies that have compared zinc orthophosphate compounds versus simple orthophosphates have shown no significant benefit from zinc additives at operational dosage (Huang, D.J.S. 1980; HDR Engineering Inc 2001).

Zinc is an environmental concern because of the adverse effects of zinc on wastewater treatment facilities and limits on the land disposal of sludge. Hence, it is important to understand

the role of zinc, if any, in corrosion inhibition and especially in lead release in a variable water quality environment.

### **Experimental Methods**

#### **The pilot distribution systems (PDSs)**

An extensive research facility was constructed for this study and consisted of seven pilot water treatment facilities, eighteen pilot distribution systems (PDSs) with individual sampling ports and cradles for individual coupon analyses, a corrosion facility with eighteen copper and lead corrosion loops, a stainless steel food grade trailer for hauling water and five trailers for housing of pilot facilities, chemical analyses and equipment storage.

The PDSs were designed to represent typical scenarios for changing water quality that were experienced in a real distribution system. These PDSs are identical and consisted of increments of PVC, lined cast iron, unlined cast iron and galvanized steel pipes connected in series. A picture of the PDSs is shown in Figure 7.1. The PDSs are operated to maintain a two-day hydraulic residence time (HRT). Standpipes are located at the beginning and end of each PDS to ensure the presence of water inside of the lines at all times.





Figure 7.1 Pilot Distribution System

A corrosion shed was built which contained eighteen loops of lead pipes, as shown in Figure 7.2, for the lead corrosion study. A portion of the flow from each PDS was discharged to the corrosion loop to simulate a consumer environment and tap monitoring for LCR (lead and copper rule) compliance. Only fourteen of the eighteen PDSs and corrosion loops were utilized in this work.

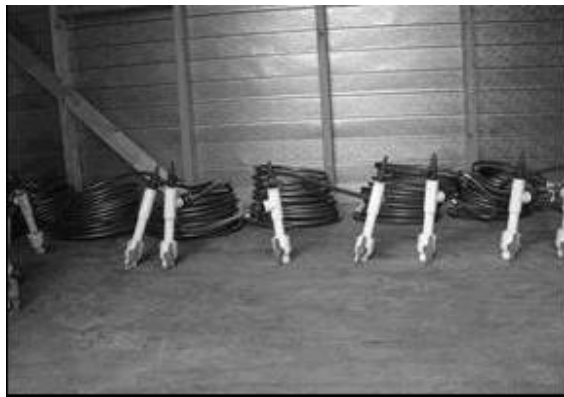


Figure 7.2 Corrosion shed and loops

### **The use of zinc orthophosphate (ZOP) inhibitor**

In the fourteen PDSs, PDS 1-12 received four different corrosion inhibitors at three different doses. The remaining two PDSs (PDS 13 and PDS14) received only pH adjustment. PDS 13 influent was adjusted to  $\text{pH}_s$  and PDS 14 influent was adjusted to  $\text{pH}_s + 0.3$ . PDS 13 and 14 served as controls or references for the project.

The ZOP dose was constant for the year of operation, and was 0.5, 1.0, and 2.0 mg/L as P in PDS 7, 8 and 9 respectively. Stock solutions of ZOP were diluted in a 40 gallon ( $151 \text{ m}^3$ ) tank and the feed rates of ZOP to the three PDSs were calibrated twice a week. The ZOP inhibitor used in this study is made by dissolving zinc sulfate into a phosphoric acid solution. The product has a ratio of 1 part Zinc to five parts  $\text{PO}_4$  with a target of 6% as Zinc and 30% as  $\text{PO}_4$ .

### **Source and blend water quality**

Conventionally treated groundwater (GW), enhanced treated surface water (SW) and desalinated water treated by reverse osmosis (RO) were blended and fed to the PDSs. The blends of GW, SW and RO were changed quarterly over one year as shown in Table 7.1. All PDSs received the same blend during each phase. The phases I and III were identical in order to evaluate seasonal effects, which were predictable by water quality.

Table 7.1  
Blend ratios of GW, SW, and RO waters used during project

Phase	Time Period	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

### **Data collecting and analysis**

Influent and effluent water quality was monitored for each of the fourteen PDSs over the year of operation. Quality assurance and quality control of both the laboratory and field determinations of water quality parameters was accomplished by taking duplicate samples and repeating at least 10% of the analyses in the laboratory and field. Blind duplicates and spikes were also used to determine the accuracy of measurements. Dynamic control charts were used to monitor precision and accuracy of laboratory and field analysis.

PDS influent water quality was typically identical except for pH, inhibitor type and inhibitor concentration. Influent and effluent water quality parameters shown in Table 7.2 were typically monitored weekly or biweekly. Key parameters of investigation like ortho-phosphorus, pH, and flow were monitored at least 3 times a week for control.

