

NON-UNIFORM COPPER CORROSION IN POTABLE WATER: THEORY AND PRACTICE

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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
In partial fulfillment of the requirements for the degree of

Master of Science
in
Environmental Engineering

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May 4, 2007
Blacksburg, Virginia

Keywords: Corrosion, Copper, Pitting, Inhibitors, Flow Electrification, Electrochemical Noise

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ABSTRACT

While it has long been known that water flow can influence non-uniform corrosion of copper pipe (Rushing 2002, Marshall 2004), it has never previously been considered a primary contributor to the problem. This work is the first to describe a fundamentally important phenomenon in aqueous non-uniform corrosion: flow electrification. A conceptual framework for flow electrification was developed from prior work on non-aqueous fluid flow in pipes, where the primary concern was prevention of electrical explosions. Thereafter, a series of experiments was aimed at monitoring flow electrification, quantifying its practical effects, and examining aspects of non-uniform copper corrosion in real situations.

Under conditions with little or no flow, in a high pH and high Cl_2 water known to cause pinholes in copper pipes, while water chemistry influenced corrosion, non-uniform corrosion was not sustained. But when flowrates were higher, flow electrification contributed to severe and sustained non-uniform corrosion, with the most serious attack manifested in the first section of pipe that encountered the flowing water. The magnitude of flow electrification increased with Cl_2 concentration, pH and flowrate. Containers dosed with inhibitors such as zinc or phosphate experienced lower electrification, current, voltage, scale resistance, and corrosion potential measurements when compared to a control without an inhibitor. Additionally, systems dosed with inhibitors had reduced rate of chlorine decay, weight loss, pit density and/or maximum depth. Zinc orthophosphate had the largest positive impact on electrochemical measures of pitting. However, experimental studies suggested that if zinc orthophosphate was dosed to a system for a period of time, and dosing was then stopped, very serious pitting could occur. A practical case study seemed to strongly confirm this hypothesis in one system.

The presence of sulfides caused the separation of anode and cathode along a pipe section, from electrification, to reverse relative to what was observed in the system with high Cl_2 and high pH. Below a certain level of sulfides, electrification ceased. It seems likely, based on measurement

of electrochemical potential (E_{Corr}) in waters of this type as a function of sulfide concentration, that the onset of pitting would be associated with decreasing E_{Corr} with time. If so, the fundamental basis of tracking E_{Corr} rise with time to predict pitting propensity would be invalidated.

Electrochemical noise programs were applied to try to differentiate between systems of low and high pitting propensity. Amplitudes of potential noise and current noise measurements drastically increased with the presence of sulfides or chlorine, confirming that tracking electrochemical noise may indicate the presence of a pitting agent. However, the electrochemical noise measurements are at best, an indirect indicator of copper pitting, and their interpretation is complicated by the co-occurrence of flow electrification.

Attempts were made to apply these insights to a case study examining pitting in two real waters in Maryland and to examine the effects of orthophosphate, chlorination, chloramination and enhanced coagulation on copper pitting propensity. Tracking of E_{Corr} suggested that the control water (without phosphate) had the greatest pitting propensity. The free chlorine system with orthophosphate maintained E_{Corr} values below the control signifying that the presence of phosphate lowered the corrosion propensity. Waters with chloramine and phosphate had the lowest E_{Corr} values and also had the least variability in E_{Corr} due to the stability of the disinfectant. There is considerable ambiguity in the results, since the copper pipes exposed to the waters in question did not develop serious pitting over the several months of the study.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Dr. Marc Edwards. Without his faith, guidance and endless encouragement, I would not have had the understanding and determination to complete this work.

I will be forever grateful to the entire Edwards research group, particularly Dr. Paolo Scardina, who provided me with a solid foundation in the understanding of copper pitting and without his help I would not have been able to make all the odds and ends possible.

Thank you also to my committee members, Dr. Andrea Dietrich and Dr. Peter Vikesland, for their support and direction.

I would like to thank my parents and family for their infinite encouragement of all of my goals and endeavors. They have supported me all my life and provided me with opportunities for which I will be eternally grateful.

To all of my friends and loved ones including Lane Slabaugh, other fellow Boilermakers, my childhood friends from Chicago and my Hokie family here at Tech, thank you for the endless support and patience of me while I pursued my dream of higher education. Thank you for all the words of wisdom, the strength to never quit, and the everlasting smiles. I would not be who I am today without each and every one of you.

Finally, thank you to the Charles E. Via, Jr. Fellowship, the Copper Development Association, and the American Water Work Association for their generous funding.

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AUTHOR'S PREFACE

The chapters in this thesis are developed in a Virginia Tech Journal article format, in which each chapter represents work of several individuals whose efforts are explicitly acknowledged, as would be the case in a peer reviewed article. Chapter 1 compiles an extensive literature review, and includes some prior work from a thesis of Gregory Sheffer of copper pitting and effects of zinc inhibitors. The remainder of Chapter 1 was done by the author of this thesis. Chapters 2 thru 4 are based on laboratory studies at Virginia Tech. Chapter 4 also contains field studies conducted at various water utilities in the United States with multiple assistants involved. Chapter 5 provides a restatement of key conclusions from the thesis. The additional authors listed in the chapters of this thesis were all members of Dr. Marc Edwards's research group. All co-authors including my advisor, Dr. Marc Edwards, performed experiments and/or contributed background information that is included in various chapters of this thesis.

CHAPTER 1: REVIEW OF COPPER PITTING CORROSION, NON-UNIFORM CORROSION INHIBITORS, AND MONITORING METHODS

Rebecca Lattyak, Gregory Sheffer, and Marc Edwards

INTRODUCTION

Corrosion of metals such as copper pipe in domestic plumbing is manifested in many ways. Uniform corrosion occurs when the entire surface of the pipe is gradually eaten away by electrochemical (oxidation-reduction) reactions. Non-uniform types of corrosion including crevice, erosion and pitting corrosion, result in a very rapid attack at small areas of pipe surface ($\approx 0.01\text{-}3\text{ mm}^2$). Over the last decade, interest in pitting corrosion, which can produce pinhole leaks in copper tubing, has increased after well-publicized instances where leaks in certain localities reached epidemic proportions. Although copper has a well-deserved reputation as a reliable household plumbing material, approximately 8% of U.S. homeowners have experienced at least one pinhole leak, although overall rates of tube failure are comparable for copper and plastics (Scardina et al. 2007).

Copper pitting corrosion can either result from holes eaten from inside-out (internal corrosion) or outside-in (external corrosion). An earlier review broadly documented different types of internal copper pitting corrosion problems and suspected links to water chemistry (Edwards et al. 1994). This review emphasizes mechanisms of internal copper pitting, monitoring techniques that can purportedly quantify a water's ability to cause internal pitting (i.e., the water's pitting propensity), and theoretical aspects of pitting inhibitors.

BACKGROUND

A pinhole leak results from the culmination of a two step process which includes pit initiation and propagation. Initiation refers to the circumstances which can cause non-uniform copper corrosion to get started. Propagation refers to the circumstances which allow initiated pits to continue growing. Pinhole leaks cannot occur if factors that cause either initiation or propagation are missing.

Pit Initiation

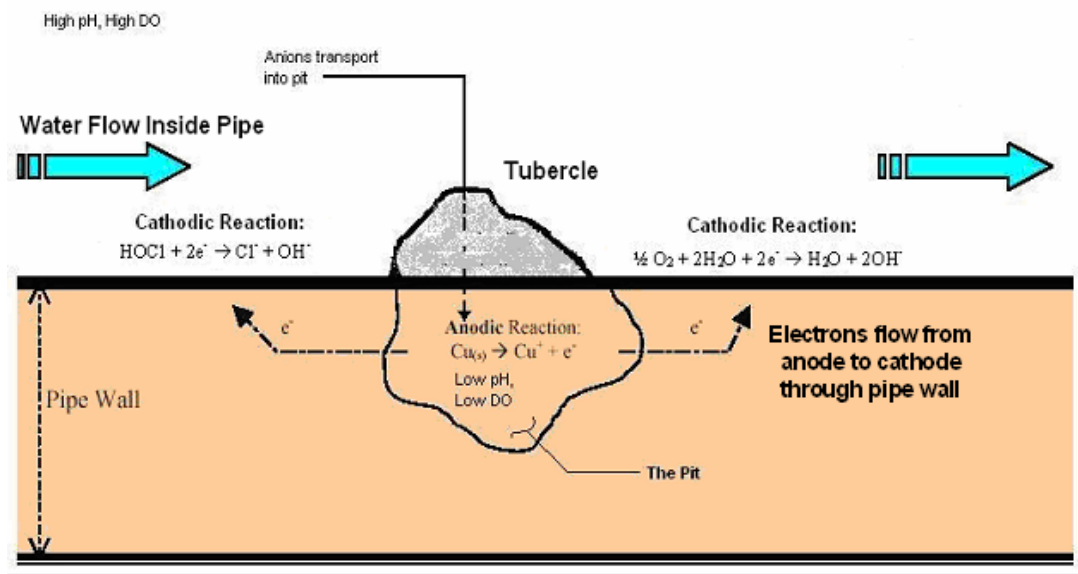
Pitting corrosion was thought to initiate from a number of factors including surface defects, particle deposition, differential flows or prolonged stagnation (Patel 1997; Sosa 1998). At least some surface defects are present in all copper tubes, including consideration of trace impurities, carbon films and other deposits (Sosa 1998). Certain manufacturing processes are known to increase the number of defects and films which might be present on a copper tube.

Another well-established phenomenon that can initiate non-uniform corrosion on metal surfaces is particle deposition or under-deposit corrosion. If particles in the water attach to a copper pipe surface, the small portion of the surface under the deposit is somewhat screened from the water, causing oxygen/chlorine levels to become depleted and marked changes in pH. In some situations, these changes tend to make copper under the deposit anodic relative to the rest of the surface, and the resulting corrosion at this point can produce further drops in oxygen/chlorine or pH, at which point the attack can become self-perpetuating. The attachment of any type of particle could cause under-deposit corrosion, including aluminum, iron, or clay like particles. The size of the particle, its adherence to the pipe, porosity, surface charge and solubility might also play an important role in ability to initiate non-uniform copper corrosion.

A number of non-uniform copper corrosion problems are initiated by phenomena associated with hydraulics (Novak 2005). These factors include erosion corrosion, gaseous cavitation, vaporous cavitation and impingement. Differential flow could also be important and is analogous to under-deposit corrosion in origin. That is, if one portion of copper tube is exposed to water at a high flow rate, whereas another part of the tube is exposed to the same water but at a lower flow or even stagnant conditions, differences in oxygen/chlorine or pH at the pipe surfaces can naturally result. These differences, in turn, can cause one portion of the pipe to become anodic relative to another portion of the pipe. For iron, the portion of pipe exposed to less flow almost always becomes anodic relative to the pipe exposed to higher flow. For copper, the section of copper exposed to low flow can become either anodic or cathodic dependent on the water's chemistry and other circumstances.