Table 7.2  
Related influent and effluent chemical monitoring for each of 14 PDSs and cradles

Parameter	Method
Alkalinity	Titration
Ammonia	NH <sub>3</sub> probe
Chlorine, Free	Spectrophotometer
Chlorine, Total	Spectrophotometer
Color, Apparent	Spectrophotometer
Conductivity	Conduct probe
Nitrite-N	Spectrophotometer
ORP	Redox probe
Oxygen, Dissolved	DO probe
pH	pH probe
Phosphorus, Ortho	Spectrophotometer
Silica	Spectrophotometer
TDS	TDS probe
Temperature	Probe
Turbidity	Turbidimeter
UV-254	Spectrophotometer
Aluminum	ICP
Calcium	ICP
Chloride	IC
Copper, Dissolved	ICP
Copper, Total	ICP
Iron, Dissolved	ICP
Iron, Total	ICP
Lead, Dissolved	ICP
Lead, Total	ICP
Magnesium	ICP
NPDOC	TOC Instrument
Phosphorus, Total	ICP
Silica	ICP
Sodium	ICP
Sulfate	IC
TKN	Digestion
Zinc, Dissolved	ICP
Zinc, Total	ICP

Surface characterization was a critical part of documenting the effects of ZOP corrosion inhibitor on lead release. The lead coupons for surface characterization study were rectangular and were housed in a cradle which received PDS effluent. Surface characterization was done on

24 coupons using X-ray Photoelectron Spectroscopy (XPS) to identify chemical components of the top surface of the corrosion layer.

## **Results and Discussions**

### **Field operation**

#### *Total phosphorus*

Figure 7.3 shows the average influent and effluent phosphorus concentrations as well as the minimum and maximum observed for each of the ZOP PDSs using a bar and whiskers format. The bars represent the average while the whiskers represent the minimum and maximum of the four phases. The measured average influent values for the reporting period were 0.54, 0.91, and 1.73 mg P/L for the low, medium and high inhibitor doses. Average effluent concentrations were 0.43, 0.82 and 1.65 for the low, medium and high inhibitor doses respectively. As shown in Figure 7.3, the average influent concentrations for all ZOP PDSs are persistently higher than the effluent values which indicated that uptake of phosphorus occurred in all PDSs receiving ZOP inhibitor in this work.

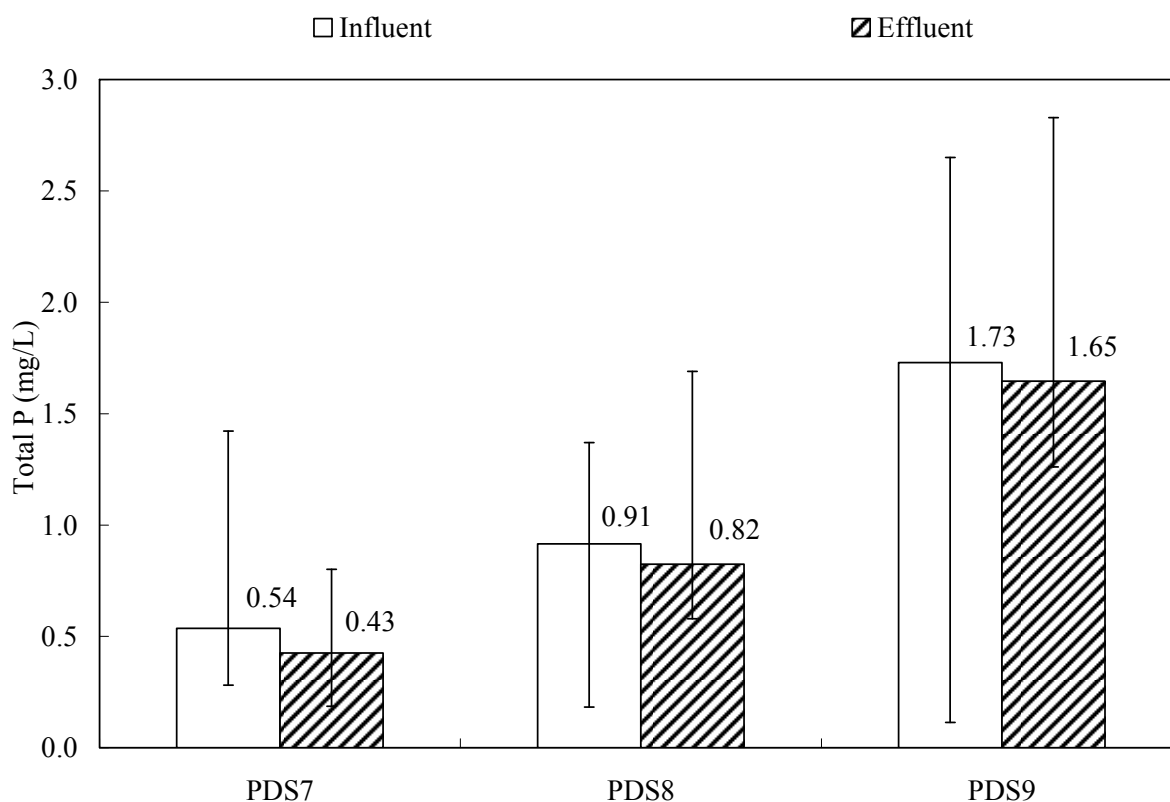


Figure 7.3 Average measured total phosphorus concentration

Average influent and effluent phosphorus concentrations are presented in Table 7.3 by phase and PDSs. Effluent values are continually lower than the feed concentrations at all inhibitor doses for all phases except for PDS 8 in Phase III. The continuous uptake of phosphorus in all ZOP PDSs for all 4 phases indicated a phosphorus-containing film may be produced on the pipe surface which could be a barrier to lead release from pipe materials. The data also indicated that variation of phase water quality did not significantly affect the mass balance of total phosphorus.

Table 7.3  
Average influent and effluent phosphorus concentrations for each phase

		PDS 7	PDS 8	PDS 9
Phase I	Influent	0.63	1.00	1.74
	Effluent	0.49	0.90	1.68
Phase II	Influent	0.54	0.88	1.77
	Effluent	0.34	0.77	1.72
Phase III	Influent	0.49	0.88	1.82
	Effluent	0.48	0.90	1.73
Phase IV	Influent	0.46	0.88	1.58
	Effluent	0.38	0.70	1.44

*Total zinc*

The measured average influent zinc concentrations for all 4 phases were noted to be 0.05, 0.13, and 0.25 mg P/L for the low, medium and high ZOP inhibitor doses. The average values as well as the minimum and maximum zinc concentrations are presented in Figure 7.4 using a bar and whiskers format.

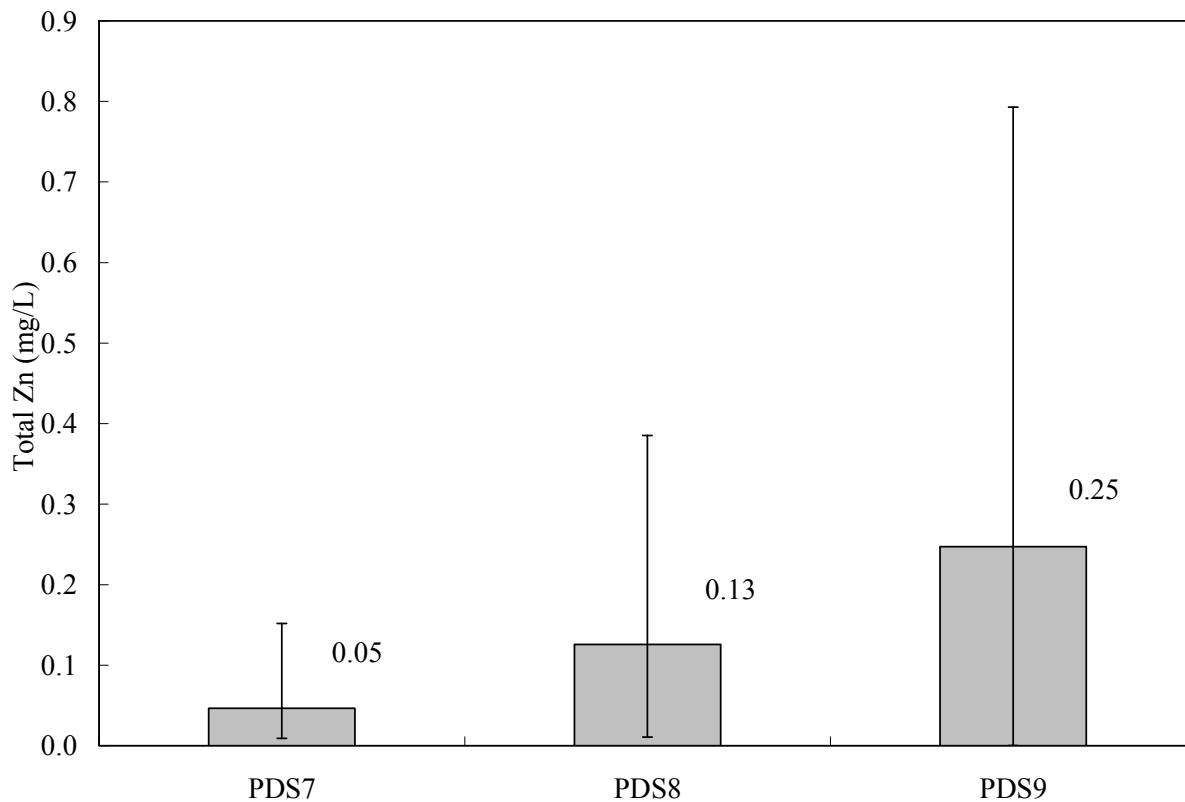


Figure 7.4 Average measured total zinc concentration

Influent zinc to PO<sub>4</sub> ratios were calculated to be 1:33, 1:21 and 1:21 for low, medium and high ZOP inhibitor doses respectively. These ratios were significantly smaller than the inhibitor manufacturer's specification which was 1 part Zinc to five parts PO<sub>4</sub> with a target of 6% as Zinc and 30% as PO<sub>4</sub>. As also shown in Table 7.4, theoretical zinc concentration calculated base on measured total phosphorus value is much higher than measured zinc concentration. This is most likely due to the precipitation of zinc phosphate ( $Zn_3(PO_4)_2$ ) in the inhibitor feed tank, which could be an operational or cost problem for utilities using ZOP.



The stock solutions of the ZOP inhibitor product were diluted in a 40 gallon (151 m<sup>3</sup>) feed tank. During field operation, a white precipitate was observed in the ZOP feed tank. Majority of this white precipitate was identified as zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) solid using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDS) (as shown in Figure 7.5) and an Ion Coupled Plasma (ICP) Spectrophotometer.