Pit Propagation

Contrary to earlier hypothesis, it has recently been established (Sosa et al. 1999) that copper pits propagate via a concentration cell mechanism, in which a small area of the copper surface (the anode) has a lower electrochemical potential than another portion of the copper surface (the cathode). Because the two areas of the copper are in electrical contact, the voltage drop arising between the anode and cathode creates a flow of electrons through the metal (Figure 1-1).



**Figure 1-1: Key reactions, locations, and elements of copper pitting
(Figure modified from Marshall 2004)**

At the anode, which is the site of the pit, the copper metal is oxidized and electrons are produced. These electrons travel through the pipe wall where they are consumed via reaction with constituents such as oxygen or Cl_2 at the cathode surface. The reactions at the cathode and anode must proceed at the same overall rate, since any electrons produced at the anode must be consumed at the cathode. In the pits, which are often less than 1 mm in diameter, the released cuprous and cupric ions react with the water and remove OH^- , O_2 and Cl_2 , driving pH down and creating a region of low dissolved oxygen. A portion of the released copper in the pit reacts further with the water to form a growing mound of corrosion products (i.e. the equivalent of iron rust but for copper) known as a tubercle.

In this mode of non-uniform attack, the cathodic surface of copper is exposed to much higher concentrations of chlorine and/or oxygen, because it is not shielded from the bulk water. This creates a lower concentration of electrons in the metal at this point to which electrons can flow for removal after they are created in the pit. Corrosion can proceed in the pit until, eventually, the entire pipe wall has been consumed and a pinhole leak can be observed.

Causes of Copper Pitting

It is known that waters can contain certain constituents that initiate pitting (e.g., particles) and others essential to propagation of pitting (e.g., oxygen, chlorine, sulfate, chloride and other constituents). In some situations it is possible to alter a water's ability to initiate or propagate pits, through either unintentional or purposeful adjustments to factors such as pH, natural organic matter, chlorine, zinc, and phosphate amongst many others. It is not currently possible to predict, with any scientific certainty, which combinations of factors will cause a high likelihood of pitting and which factors would cause a low likelihood of pitting. From a practical perspective, it is nonetheless useful to consider the practical ability of a water to initiate and propagate pits, which is henceforth termed the water's *pitting propensity*.

For the most part, laboratory attempts to scientifically prove that certain combinations of factors could cause pitting were unsuccessful. This changed when a specific recipe for a water with aluminum particles, free chlorine and high pH gave unambiguous signs of causing severe pitting of copper under conditions representative of water distribution systems (Rushing 2002). Marshall (2004) proved that this recipe could cause multiple pinhole leaks to form in copper tubing in less than one year. The identification of a known pitting water is useful, because it demonstrates that aggressive water alone can cause pitting, and it also allows testing of physical and chemical parameters which make pitting worse or better. Finally, it can be used to examine the effectiveness of techniques that purportedly monitor a water's pitting propensity.

Other combinations of physical, chemical and biological factors are also strongly suspected to cause pitting. Pinholes are also believed to result from erosion corrosion, gaseous cavitation, sulfide attack, and other types of microbial activity such as localized acid production (Table 1-1). The presence of one particular microbe, sulfate-reducing bacteria (SRB), has been of specific

interest and has long been recognized for its possible involvement in localized corrosion of potable water iron pipelines (Starkey 1958; Gaylarde 1992; Seth and Edyvean 2006). Sulfate-reducing bacteria chemically transform sulfate compounds into sulfides, which can increase corrosion rates on copper by more than two orders of magnitude even at a pH of 9.2 (Jacobs and Edwards 2000). The presence of hydrogen sulfide has also been associated with taste and odor problems in potable water systems. Even though SRB are obligate anaerobes, they nonetheless rapidly colonize surfaces in water distribution systems on where oxygen has been removed by biochemical reactions (Seth and Edyvean 2006).

Scardina et al. (2007) recently discovered that SRB are often growing under copper pits, and are presumably involved with pit growth and pinhole leak failures. Using new techniques, detection of sulfides and sulfate-reducing bacteria has been confirmed in at least four recent outbreaks of pinhole leaks. Through various detection methods, Scardina identified local production of H₂S in and around pits by SRBs. Additionally, sulfide-induced corrosive attack is reported to be difficult to alleviate once started. For example, Jacobs (1998) could not stop sulfide-induced corrosion through de-aeration, maintaining a chlorine residual, or super-chlorination. It has been suggested that H₂S concentrations as low as 0.007 mg/L have led to sulfide-induced corrosion (Gudas and Hack 1979), and Myers and Cohen (2005) have alluded to leaks caused by sulfide levels as low as 0.02 mg/l of H₂S. Finally, Jacobs (2000) reported that sulfide containing scale increased both the anodic and cathodic reactions rates, resulting in an overall increased corrosion rate. Clearly, sulfides and SRB have been strongly linked to aggressive attacks on copper and pitting corrosion.

Table 1-1: Summary of suspected copper pitting mechanisms (Sheffer 2006)

Suspected Pitting Mechanism	Scientific Certainty	Cause	Characteristic Water	Possible Factors in Water Reducing the Frequency of Failure	Characteristic Location of Worst Pitting
Sulfide Attack	Nearly 100%	Direct corrosion	Any raw water with sulfides or sulfate reducing bacteria (SRB)	Natural organic matter (NOM), high pH, molybdenum, phosphate	Near colonies of SRB
Cl ₂ -Al-high pH	100%	Aluminum deposits cause non-uniform attack	pH > 7.8 Cl ₂ > 2.5 ppm Cold water	NOM, phosphate	Pipes in frequent flow and at locations with highest residual
Chloramine-Al	100%	Same as above	Same as above, but seems to be hot water	Lower temperatures, lower velocity of water in pipes	Both hot and cold, but hot water recirculation lines worst impacted
High Cl ₂ -high pH	Strongly suspected	Chlorine oxidant and non-uniform attack	pH > 8.5 Chlorine > 0.5 ppm Cold water	Unknown	Pipes with frequent flow and close to treatment plant
Gaseous Cavitation	Strongly suspected	Bubble impingement	Dissolved gas supersaturation, hot and cold water	Surfactants such as polyphosphate and NOM might reduce gaseous cavitation	Near bends and flow constrictions
Particle/Water Erosion Corrosion	Suspected	Non-uniform wearing of pipe	Both hot and cold, although hot is more susceptible	Lower velocity of water, colder temperatures, lower turbidity	Near bends
Deposition Corrosion	Suspected	Concentration cells caused by varied oxidant access to surface	Lines or mounds of deposits other than copper	Filter particles from water, reduced oxidant concentration	Deposits often preferentially found on pipe bottom or outside of bends
Other microbial	Strongly suspected	Concentration cells caused by bacteria	Low alkalinity and poorly buffered water, lack of disinfectants	Low concentrations of AOC, phosphate, fixed N or K limit growth	Farthest reaches of treatment plant

Inhibition of Copper Pitting: Theory and Practice

Chemicals that can inhibit pitting corrosion can either be naturally present in a water supply or added purposefully by the utility. There are other methods for addressing pinhole leak problems that can include re-plumbing with new copper, re-plumbing with PVC, patching leaks, or lining

pipes in-situ with epoxy coatings. Amongst these options, addition of an inhibitor to the water is often the only low cost means of controlling pitting throughout a system.

It is important to understand the mechanisms by which inhibitors operate. Although anodic and cathodic corrosion reactions must occur at the same rate, it often happens that the overall rate of pit growth is determined by one of these reactions almost exclusively. Corrosion reactions are said to be under cathodic control, if the overall rate is limited by the rate of reduction reactions at the cathode. Conversely, they are under anodic control if the overall rate is limited by oxidation reactions at the anode. In instances of copper pitting in potable water, the rate of pit growth is often believed to be limited by the rate of the cathodic reaction (Nguyen 2005). Conceptually, the driving force of the cathodic reaction can be decreased by higher OH^- concentrations (e.g., higher pH), which can reduce the rate of electron consumption at the cathode according to LeChatlier's Principle. This is one reason why the overall corrosion rate of metals in potable water is reduced by raising pH.

To better conceptualize inhibitor action in relation to pitting corrosion, the schematic of a active pit in Figure 1-1 can be considered as a divided cell, in which two copper samples are exposed to different chemical environments representative of conditions at anodic and cathodic locations on the pipe (Figure 1-2). Specifically, the cathodic copper surface is in contact with water of relatively high pH, high dissolved oxygen and/or chlorine, and low Cu^+ and Cu^{2+} concentrations. However, the small anodic copper surfaces representing pits are exposed to an environment of low pH, low DO, and high Cu^+ and Cu^{2+} concentrations. As a result of the different chemical environments, the two pieces of copper essentially form a battery. In this representation of a pit, an ammeter can be connected between anodic and cathodic samples, and the measured flow of electrons can provide direct insight to the rate of pitting. In practice for a real pipe, it is not possible to measure the flow of electrons through the metal directly, although it is present.

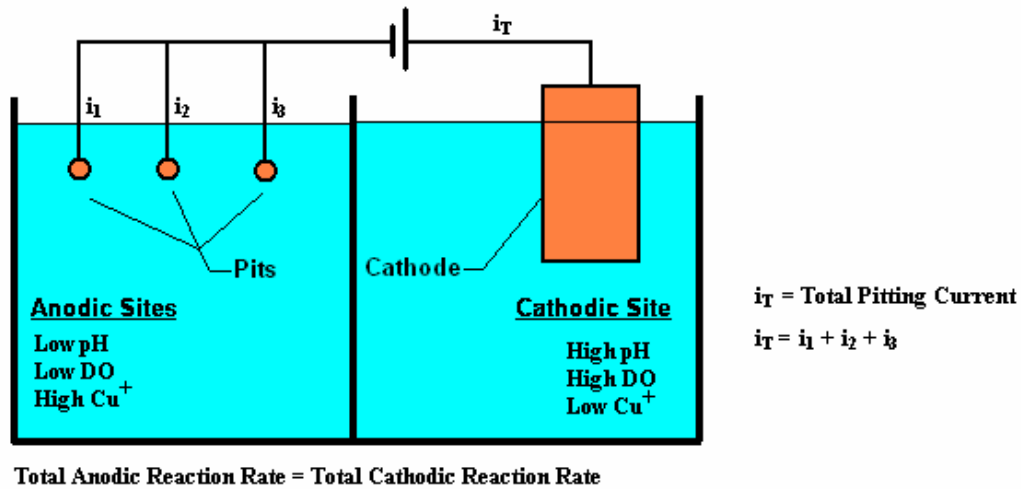


Figure 1-2: Divided Cell - Conceptual illustration of copper pitting process (Sheffer 2006).

Inhibitors of pitting corrosion have been divided into three fundamental classes: cathodic (those that hinder the cathodic reaction), anodic (those that hinder the anodic reaction), and mixed (those that hinder both halves of the oxidation-reduction reaction). Evans further subdivided the anodic and cathodic inhibitors into the following four cases (1936):

1. Anodic Control; Anodic Inhibitor
2. Anodic Control; Cathodic Inhibitor
3. Cathodic Control; Anodic Inhibitor
4. Cathodic Control; Cathodic Inhibitor

Evans then made a compelling argument, based on theory, laboratory and practical data, that corrosion inhibitors should be classified as ‘safe’ or ‘dangerous’ relative to pitting. Depending upon which reaction is controlling the overall rate of an attack (anodic or cathodic), certain concentrations of inhibitors may actually increase either the number of pits or the rate of their growth through the pipe wall, hence the designation of ‘dangerous’ (Evans 1936; Evans 1939).

Sheffer (2006) summarized the practical effects of each of Evans’s cases. Key factors that are considered include quantity of metal corroded (total corrosion), the expected area attacked, and the expected intensity of corrosion (rate of attack per unit area at pits or anodes).

Case I. Anodic Control; Anodic Inhibitor

In this case, added inhibitor stifles the attack through an unknown reaction(s) at the anode. For instance, this could occur via orthophosphate addition, if orthophosphate formed an impermeable layer inside the pit or above the tubercle. As the level of inhibitor is progressively increased, more of the pits are affected, and the number of pit sites and anodic area is decreased. The overall amount of corrosion is decreased. Because the reaction is under anodic control, for the pits in which attack is not completely stopped, the intensity of attack will nonetheless decrease. The net result is that for addition of an anodic inhibitor to a situation under anodic control, all aspects of pitting improve with increasing inhibitor concentration. Figure 1-3 illustrates a qualitative plot of how each measure of corrosion is affected as inhibitor dose is increased for this case, with corrosion intensity indicating the rate of attack at the strongest anode in the system.

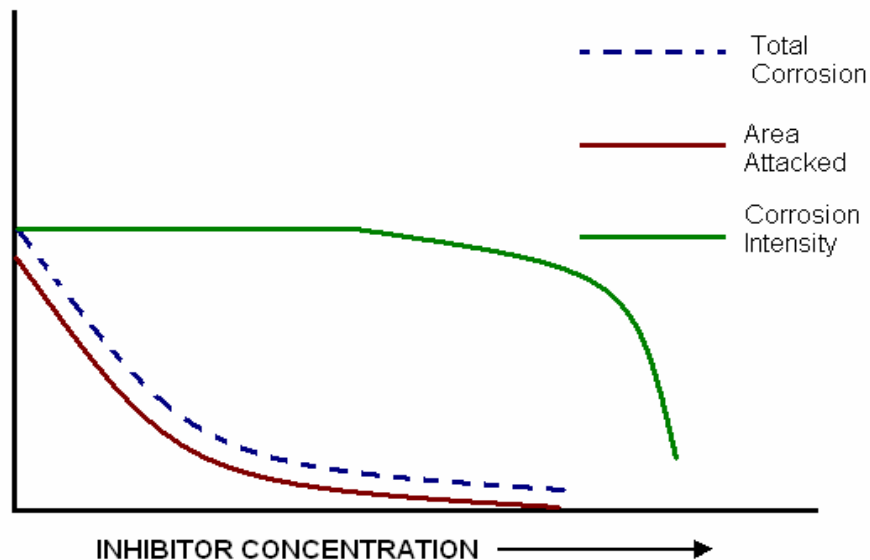


Figure 1-3: Case I - Anodic Control; Anodic Inhibitor

Case II. Anodic Control; Cathodic Inhibitor

In this situation, the addition of low levels of cathodic inhibitor will not immediately decrease the total corrosion, but as inhibitor dose is increased a point will eventually be reached at which

cathodic reactions becomes so impeded that the total corrosion will begin to decrease. As the number of cathodic sites or area decreases, if anything, the area subject to anodic attack will increase. The intensity of corrosion at the worst anodes is invariably decreased as the concentration of inhibitor increases. Thus, similar to Case I, addition of a cathodic inhibitor to a situation where pitting is under anodic rate control, is inherently safe and there is no threat of worsening corrosion. Figure 1-4 illustrates a qualitative plot of how each measure of corrosion is affected as inhibitor dose is increased in Case II conditions.

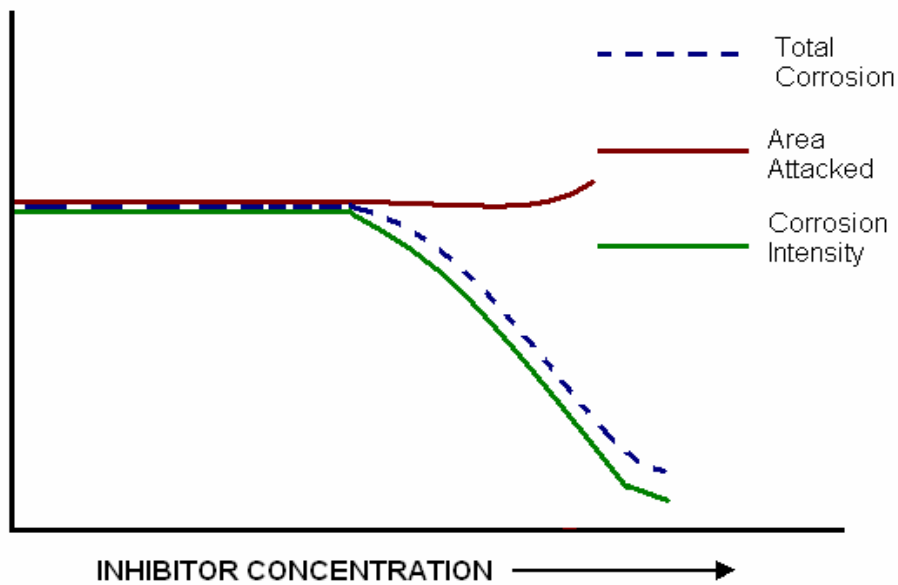


Figure 1-4: Case II - Anodic Control; Cathodic Inhibitor

Case III. Cathodic Control; Anodic Inhibitor

There are interesting and important consequences of adding an anodic inhibitor to a cathodically controlled corrosion process. Similar to Case I, increasing doses of an anodic inhibitor will progressively reduce the number of active pits or *anodic area* subject to attack. However, since the overall rate of corrosion is controlled by the cathodic reaction, total corrosion will remain the same or will increase, since the cathodic area is the same or increases if anodes are converted to cathodes. The net effect of having the same corrosion rate, with fewer anodic sites, is that the intensity of the attack at the remaining active anodes will increase. This condition is a dangerous proposition. Essentially, under-dosing of an anodic inhibitor to a pitting condition under

cathodic control, will decrease the number of pits but will increase the rate of attack at those which remain. Only when a sufficient concentration of inhibitor is added to stop attack at nearly every pit, will benefits of the inhibitor become obvious (Figure 1-5).

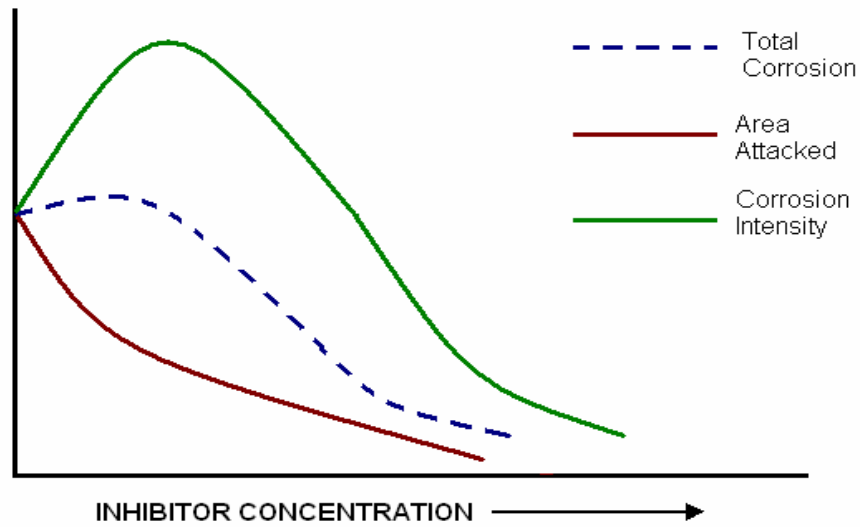


Figure 1-5: Case III - Cathodic Control; Anodic Inhibitor

Case IV. Cathodic Control; Cathodic Inhibitor

In a corrosion process controlled by the cathodic reaction, the addition of a cathodic inhibitor will steadily decrease the overall rate of attack. Although the area subject to anodic attack will, if anything, slightly increase as seen in Case II, the intensity of attack will decrease steadily. Therefore, for corrosion controlled by the cathodic reaction, the addition of a cathodic inhibitor is a 'safe' approach and usually sufficient for practical purposes (Figure 1-6).

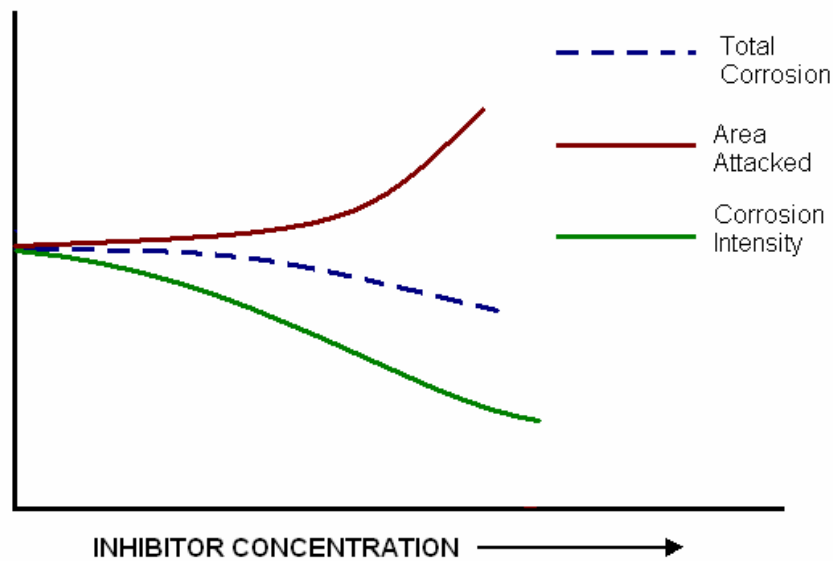


Figure 1-6: Case IV - Cathodic Control; Cathodic Inhibitor

Zinc and Orthophosphate Inhibitor Addition

Currently, about 58% of U.S. water utilities add phosphate inhibitors to water to control corrosion (Scardina et al. 2007). Of those utilities adding phosphate inhibitors, about 40% use phosphate in the form of zinc phosphate. Early research, mostly on iron corrosion, provided strong experimental evidence for benefits of zinc as a general inhibitor to corrosion (Evans 1936; Evans 1939). Later work by Jonassen (1958), Zin et al.(2004), Oelsen (1998), Mayer (2000) and AWWARF (1996) pointed to the potential importance of zinc’s interaction with calcium, phosphate and carbonates in forming scales that protect pipes and inhibit corrosion for steel, concrete and other materials.