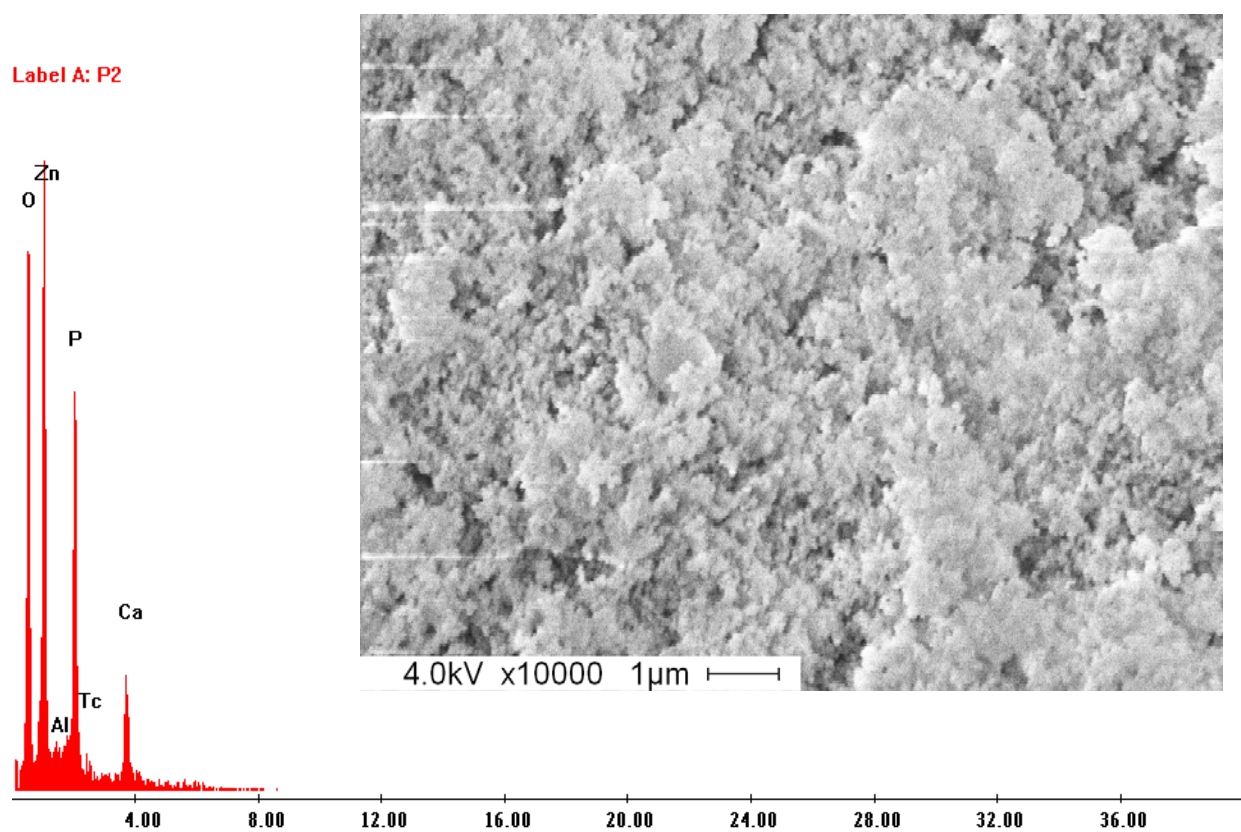


Figure 7.5 EDS analysis results and SEM image (4.0kV×10000)

The solubility modeling for zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was undertaken to simulate addition of the ZOP inhibitor directly to the PDSs. The modeling results are shown in Table 7.4.

Taking into account the effects of ionic strength, the solubility calculations were consistent with the precipitation of  $\text{Zn}_3(\text{PO}_4)_2$  in the feed tank. The results also suggested that  $\text{Zn}_3(\text{PO}_4)_2$  would not precipitate if the inhibitor feed tank was bypassed and ZOP inhibitor was added directly to the PDSs. Since  $\text{Zn}_3(\text{PO}_4)_2$  would not be expected to precipitate in the PDSs or in actual use, the precipitation of zinc phosphate precipitation wasn't and would not be a factor in inhibiting lead release by ZOP inhibitor as indicated by equilibrium calculations.

Table 7.4  
ZOP solubility modeling

	Stock	Feed Tank	PDS 7	PDS 8	PDS 9
pH	1	6.7	7.9	7.8	7.7
P (mg/L)	123974	19.30	0.55	0.92	1.65
PO <sub>4</sub> (mg/L)	379920	59.15	1.69	2.82	5.06
Calculated Zn (mg/L)	75984	11.829	0.337	0.564	1.011
$\text{Zn}_3(\text{PO}_4)_2$ Precipitation	No	Yes	No	No	No

### **ZOP inhibitor performance**

A summary of the total and dissolved lead release data for each of the PDSs receiving zinc orthophosphate inhibitor is shown in Table 7.5. This data is segregated by Phase and by PDS. It can be seen that the majority of the lead released in the PDSs was in the particulate form. There was no apparent improved inhibition (reduction) of lead release as ZOP dose increased. Many of the reported lead values were below or very close to the detection limit (0.001 mg/L) for lead analysis, which indicates the maximum reduction or inhibition of total lead was achieved by the lowest inhibitor dose. This is expected if ZOP inhibition is caused by an inhibitor generated film or scale which is maximized under these conditions at the lowest ZOP dose.