Since the late 1980’s, researchers and the water industry have been primarily concerned with control of lead and copper leaching to potable water from lead pipe, copper pipe, brass and lead solder. In the few cases where zinc was examined in that work, generally speaking, no conclusive benefits from zinc have been found (Edwards, Hidmi et al. 2002; Edwards and McNeill 2002). This recent data has contributed to newfound skepticism regarding potential benefits of zinc. Many in the water industry have begun to openly question whether use of zinc has any noteworthy benefits in control of corrosion. However, it is also well understood that control of metals leaching to water has little to do with protecting pipe materials from

degradation due to uniform and non-uniform corrosion. It is presumptuous, to say the least, to discount extensive prior research on control of uniform and non-uniform corrosion due to zinc, based on recent studies of metals leaching.

Laboratory studies by Marshall strongly suggested that orthophosphate dosing might reduce the frequency of pinhole leaks in water for a utility in Maryland (2004). Subsequent full scale dosing of phosphate at the utility confirmed the benefits of phosphate in reducing (but not eliminating) the frequency of pinhole leaks experienced by customers. More recently, a project investigating copper pitting corrosion at a utility in Florida, suggested that increased pitting occurred in consumer's homes after the utility began dosing with orthophosphate at lower pH values (Sheffer 2006). This trend is consistent with expectations based on analysis by Evans and Sheffer in the preceding section, given that orthophosphate is widely considered to be an anodic inhibitor, and pitting is predicted to increase if the reaction was cathodically controlled at low levels of inhibition (Figure 1-7). Further investigation of inhibitors at the Florida utility suggested that zinc phosphate may have advantages relative to phosphate alone (Sheffer 2006). That result highlighted a need for laboratory studies into the possible role of zinc in stopping non-uniform copper corrosion. Likewise, it is desirable to better understand the role of phosphate dose in controlling copper pitting corrosion, given the potential downside of under-dosing inhibitor.

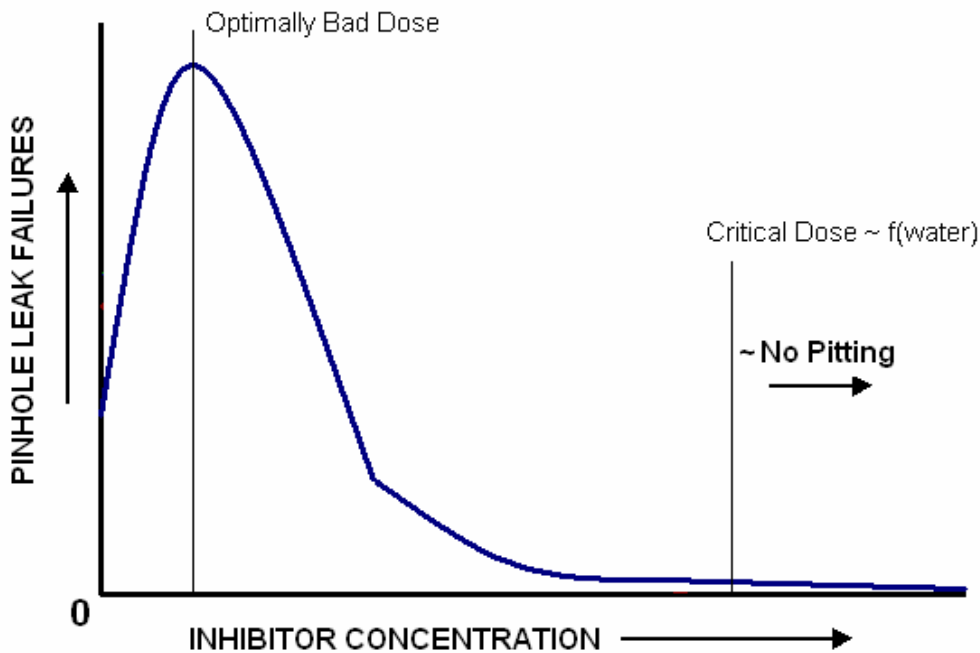


Figure 1-7: Predicted anodic inhibitor response curve for pitting under cathodic control (Sheffer 2006)

Natural Organic Matter

It has long been understood that the presence of natural organic matter can stop copper pitting through a variety of reactions (Edwards, Ferguson et al. 1994; Edwards and Boulay 2001). However, like phosphate, there is very little understanding as to the effect of different concentrations of NOM. Recent EPA regulations, such as the Disinfection/Disinfection Byproducts Rule, prompt concern since utilities are now required to remove the NOM and this would be expected to increase copper pitting in at least some cases (Edwards, Ferguson et al. 1994). Therefore, it would be important to better understand the concentration dependence of NOM on copper pitting corrosion.

Monitoring of Pitting Propensity

The corrosivity of water flowing through copper tube is believed to be a key factor in explaining disparate pitting propensity from one locality to another. In some situations, changes in water treatment practice (e.g., coagulation, disinfection and pH) can render a water that was previously non-corrosive into a water that was highly corrosive, and vice versa. It would obviously be of

high importance to measure the pitting propensity of a water, or tendency to cause pitting corrosion and pinhole leaks. If such a method were available, its use could prevent changes to water that caused problems, or be used to identify ways of rendering a corrosive water non-corrosive.

There is a long history of rapid tests that purportedly measure pitting propensity. Since pinhole leaks have only recently been reproduced scientifically, under laboratory conditions, all prior work on the subject must be deemed speculative, as the accuracy of each method could never be tested. Due to the high economic costs of pitting, these unproven methods have nonetheless received widespread use, in large part because it is unacceptable to do nothing, and due to a lack of viable alternatives.

Methods used to track pitting propensity have included macrocells with separate anode and cathode, multi-electrode arrays, and cyclic voltammetry. Macrocells physically separate the anodic and cathodic copper surfaces, which are placed in potable water solutions (i.e. Mattsson and Fredricksson 1968; Singh, Galyon et al. 1992) The metals are electrically connected with a wire which allows electrons to flow freely between each area and a pitting current can be measured with an ammeter. Typically, more aggressive waters are those in which the current either increased, or remained at a sustained value. Waters likely to passivate pits cause currents between anodic and cathodic areas to drop. In prior work, these methods have required the use of catalysts to artificially initiate pit growth in the system, and therefore, it is uncertain whether the results are representative of pits found in practice.

Multi-electrode arrays developed by Goodman and Lucey allowed water flow at a low rate over a small area composed of a single cathode wire and twelve anode wires (1984). Uniform corrosion occurs when the currents passing through all twelve wires are similar. The general idea of the method is that pitting corrosion is more likely when a water tends to make a greater percentage of the artificially applied current flow through one of the wires.

Finally, cyclic voltammetry involves the application of voltage in the positive direction until a predetermined potential is reached. The voltage is then applied in the reverse direction until the

original potential is achieved. If current measurements form a clockwise loop, it is believed that pitting will likely occur in the water (Singh et al 1993). Similar to the multi-electrode array, this method does not provide any insight to the cathodic reaction. Nor does it provide insights to pit initiation. Therefore, more advanced methods which can not only monitor, but also predict corrosion have been investigated for optimization of corrosion control including pitting currents, corrosion potential (E_{Corr}), and electrochemical noise.

Electrochemical Rise

Corrosion potential, or E_{Corr} , reflects the oxidation-reduction potential that is produced from the balance of anodic and cathodic reactions occurring on a metal surface at a given time. While the sum of the anodic (oxidation) reaction rates must be equal to the sum of the cathodic (reduction) reaction rates over the pipe surface, that balance is achieved by an adjustment in the electron activity in the metal. When E_{Corr} is high, the metal is of relatively low electron activity, and higher E_{Corr} values result from the presence of electron acceptors such as oxygen or free chlorine in the water supply. Gold naturally has a high propensity to accept electrons, and an extremely low propensity to create electrons from corrosion, resulting in a very high electrochemical potential or E_{Corr} value. Alternatively, iron has a high propensity to release electrons via corrosion and a low propensity to accept electrons, resulting in a low E_{Corr} when immersed in water.

In terms of corrosion monitoring of copper, changes in E_{Corr} represent how the metal is changing with time in its ability to accept or release electrons. Based on previously described theory of pitting corrosion, the worst case actually occurs when the majority of the pipe surface is cathodic or has a high E_{Corr} , as this indicates that there is a relatively large cathode and a small anode. In such situations, the intensity of the attack at the very small anode surface can be highest.

Over the years, it was noted that in many waters with a high pitting propensity, that the electrochemical potential tends to rise slowly until it reaches a critical value that is believed to be associated with the onset of pitting (Pourbaix 1969). In contrast, waters with low pitting propensity displayed values below this critical value, or E_{Corr} even dropped with time suggesting passivation of the surface. The critical value necessary for the onset of pitting varies from study

to study (Table 1-2). Tracking of electrochemical potential has been applied in both field and laboratory studies, and is currently the most widely accepted test method for tracking pitting tendencies (Edwards and Ferguson 1993). However, under no circumstances should this method be construed as a direct measure of pitting. Rather, based on the literature, conditions which cause a rise in copper E_{Corr} tend to also occur in waters that cause pitting.

**Table 1-2: Critical E_{Corr} Values from Various Publications
(Data modified from Nyugen 2005)**

Type of Pitting	E_{crit} (vs Ag-AgCl)	Reference
Soft-water	495	Page, 1973
Soft-water	49	Al-Kharafi et al., 1989
Hot-Water	195	Fujii et al., 1984
Cold-Water	215	Pourbaix, 1969
Cold-Water	145-215	Cornwell et al., 1973

Virginia Tech Apparatus

A macrocell was developed to determine whether differential flow could cause initiation and propagation of pits in test waters (Nguyen 2005). This apparatus simulates pits through a macrocell with a separate anode (pit wire) and cathode (copper pipe) connected via an external wire. The connection between the pipe and the pit wire allow measurement of pitting current, potential, and resistance on the artificial pits with a simple multimeter. As opposed to other indirect methods such as E_{Corr} , these pit wires provide a real and direct measurement of copper pitting corrosion, if a pit can be “grown” on the tip of the pit wire. Direct measurement of the pitting current can determine whether pits can be initiated, and also sustained, in a given water under the conditions of study.

Electrochemical Noise (ECN)

Another alternative for real-time, online corrosion monitoring includes the use of electrochemical noise. ECN techniques have been utilized to track corrosion processes since the

late 1960's (Iverson 1968). The use of ECN has become more wide spread because it is inexpensive, fast and non-destructive (Smith and Francis 1990; Legat and Dolecek 1995; Kane, Eden et al. 2003; Duranceau, Townley et al. 2004; Giriga, Mudali et al. 2005).

Electrochemical noise refers to changes in E_{Corr} , or corrosion currents between coupled metals, that occur on a random basis. The technique measures signals generated from the electrochemical reactions (anodic and cathodic) occurring at the metal-solution interface through the use of two electrodes (working and counter) attached to identical pieces of copper. When used in zero resistance ammeter (ZRA) mode, no external potential or current is imposed on the metals, and therefore, corrosion is proceeding naturally. When measured simultaneously, current between the two electrodes and potential versus a reference electrode (Ag-AgCl) are measured in sets of block periods. Statistical analysis is applied to each data block in order to calculate the I_{rms} and V_{rms} values. These are root mean square (RMS) values which are calculated using the following equations:

$$I_{\text{rms}} = \frac{I_{\text{max}}}{\sqrt{2}}$$

$$V_{\text{rms}} = \frac{V_{\text{max}}}{\sqrt{2}}$$

I_{max} and V_{max} values represent half of the peak-to-peak current and potential amplitudes, respectively. Additionally, ECN programs can typically calculate mean current and potential values from the data blocks which should correlate to the galvanic current and potential (E_{Corr}).

Electrochemical noise has been thought to distinguish between different types of corrosion. Previous work has found that noise recordings in systems undergoing pitting were much larger than in systems corroding uniformly (Giriga, Mudali et al. 2005). Work by Smith and Francis reported successful application of noise programs to characterize the surface of copper tubes, specifically copper tubes with carbon residues or films (Smith and Francis 1990). Their work also explicitly mentioned that ECN methods are not meant to indicate a measure of the carbon on the copper, but only the corrosion that occurs.

While the data acquisition is relatively quick and efficient, interpretation of the analysis can be complex. A recent study evaluating differences in noise between a water thought to cause pitting, and a relatively non-aggressive water, found a notable increase in the amplitude of the noise measurements in the water known to cause copper pitting when compared to the benign water (Sandenbergh, Pistorius et al. 1996). However, perplexing limitations to the use of ECN techniques have also been reported. The same study discovered that electrochemical noise was highly dependent upon flow, and nearly stagnant conditions resulted in low levels of noise. It is also clear that there is a strong relationship between E_{CORR} and noise and the concentration of free chlorine in water (Rushing 2002; Rushing and Edwards 2004). To the extent this occurs, electrochemical noise may reflect the presence of redox active “pitting agents” in the water, and therefore, may have nothing to do with formation of pits on the pipe surface.

ECN methods, having only recently been applied to the study of pitting corrosion of copper tubes in potable water, have been extensively investigated for corrosion monitoring (Table 1-3). Of the studies listed, only one acknowledged that the water chemistry has a direct effect on the noise measurements. It is therefore of high interest, to examine the relationship between electrochemical noise and pitting agents such as chlorine and sulfides.

Table 1-3: Summary of Recent Studies Employing ECN Methods for Corrosion Detection and Monitoring

Reference	Flowrate(s)	Chlorine/Sulfide Presence	Pit Formation	General Conclusions
Smith and Francis 1990	1 L/min for 2 hrs, every 12 hrs.	Study tested only synthetic water. Therefore, it is unlikely that either chlorine or sulfides were present in the system.	Study identified pits in a select number of the copper tubes were tested. All the tubes contained a carbon film.	The study concluded that ECN was higher for pipes with carbon films than without them..
Sandenbergh, Pistorius et al. 1996	Effects of flowrate on ECN were examined. Study tested flowrates at 200 mL/min and 50 mL/min.	Chlorine and sulfide levels were not reported. Water was derived from two sources: one with high pitting propensity and the other known to be non-aggressive.	Pit formation/depth was not reported.	Suggested that ECN measurements are dependent upon flow, and that at low flow rates low noise was observed. Concluded that noise measurements were not direct indicators of pitting corrosion.
Rushing et al. 2002 and 2004	Flow was circulated through two 1' copper pipe sections at a rate of 6 L/min for 5 minutes every three hours.	Study used synthetic water with high chlorine. b	Pits were not detected on the surfaces of the samples, even though it is known the water can cause pitting.	E_{corr} varied dramatically with level of chlorine and onset of flow.
Kane, Eden et al. 2003	Flow and static conditions tested.	Presence and monitoring of chlorine and sulfides were not reported.	Pit formation/depth was not reported. However, pitting factors and corrosion rates were calculated.	Study observed variations in noise and calculated pitting factors between flow and static conditions. While the study completed testing on a variety of metals, copper exhibited the greatest differences between test conditions.
Duranceau, Townley et al. 2004	Exact flowrate was not reported and tested only in some of the cases studied. Flow was intermittent to simulate use of domestic plumbing.	Study examined real waters. Complete analysis of water composition was conducted including total sulfide levels. Chlorine residuals were also monitored, but levels were not reported.	Short term testing did not result in formation of any large pits.	ECN techniques were reported to have accurately detected and monitored pitting, even though no large pits were obtained.

SUMMARY AND RE-STATEMENT OF GOALS

Copper pitting corrosion can be a serious problem in some affected communities. The science of pitting suggested that water flow rates can be an important factor in initiation and propagation of pits, yet there is virtually no research that has explicitly examined flow rate as a critical variable to pitting. This work will be the first to do so. Moreover, the impacts of various inhibitors to pitting corrosion tendencies under a range of circumstances will be examined as part of that evaluation.

REFERENCES

American Water Works Association Research Foundation and DVGW-Technologiezentrum Wasser (1996). Internal Corrosion of Water Distribution Systems, Second Edition. Denver, CO, American Water Works Association.

Duranceau, S. J., D. Townley, et al. (2004). Optimizing Corrosion Control in Water Distribution Systems, AWWARF.

Edwards, M. and N. Boulay (2001). "Organic Matter and Copper Corrosion By-Product Release: A Mechanistic Study." Corrosion Science **43**(1): 1-18.

Edwards, M. and J. F. Ferguson (1993). "Accelerated Testing of Copper Corrosion." Journal of American Water Works Association **85**(10): 105-113.

Edwards, M., J. F. Ferguson, et al. (1994). "The Pitting Corrosion of Copper." Journal of American Water Works Association **86**(7): 74-90.

Edwards, M., L. Hidmi, et al. (2002). "Phosphate Inhibition of Soluble Copper." Corrosion Science **44**(1057-1071).

Edwards, M. and L. S. McNeill (2002). "Effect of Phosphate Inhibitors on Lead Release from Pipes." Journal of American Water Works Association **94**(1): 79-90.

Evans, U. R. (1936). "Inhibitors- Safe and Dangerous." Transactions of the Electrochemical Society **69**: 213-231.

Evans, U. R. (1939). "The Classification of Anodic and Cathodic Inhibitors." Transactions of the Electrochemical Society **76**: 215-230.

Gaylarde, C. C. (1992). "Sulfate-Reducing Bacteria which do not Induce Accelerated Corrosion." International Biodeterioration and Biodegradation **30**: 331-338.

Giriga, S., U. K. Mudali, et al. (2005). "Electrochemical Noise Technique for Corrosion Assessment - A Review." Corrosion Reviews **23**(2-3): 107-170.

Gudas, J. P. and H. P. Hack. (1979). "Sulfide Induced Corrosion of Copper Nickel Alloys." Corrosion. **35**: 67-73.

Goodman, P. D. and V. F. Lucey (1984). An Electrochemical Pitting Corrosion Test Cell for Waters. Contractor Report: Technology for the Copper Industry, International Copper Research Association, Inc.

Iverson, W. P. (1968). Journal of Electrochem. Soc. **115**(6): 617.

Jacobs, S. (1997). Sulfide-Induced Corrosion of Copper in Drinking Water. Civil, Environmental and Architechtural Engineering. Boulder, Colorado. University of Colorado. **Master of Science**.

Jacobs, S. and M. Edwards (2000). "Sulfide Scale Catalysis of Copper Corrosion." Water Research **34**(10): 2798-2808.

Jonassen, H. B. (1958). Corrosion **14**: 375-376.

Kane, R. D., D. C. Eden, et al. (2003). Evaluation of Potable Water Corrosivity Using Real Time Monitoring Methods. Houston, Texas, NACE International.

Legat, A. and V. Dolecek (1995). "Corrosion Monitoring System Based on Measurement and Analysis of Electrochemical Noise." Corrosion **51**(4): 295-300.

Luther, V. H. and B. Hampel (1957). "Static Electrification of Hydrocarbons After Reaction with Oxygen." Erodel and Kohle **10**: 297-300.

Marshall, B. J. (2004). Initiation, Propagation, and Mitigation of Aluminum and Chlorine Induced Pitting Corrosion. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.

Mattsson, E. and A. M. Fredricksson (1968). "Pitting Corrosion in Copper Tubes- Cause of Corrosion and Counter-Measures." British Corrosion Journal **3**(September): 246-257.

Mayer, I. and J. D. B. Featherstone (2000). Journal of Crystal Growth **219**: 98-101.

Murray-Ramos, N. A. (2006). Examining Aspects of Copper and Brass Corrosion in Drinking Water. Environmental Engineering. Blacksburg, Virginia. Virginia Polytechnic Institute and State University. **Master of Science**.

Myers, J. and Cohen, A. (2005). Copper-tube Corrosion in Domestic Water Systems. *Boiler Systems Engineering (American Boiler Manufacturer's Association)*.