Table 7.5  
Lead release summary for ZOP PDSs

Phase	PDS	Dose	Dissolved Pb			Total Pb		
			Avg	Max	Min	Avg	Max	Min
I	7	0.64	0.000	0.001	0.000	0.000	0.002	0.000
	8	0.99	0.000	0.002	0.000	0.000	0.003	0.000
	9	1.78	0.000	0.002	0.000	0.002	0.019	0.000
II	7	0.54	0.000	0.002	0.000	0.000	0.001	0.000
	8	0.89	0.000	0.001	0.000	0.000	0.002	0.000
	9	1.77	0.001	0.002	0.000	0.001	0.007	0.000
III	7	0.49	0.000	0.001	0.000	0.000	0.001	0.000
	8	0.88	0.000	0.000	0.000	0.001	0.001	0.000
	9	1.82	0.000	0.001	0.000	0.001	0.001	0.000
IV	7	0.46	0.000	0.001	0.000	0.001	0.001	0.000
	8	0.88	0.000	0.001	0.000	0.001	0.001	0.000
	9	1.58	0.001	0.002	0.000	0.001	0.005	0.000
All	7	0.54	0.000	0.002	0.000	0.000	0.002	0.000
	8	0.91	0.000	0.002	0.000	0.001	0.003	0.000
	9	1.74	0.000	0.002	0.000	0.001	0.019	0.000

Average output total lead concentrations of the entire study for PDSs treated with ZOP inhibitor and pH inhibition were compared in Figure 7.6 to analyze the performance of ZOP inhibitor. As shown in the graph, there was some improvement for total lead release control in PDS 14 ( $\text{pH}_s + 0.3$ ) compared to PDS 13 ( $\text{pH}_s$ ). The annual average corrosion loop concentrations for PDS 13 and PDS 14 were 0.014 and 0.006 mg/L, respectively. Hence increasing pH 0.3 units reduced total lead release by approximately one-half. In the absence of a control strategy (either pH elevation or inhibitor addition), compliance with the action level (90<sup>th</sup>

percentile concentration) of 0.015mg/L would be problematic for the expected water quality in the TBW MGs distribution systems.

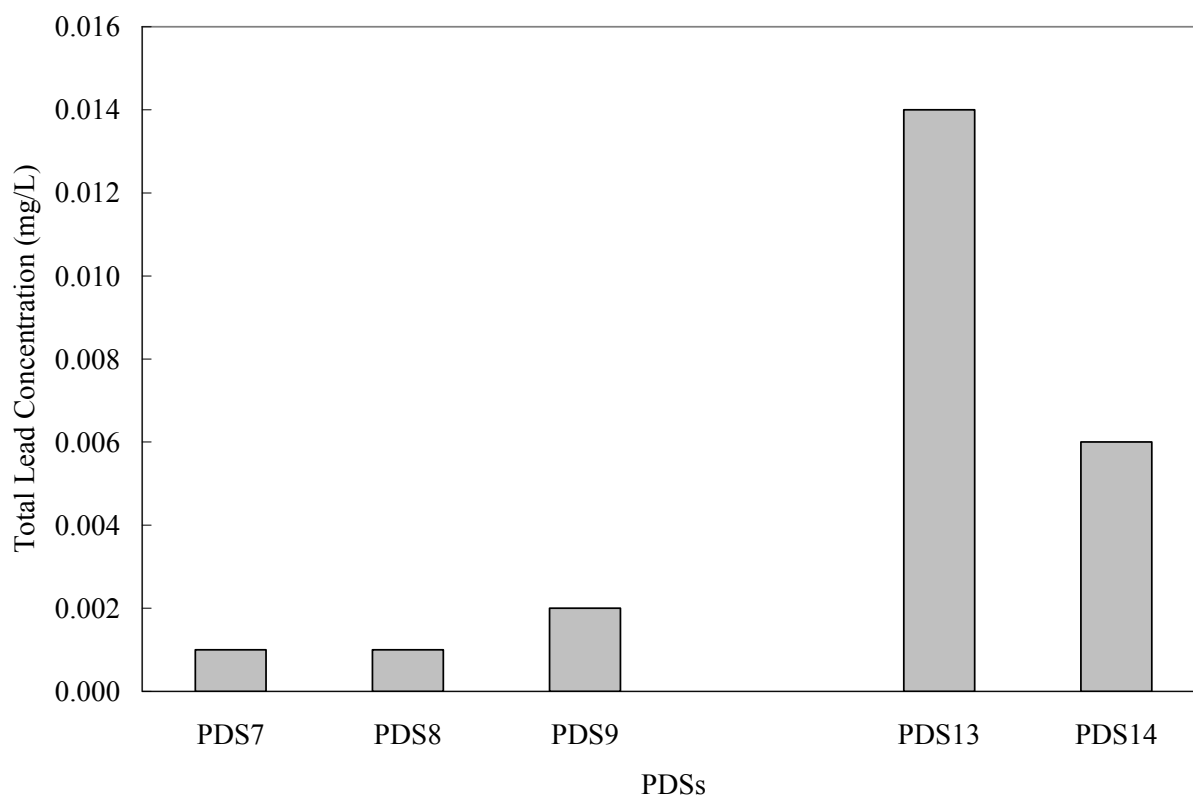


Figure 7.6 Data summary for total lead concentration

The average lead concentrations for ZOP PDSs displayed a clear benefit in comparison to the  $\text{pH}_s$  control and pH elevation. Relative to operation at  $\text{pH}_s$ , the annual average corrosion loop concentrations were reduced by 80 to 90 %. Apparently, ZOP inhibitor is a better choice for lead release control than pH inhibition. ZOP inhibitor actually exhibited the best performance in lead release control compared to other inhibitor studied in this work including blend orthophosphate (BOP), orthophosphate (OP), silicate (Si) and pH elevation ( $\text{pH}_s+0.3$ ). Considering the similarity