- Nguyen, C. K. (2005). Interactions Between Copper and Chlorine Disinfectants: Chlorine Decay, Chloramine Decay and Copper Pitting. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.
- Novak, Julia Ann. (2005). Cavitation and Bubble Formation in Water Distribution Systems. Environmental Engineering. Blacksburg, Virginia. Virginia Polytechnic Institute and State University. **Master of Science**.
- Olesen, P. T., T. Steenberg, et al. (1998). "Electrolytic Deposition of Amorphous and Crystalline Zinc-Calcium Phosphates." Journal of Materials Science **33**(12): 3059-3063.
- Patel, Sapna. (1997). Measurement of Localized Galvanic Currents during Copper Pitting Corrosion using a Novel Electrochemical System. Civil, Environmental and Architechtural Engineering. Boulder, Colorado. University of Colorado. **Master of Science**.
- Pourbaix, M. (1969). "Recent Applications of Electrode Potential Measurements in the Thermodynamics and Kinetics of Corrosion of Metals." Corrosion. **25** (6): 267-281.
- Rushing, J. C. (2002). Advancing the Understanding of Water Distribution System Corrosion: Effects of Chlorine and Aluminum on Copper Pitting, Temperature Gradients on Copper Corrosion, and Silica on Iron Release. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.
- Rushing, J. C. and M. Edwards (2004). "Effect of Aluminum Solids and Free Chlorine on Copper Pitting Corrosion." Corrosion Science **46**(12): 3069.
- Sandenbergh, R. F., P. C. Pistorius, et al. (1996). Characterization of the Pitting Corrosion Tendency of Copper in Water Using Electrochemical Techniques. 13th ICC.
- Scardina, P., M. Edwards, et al. (2007). Non-Uniform Corrosion in Copper Piping - Assessment. AWWARF.
- Seth, A. D. and R. G. J. Edyvean (2006). "The Function of Sulfate-Reducing Bacteria in Corrosion of Potable Water Mains."
- Sheffer, G. J. A. (2006). Investigation of Copper Pitting Propensity Using Bench and Field Scale Testing. Environmental Engineering. Blacksburg, Virginia. Virginia Polytechnic Institute and State University. **Master of Science**.
- Singh, P., G. T. Galyon, et al. (1992). Potentiodynamic Polarization Measurements for Predicting Pitting of Copper in Cooling Waters. The NACE Annual Conference and Corrosion Show, NACE
- Smith, S. and R. Francis (1990). "Use of Electrochemical Current Noise to Detect Initiation of Pitting Conditions on Copper Tubes." British Corrosion Journal **25**(4).

Sosa, Melanie. (1998). Investigation of Copper Pit Initiation, Propagation and Pssivation. Civil, Environmental and Architechtural Engineering. Boulder, Colorado. University of Colorado. **Master of Science**.

Sosa, M., S. Patel, et al. (1999). "Concentration Cells and Pitting Corrosion of Copper." Corrosion **55**(11): 1069-1076.

Starkey, R. L. (1958). "The General Physiology of the Sulphate-Reducing Bacteria in Relation to Corrosion." Producers Monthly: 12-30.

Zin, I. M., S. B. Lyon, et al. (2004). "Inhibition of Steel and Galvanized Steel Corrosion by Zinc and Calcium Ions in the Presence of Phosphate." Corrosion Engineering, Science and Technology **39**(2): 167-173.

CHAPTER 2: BENCH SCALE STUDIES OF ZINC, PHOSPHATE, AND NOM INHIBITION OF COPPER PITTING TENDENCIES UNDER LOW FLOW CONDITIONS

Rebecca Lattyak and Marc Edwards

ABSTRACT

All levels of orthophosphate greater than 0.2 mg/L as P reduced non-uniform corrosion tendencies in a macrocell apparatus with low flow, and zinc orthophosphate provided the best overall control. However, in this high pH and high Cl₂ water known to cause pitting, pits representative of those found in practical situations were not reproduced in any of the conditions tested. It was clear that flow rate needs additional research as a contributing factor to pitting.

INTRODUCTION

Pitting corrosion of copper drinking water pipes in consumers' homes remains problematic in certain regions of the United States. Relatively little is known regarding possible remedies to pitting. Recently, Marshall (2004) determined that a specific recipe of water at high pH, containing chlorine and aluminum, could cause pinhole leaks in copper pipe. This is the first time that pinholes were reproduced in the laboratory under scientifically reproducible conditions. Follow-up work by Marshall, using electrochemical techniques, indicated that dosing of orthophosphate would be predicted to reduce the rate of pinhole leaks in this water. Subsequent full scale dosing of phosphate at the utility confirmed the benefits of phosphate in reducing (but not completely eliminating) the frequency of pinhole leaks experienced by customers.

This work studied pitting in the Marshall water as a function of orthophosphate dose and natural organic matter concentration at low flow conditions using a bench-scale apparatus. Other research had suggested that zinc in combination with phosphate may have synergistic benefits in reducing pitting attack, so zinc orthophosphate inhibitor was also tested.

METHODS AND MATERIALS

The general approach used in this work replicated the essential features of a pit in the Marshall water using a low flow divided macrocell (Figure 2-1). Two copper samples are involved,

including 1) a small area of copper shielded from flow and bulk oxidants such as chlorine and oxygen, reproducing chemical conditions which might occur under a deposit in a real situation, and 2) a larger area of copper exposed to bulk water and modest flow, reproducing conditions for copper surfaces which are not under a deposit. When exposed to the high pH and high Cl_2 water that was shown to cause pitting by Marshall 2004, it was anticipated that a differential voltage would naturally arise between the two pieces of copper, and the resulting current between the samples could be measured using an ammeter. This flow of electrons from the anode to the cathode is termed a “pitting current,” as it contributes to the rate at which copper is corroded at the anode.

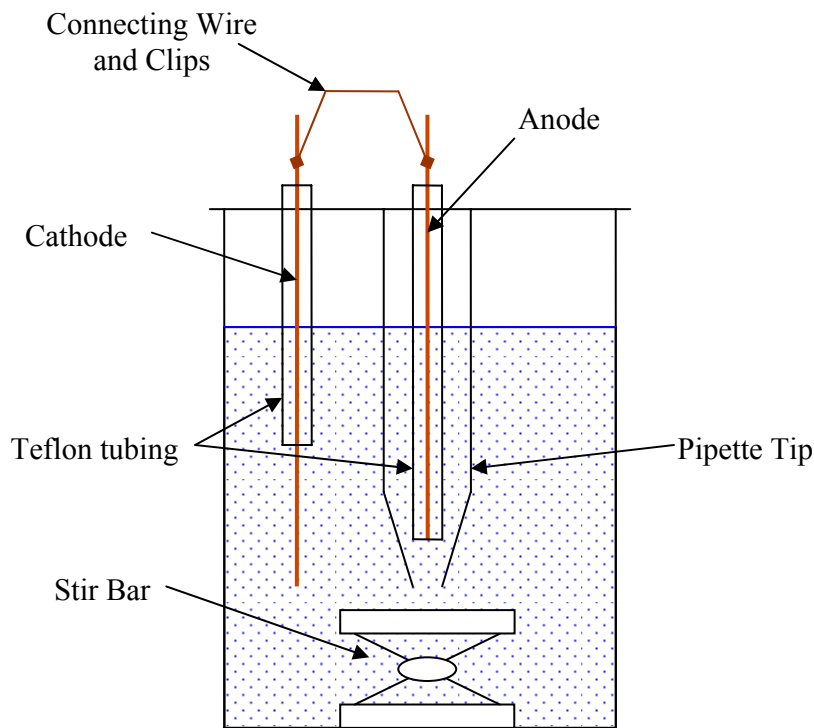


Figure 2-1: Schematic of Experimental Setup

Each test was conducted in 1 liter glass containers, covered with plastic to minimize air exchange, and stirred with a magnetic bar suspended in a plastic cage at 275 revolutions per minute (Figure 2-1 and Figure 2-2).

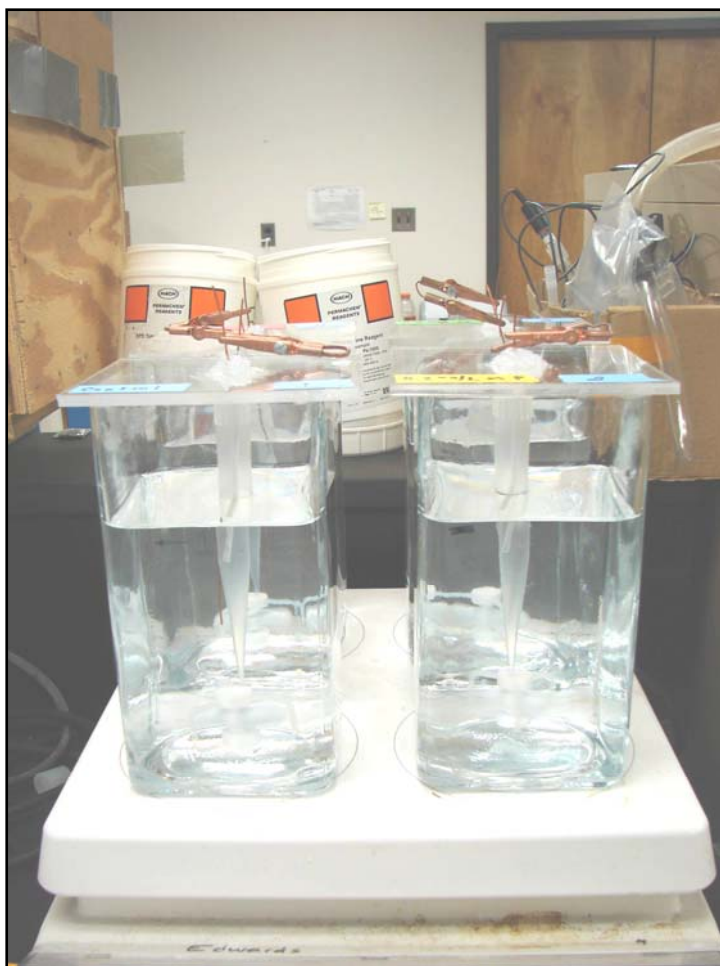


Figure 2-2: Experimental Setup with 4 Test Cells

Each test cell had two separate copper wire specimens, including the section believed destined to become anodic, which was located within a plastic pipette tip to partially shield the copper from the bulk water and to create an occluded cell. The cathode copper surface was composed of 18 gauge electrical grade bare copper wire inserted into Teflon tubing (ID = 1/16", OD = 1/8") and sealed with silicone sealant. Five cm (about 2 inches) of this wire was exposed to the water and the remainder was sealed under the tubing. The anode, or pit, was made by inserting the same 18 gauge electrical grade bare copper wire into Teflon tubing and sealing both ends with silicone sealant. The end of the wire (1 mm²) was cut flush with the tubing and sanded to a smooth, circular copper surface using a small handheld sanding tool with 60 grit sandpaper. The cathode to anode surface area was about 16:1.