of OP inhibitor and ZOP inhibitor, the higher average total lead releases for OP PDSs indicated that addition of zinc in ZOP inhibitor was beneficial for reducing lead release.

There is not any apparent improved inhibition of lead release with the increase in ZOP dose based on Figure 7.6. However, since the detection limit for dissolved lead is 0.001 mg/L which is very close to the average measured data in all ZOP PDSs, the effects of increasing ZOP dose on lead release control was difficult to discern.

A statistical comparison of the mean lead concentrations (one tailed, paired data, t-test for equality of means) between the control (PDS 13) and the corrosion control treatments (PDS 14, PDS 07 to PDS 09) is reported in Table 7.6. A reduction in lead release was observed for pH elevation in all phases. This reduction was statistically significant for three out of five comparisons (Phase II, Phase III, and composite). ZOP Inhibitor addition also reduced average lead release at all doses and phases, and was statistically significant for 14 out of 15 comparisons. ZOP inhibitor was effective for all blends and water qualities regardless of blends (including groundwater or elevated alkalinity in Phase I and Phase III).

Table 7.6  
Comparison of ZOP inhibitor to pH<sub>s</sub> control for total lead

Treatment Dose	PDS 13 pH pH <sub>s</sub>	PDS 14 pH pH <sub>s</sub> +0.3	PDS 07 ZOP Low	PDS 08 ZOP Med	PDS 09 ZOP High
Phase I					
Average	0.006	0.003	0	0.001	0.002
StDev	0.006	0.005	0.001	0.001	0.005
n	14	14	14	14	14
Significant		No	Yes	Yes	No
p-value		0.129	0.002	0.002	0.074
Phase II					
Average	0.012	0.008	0	0	0.001
StDev	0.007	0.007	0	0	0.002
n	13	13	13	13	13
Significant		yes	yes	yes	yes
p-value		0.048	< 0.001	< 0.001	< 0.001
Phase III					
Average	0.032	0.01	0	0.001	0.001
StDev	0.019	0.009	0	0	0
n	13	13	13	13	13
Significant		Yes	Yes	Yes	Yes
p-value		< 0.001	< 0.001	< 0.001	< 0.001
Phase IV					
Average	0.004	0.003	0	0.001	0.001
StDev	0.003	0.003	0	0.001	0.001
n	12	12	12	12	12
Significant		No	Yes	Yes	Yes
p-value		0.153	< 0.001	0.001	0.006
Composite					
Average	0.013	0.006	0	0.001	0.001
StDev	0.015	0.007	0	0.001	0.003
n	52	52	52	52	52
Significant		Yes	Yes	Yes	Yes
p-value		< 0.001	< 0.001	< 0.001	< 0.001

## Surface characterization by XPS

The coupons exposed to ZOP, OP and pH inhibition were analyzed by XPS for comparison. The XPS scanning consists of a two-step process: the initial “survey” scan conducted over a broad range of energy levels to identify all possible elements present on the coupon and the high resolution scan, over a narrow range of energy levels, for establishing the chemical states present for a given element.

A representative XPS survey scan for lead coupon exposed to medium dose of ZOP inhibitor (1mg/L) is shown in Figure 7.7. Lead, tin, oxygen, carbon, calcium and zinc are indicated on the survey by pronounced peaks.

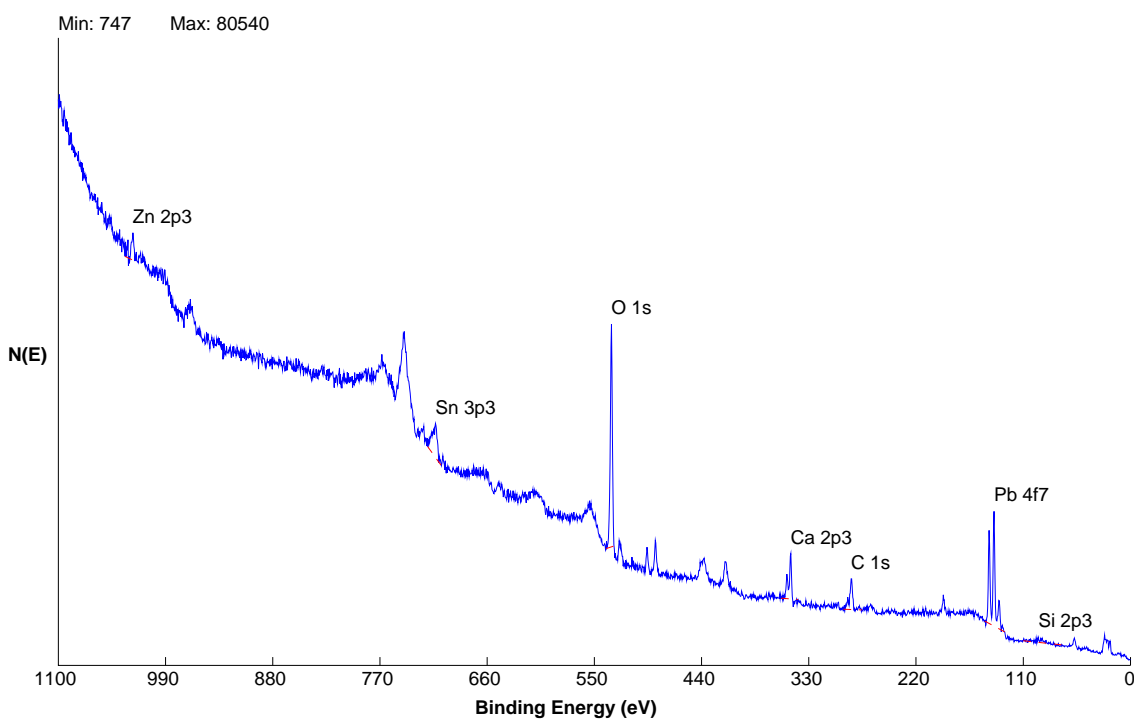


Figure 7.7 Representative XPS survey scan for a lead coupon exposed to ZOP inhibitor in Phase III

The number of coupons where each element was detected out of the total number of coupons exposed to ZOP inhibitor, OP inhibitor and pH control treatment are presented in Table 7.7. Carbon, oxygen, lead and tin were detected in the lead scale on most coupons. Phosphorus was found on six out of eight coupons incubated in phosphate based inhibitors and zero out of eight coupons in non-phosphate environment. Zinc was detected only on four of the twelve coupons exposed to OP inhibitor and pH inhibition, which were most likely released from the galvanized steel pipe. By contrast, under ZOP inhibitor treatment, zinc was found in the lead scale on four out of four coupons. These suggested phosphorous and zinc were deposited on the pipe surface and a solid film containing phosphorous and zinc was produced which could inhibit lead release.

Table 7.7  
Number of coupons containing detected elements from XPS scan

Detected element	No. of coupons where indicated element was detected		
	ZOP (4 total)	OP (4 total)	pH (8 total)
Carbon (C)	4	3	6
Calcium (Ca)	2	2	3
Lead (Pb)	4	4	7
Tin (Sn)	4	4	7
Oxygen (O)	4	4	8
Phosphorous (P)	3	3	0
Zinc (Zn)	4	2	2

High resolution spectra for lead were deconvoluted to identify lead corrosion products and to determine their relative abundance. Lead corrosion products  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$



(hydrocerussite),  $\text{PbCO}_3$  (cerussite),  $\text{PbO}$ , and  $\text{PbO}_2$  are possible in scales on lead coupons. Since significant amount of phosphorus was identified in the scale, being found mostly in the form of orthophosphate ( $\text{PO}_4^{3-}$ ), a lead orthophosphate solid like hydroxypyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ) may also existed on the surface of the coupons exposed to ZOP inhibitor.

Zinc deposits were present in the lead scales for all of the coupons exposed to ZOP inhibitor. No zinc compound was identified on most of coupons incubated in other treatments, which suggested ZOP inhibitor addition was the primary source of zinc on the lead scale and produced a zinc-containing film on the pipe surface. The lack of zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) scale in the presence of ZOP indicates that zinc phosphate precipitation was not a factor in inhibiting lead release, which was also indicated by equilibrium model presented previously..

### **Thermodynamic model development**

Thermodynamic modeling of the various blends was accomplished to predict dissolved lead at equilibrium. A thermodynamic model was constructed by assuming a lead solid was the controlling solid phase. Dissolved lead concentrations were calculated by assuming free dissolved lead is in equilibrium with the controlling solid phase. Concentrations of other dissolved lead complexes were determined using the appropriate equilibrium constants. This thermodynamic approach is limited to a prediction of dissolved lead, and will under predict total lead release.

The equilibrium model used to predict dissolved lead during previous TBW project (Taylor, J.S., et al 2005) was expanded to include phosphate, sulfate and chloride complexes. The developed thermodynamic model is shown below:

$$\begin{aligned}
\text{Pb}_T = & [\text{Pb}^{2+}] + 4[\text{Pb}_4(\text{OH})_4^{4+}] + 2[\text{Pb}_2\text{OH}^{3+}] + [\text{PbOH}^+] + 3[\text{Pb}_3(\text{OH})_4^{2+}] \\
& + 6[\text{Pb}_6(\text{OH})_8^{4+}] + [\text{Pb}(\text{OH})_2^0] + [\text{Pb}(\text{OH})_3^-] + [\text{Pb}(\text{OH})_4^{2-}] + 3[\text{Pb}_3\text{CO}_3^{4+}] \\
& + 2[\text{Pb}_2\text{CO}_3^{2+}] + [\text{PbCO}_3^0] + [\text{Pb}(\text{CO}_3)_2^{2-}] + [\text{PbHCO}_3^+] + [\text{PbSO}_4^0] \\
& + [\text{Pb}(\text{SO}_4)_2^{2-}] + [\text{PbCl}^+] + [\text{PbCl}_2^0] + [\text{PbCl}_3^-] + [\text{PbCl}_4^{2-}] + [\text{PbH}_2\text{PO}_4^+] \\
& + [\text{PbHPO}_4^0]
\end{aligned}
\tag{Equation 7.2}$$

XPS analysis revealed that both cerussite ( $\text{PbCO}_3$ ) and hydrocerussite ( $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ) were the predominant lead corrosion scales present on the lead coupons exposed to ZOP inhibitor. Solubility modeling indicated that hydrocerussite ( $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ) may limit the solubility of lead within the pH range of the study. Cerussite and hydrocerussite were considered separately as the predominant lead corrosion scales or controlling solid phase.