The Marshall pitting water (Marshall 2004) was synthesized using the following recipe: 25.0 mg/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 56.85 mg/L NaHCO_3 , 41.296 mg/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 2.0 mg/L aluminum solids, 6.0 mg/L chlorine and pH 9.1-9.3. For specifics of preparing this solution refer to Marshall (2004). The high chlorine concentration was utilized to maximize the likelihood of initiating pitting.

Three sets of experiments were conducted with four experiments in each set. In the first set of tests, zinc was tested at a level of 1 mg/L as ZnCl_2 , orthophosphate was tested at a level of 1 mg/L as P (from Na_2HPO_4), and zinc and phosphate were tested together at 1 mg/L as Zn^{+2} and 1 mg/L as P. A control was run without inhibitor for comparison the fourth test. In the second set of tests, a control was tested along with three levels of orthophosphate inhibitor including 0.2, 0.5 and 2.0 mg/L as P. The third set of tests examined four conditions that included a control and three levels of natural organic matter including 0.05 mg/L NOM as carbon, 0.3 mg/L NOM and 3.0 mg/L NOM.

The pH was maintained at 9.2 +/- 0.1. Initially, no inhibitors were added to any of the test waters, attempting to allow non-uniform corrosion and pitting currents to establish. Once relatively stable pitting currents were obtained, the desired modification was added at the targeted concentration. A second dose of inhibitor was added once per week and the water was completely changed every other week. Thus, the actual dose of inhibitor (phosphate, zinc or NOM) delivered to the water ranged from the target level to twice the target level, and the actual concentration of inhibitor in the water at a given time would depend on how much of the inhibitor was removed by reactions with the copper. In a few cases it was deemed desirable, after testing was completed at pH 9.2, to lower the pH of the water in the apparatus to pH 8.2 and/or pH 7.2.

Monitoring Corrosion: Electrochemical Measurements

Measurements of voltage between the anode and cathode, the current between the anode and cathode, and E_{Corr} of each copper sample versus an Ag-AgCl reference electrode were made periodically using a Fluke 189 True RMS Multimeter. In general, the anode and cathode were connected via a copper wire at all times, except when they were briefly connected in a voltage

mode using the ammeter during which time resistance of the connection is very high. It was believed that the electrical connection between the wires and resulting flow of electrons helps to sustain the pitting reaction. That is, release of Cu^+ inside the pit tends to remove oxygen and drop pH in the pit relative to the bulk water (Figure 1-1), which maintains an electrochemical potential between the anode and cathode which drives pitting.

In this work, a positive current indicates that the electrons are flowing from the anode to the cathode and that pit growth and propagation is occurring. Conversely, a negative pitting current indicates that electrons are flowing from the cathode to the anode, and the pit is actually the cathode. The magnitude of the measured current is proportional to the rate at which electrons are flowing, and therefore, is related to the rate of pit growth. Therefore, a higher positive current implies that pitting is occurring at the anodic wire at a faster rate. Likewise, a positive voltage indicates that the smaller pit wire is anodic relative to the larger wire exposed to bulk flow, whereas a negative voltage indicates that the smaller pit wire has become cathodic relative to the larger wire exposed to bulk flow.

Typical behavior of the anode and cathode during the initial exposure period when no inhibitor was added, which lasted a minimum of 1 week, is illustrated in Figure 2-3. There is obvious statistical variability between measured currents in the otherwise identical cells in the early phases of an experiment, and indeed, it takes time before a significant pitting current is generated. But after the initial exposure the currents between the different cells rose to within +/- 50% of each other, and the experiment was initiated by dosing inhibitor to the water. Thus, the differential flow of water was successful in initiating non-uniform corrosion in this water.

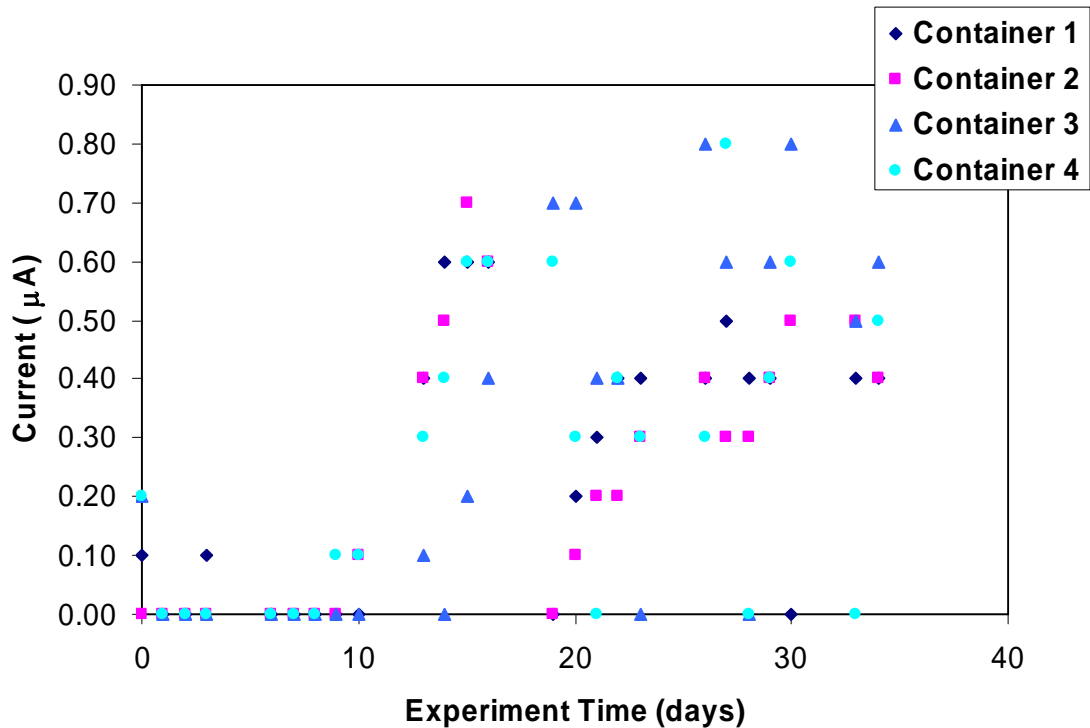


Figure 2-3: Baseline Currents Established before Inhibitor Addition

E_{Corr} measurements were gathered using an Ag-AgCl reference electrode. Electrodes were maintained on a regular basis and cross-checked with one another to ensure consistent and accurate data collection. Higher E_{Corr} values for the cathode and lower E_{Corr} values for the anode indicate a stronger driving force for pitting. Total chlorine was monitored daily in order to determine chlorine decay rates.

RESULTS

Experimental results are presented in three sections representing the three phases of experiments.

Effects of Zinc and Phosphate Alone and In Combination

Clear trends became discernable immediately after addition of the different inhibitor types (Figure 2-4). Initially, the E_{Corr} of the connected pit wire and bulk water copper was +120-180 mV. After making the modifications to the water, E_{Corr} rose to as high as 609 mV in the case of 1 mg/L Zn^{+2} , and erratically fluctuated between +110-600 mV. E_{Corr} was relatively stable at 120-240 mV for the control with no inhibitor, but was about 90 mV lower in the same water

dosed with orthophosphate. Although the system dosed with zinc orthophosphate had the second highest E_{Corr} before adding the inhibitor, within 9 days it became the lowest and remained the lowest for the rest of the experiment. As a general rule, lower or more stable E_{Corr} is thought to be indicative of reduced pitting tendencies. In a normal situation on a pipe, it is not possible to measure ΔV and pitting current, but the divided cell apparatus allowed these measurements.

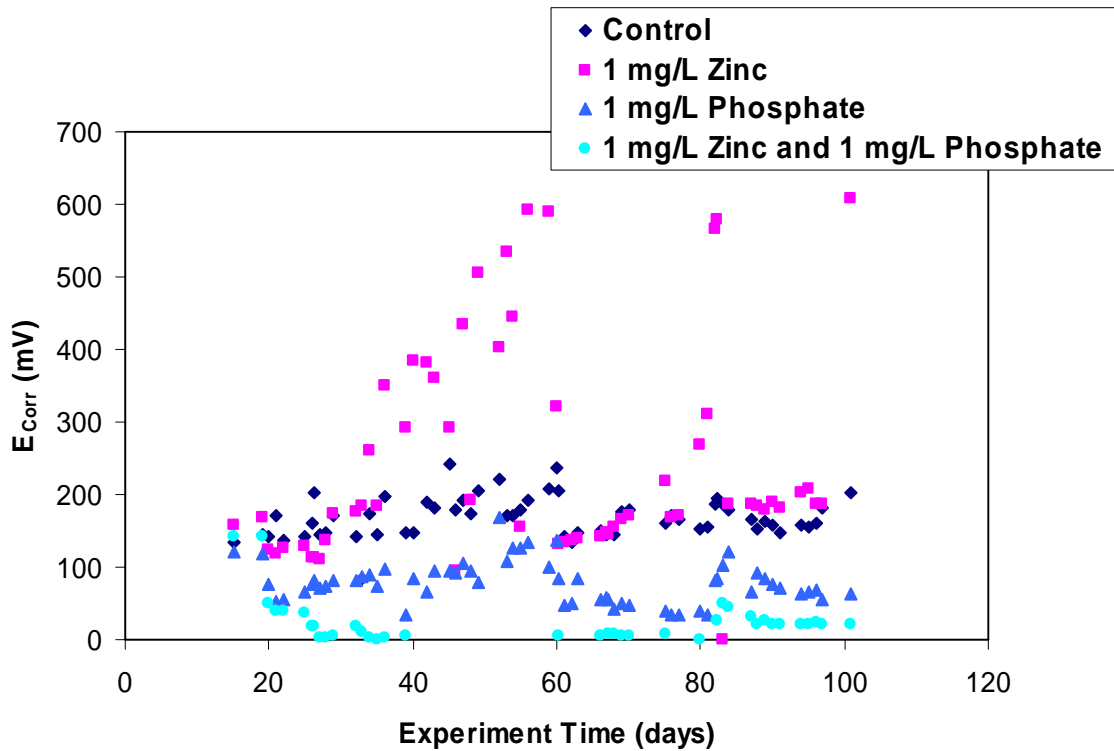


Figure 2-4: E_{Corr} Measurements for Zinc, Phosphate, and Zinc Phosphate Inhibitors

The measurements of pitting currents unambiguously support the conventional interpretation of E_{Corr} in these tests. Specifically, the combination of zinc and phosphate, or phosphate alone, which dropped E_{Corr} , also dropped the pitting current between the anode and cathode from 0.6 to 0.0 μA and currents remained undetectable for the rest of the experiment (Figure 2-5). However, within about 20 days in this test, the pitting current dropped to very low levels in all of the conditions including the control, indicating that pitting between the two pieces of copper was not sustainable using the existing apparatus and configuration.