As mentioned above, ZOP demonstrated a significant improvement in the control of lead. Since phosphate was identified on most lead coupons incubated in ZOP inhibitor, the presence of a less soluble lead orthophosphate compound would explain the decrease in lead release with the application of ZOP. Therefore, the equilibrium model was also applied assuming hydroxypyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ) as the controlling solid phase.

The thermodynamic modeling results were presented in Table 7.8. The thermodynamic models predicted lead releases much higher than any observed during the study for all three models. The results implied that the system was not at equilibrium during the collection of the sample. Lead release may be diffusion limited because of the lack of lead surface, therefore dissolved lead concentration could not reach equilibrium between the lead coupon and the volume of water contained in the corrosion loops during the 6 hour stagnation time.

Table 7.8  
Lead thermodynamic modeling of BOP

Inhibitor	Phase	Actual Lead Release (mg/L)		Modeled Lead Release (mg/L)		
		Diss Pb	Total Pb	Hydroxypyromorphite	Hydrocerussite	Cerussite
ZOP	1	0.000	0.000	0.062	0.188	0.200
	2	0.000	0.000	0.040	0.196	0.204
	3	0.000	0.001	0.058	0.187	0.200
	4	0.000	0.001	0.046	0.199	0.202
	All	0.000	0.001	0.054	0.196	0.201

As also shown in the table, assuming hydroxypyromorphite was the controlling phase, dissolved lead was significantly decreased and was much closer to the actual data, which indicated that the improvement of lead release control observed with PDSs treated with ZOP inhibitor is most likely due to the formation of a less soluble lead orthophosphate solid which inhibit lead release from pipe materials.

### **Conclusion**

The continuous uptake of phosphorus in all ZOP PDSs for all 4 phases indicated a phosphorus-containing film may be produced on the pipe surface which could be a barrier to lead release from pipe materials. Variation of phase water quality did not significantly affect the mass balance of total phosphorus.

Zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was found to precipitate in the inhibitor feed tank. Solubility modeling indicated  $\text{Zn}_3(\text{PO}_4)_2$  would not precipitate if ZOP inhibitor was added directly to the PDSs. Since  $\text{Zn}_3(\text{PO}_4)_2$  would not be expected to precipitate in the PDSs or in actual use, the

precipitation of zinc phosphate precipitation wasn't and would not be a factor in inhibiting lead release by ZOP inhibitor as indicated by equilibrium calculations.

Increasing pH 0.3 units could reduce total lead release by approximately one-half. The actual average lead concentrations for ZOP PDSs displayed a clear benefit in comparison to the  $\text{pH}_s$  control and pH elevation ( $\text{pH}_s+0.3$ ). In the absence of a control strategy (either pH elevation or inhibitor addition), compliance with the action level (90<sup>th</sup> percentile concentration) of 1.30 mg/L would be problematic for the expected water quality in the TBW MGs distribution systems.

A statistical comparison of the mean lead concentrations between the control PDS and the corrosion control treatments indicated that ZOP inhibitor achieved a reduction in average lead concentration at all doses for all study phases. ZOP inhibitor proved to be effective for all blends and water qualities that were examined, including blends that were enriched in groundwater with an associated elevated alkalinity.

ZOP inhibitor exhibited the best performance in lead release control compared to other inhibitor studied in this work including blend orthophosphate (BOP), orthophosphate (OP), silicate (Si) and pH elevation ( $\text{pH}_s+0.3$ ). The coupons exposed to ZOP, OP and pH inhibition were analyzed by XPS. Surface characterization results suggested phosphorous and zinc were deposited on the pipe surface and a solid film containing phosphorous and zinc were likely produced which could inhibit lead release. Lead corrosion products  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  (hydrocerussite),  $\text{PbCO}_3$  (cerussite),  $\text{PbO}$ ,  $\text{PbO}_2$ , and  $\text{Pb}_5(\text{PO}_4)_3\text{OH}$  (hydroxypyromorphite) are possible in scales on lead coupons.

Based on surfaces characterization analysis, ZOP inhibitor addition was the primary source of zinc on the lead scale and produced a zinc-containing film on the pipe surface. Zinc phosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) was not found on the scale which is consistent with the solubility modeling result.

Cerussite, hydrocerussite and hydroxypyromorphite were considered separately as the controlling solid phase to develop the thermodynamic model. Modeling results implied that the system was not at equilibrium and hydroxypyromorphite model was much closer to the actual data which confirmed that the improvement of lead release control was most likely due to the formation of a less soluble lead orthophosphate solid.

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