The anodes in the apparatus were replaced with new wires on day 67. This differed from the earlier approach in which pitting was established on the wires before exposure to the inhibitors. As before, pitting currents gradually developed on the wires after a period of time, in all cases except for the zinc phosphate. Thus, zinc phosphate had unique benefits in both speed of stopping established pitting currents and also in preventing new currents from arising when clean copper anode wires were added to the system.

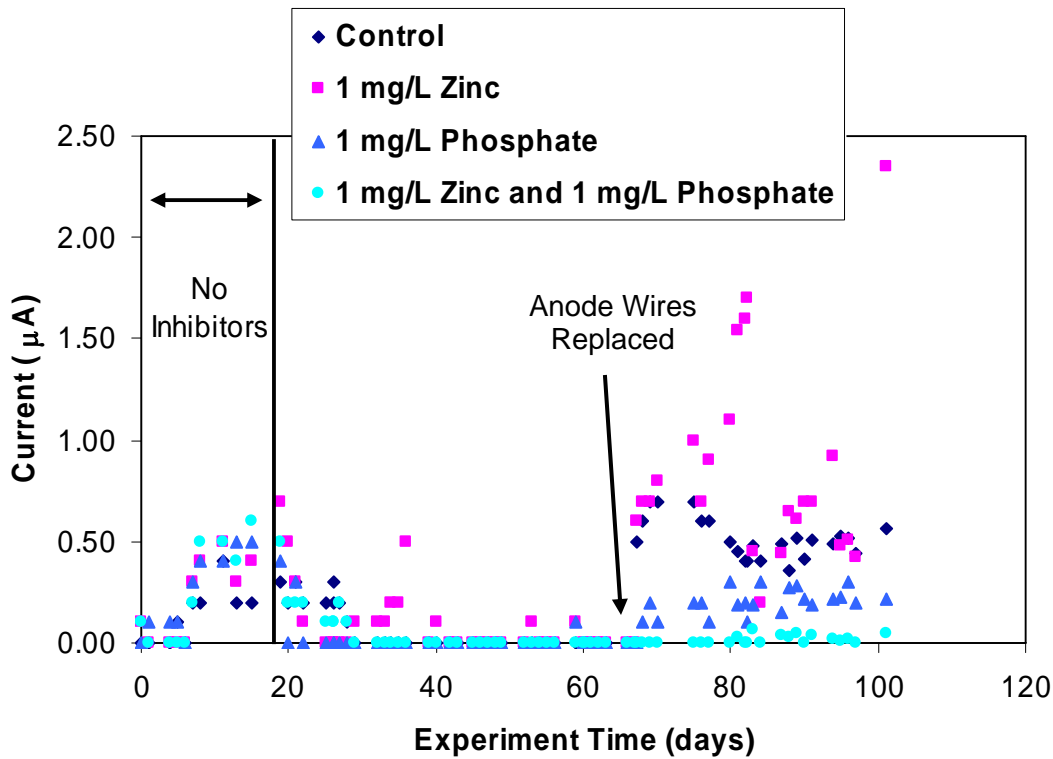


Figure 2-5: Pitting Currents for Zinc, Phosphate, and Zinc Phosphate Inhibitors

The pitting currents were highest for zinc, as they reached levels as high as 2.35 μA , which translates to corrosion rates of about 235 $\mu\text{A}/\text{cm}^2$ on the anode wire surface. A pit growing at this rate on a pipe would completely penetrate the wall of a typical Type M copper tube in only 3 months. Even a pitting current of about 0.23 μA , observed in the presence of phosphate is relatively high, because if it was sustained it would penetrate the wall of a Type M tube in only 30 months (2.5 years).

The voltage between the anode and cathode for the phosphate, the control and the zinc all show relatively stable or upward trends, with the largest uptrend in the water with only zinc (Figure 2-6). The zinc voltage difference between the anode and cathode reached above 0.5 V. The water modified with phosphate had similar voltage drops relative to the control. The voltage drop in the system with zinc and phosphate, not only decreased, but eventually resulted in negative values. The negative sign indicates that the direction of the flow of electrons reversed, and the portion of the copper that was once anodic and was being sacrificed, was actually being protected. This is a unique advantage of zinc phosphate relative to other inhibitors in this system, and this tendency has also been observed previously in field studies.

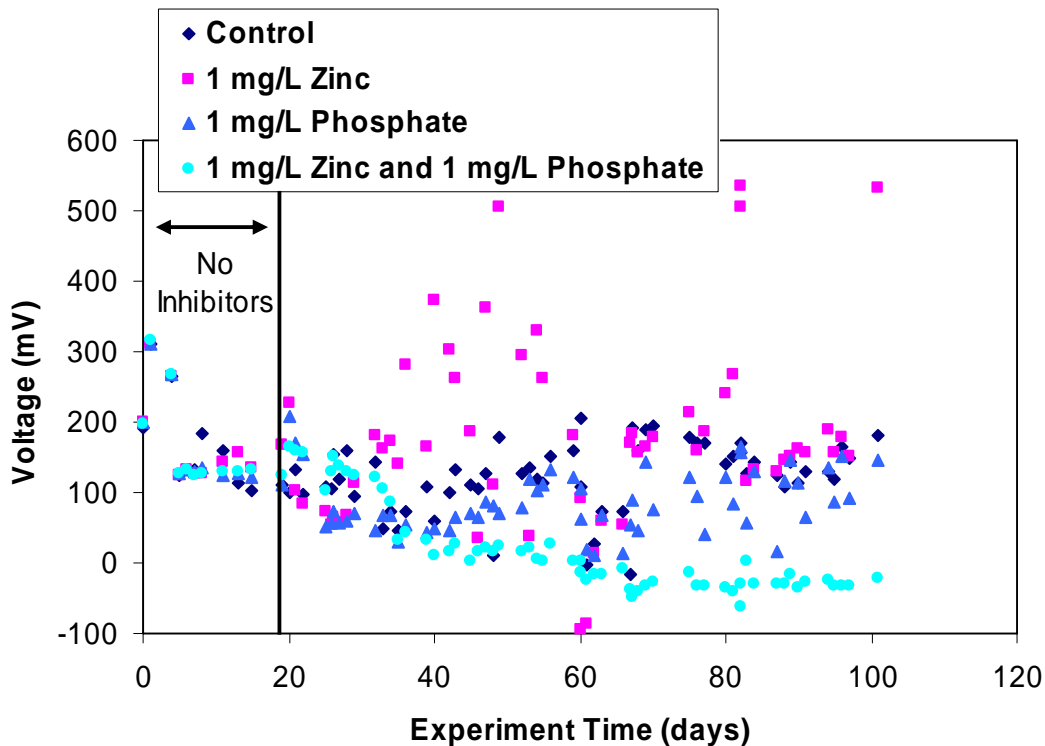


Figure 2-6: Voltages for Zinc, Phosphate, and Zinc Phosphate Inhibitors

Chlorine consumption occurring at the cathode can drive the corrosion reaction at the anode, since the cathodic reaction is often the rate limiting step. Chlorine decay rates were calculated for each condition and may be indirectly related to the corrosion rate (Figure 2-7). The error bars indicate a 95% confidence interval. Statistical analysis showed that addition of the inhibitors reduced the chlorine decay relative to the control. The most significant reduction occurred when

zinc was used in combination with phosphate. This corresponds to earlier trends noting a unique benefit from the combination of zinc and phosphate, although it is not clear whether the benefit is additive or synergistic.

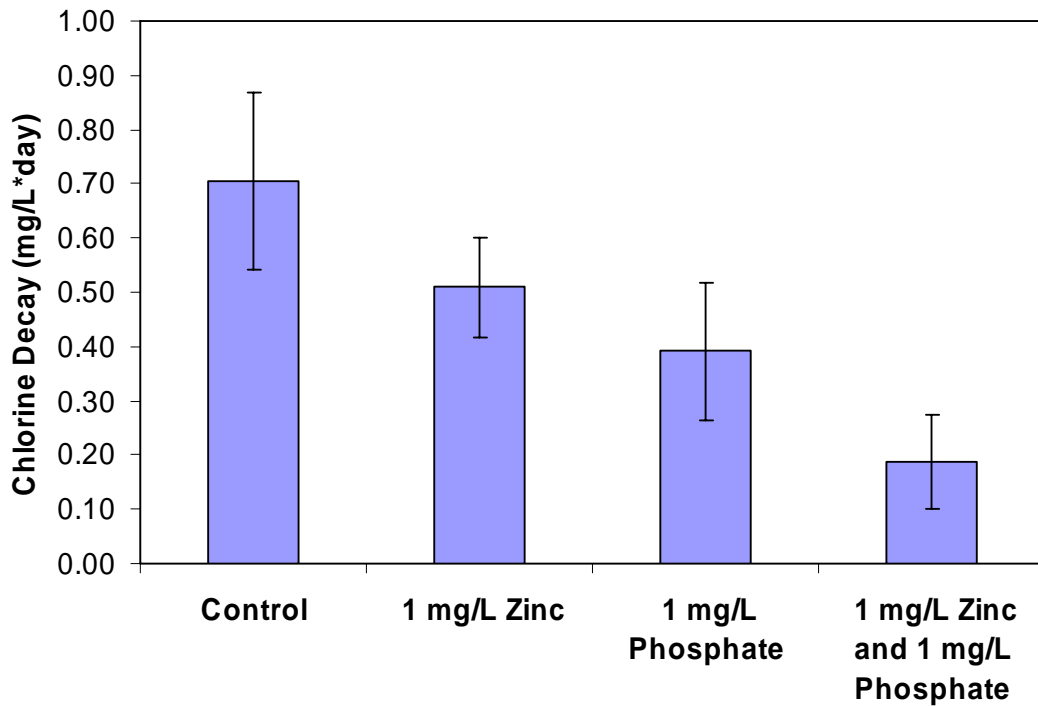


Figure 2-7: Chlorine Decay for Zinc, Phosphate, and Zinc Phosphate Inhibitors

Midway through the experiment, the anode wires were removed and photographed (Figure 2-8). Both the control and the condition with only zinc showed a black scale on the anode, which is consistent with anodic deposits observed by Marshall over pits (2004). The condition with phosphate had a green scale similar to that observed by Marshall on pipes exposed to phosphate in this water type. Finally, the condition with both zinc and phosphate had little to no noticeable buildup of deposits.

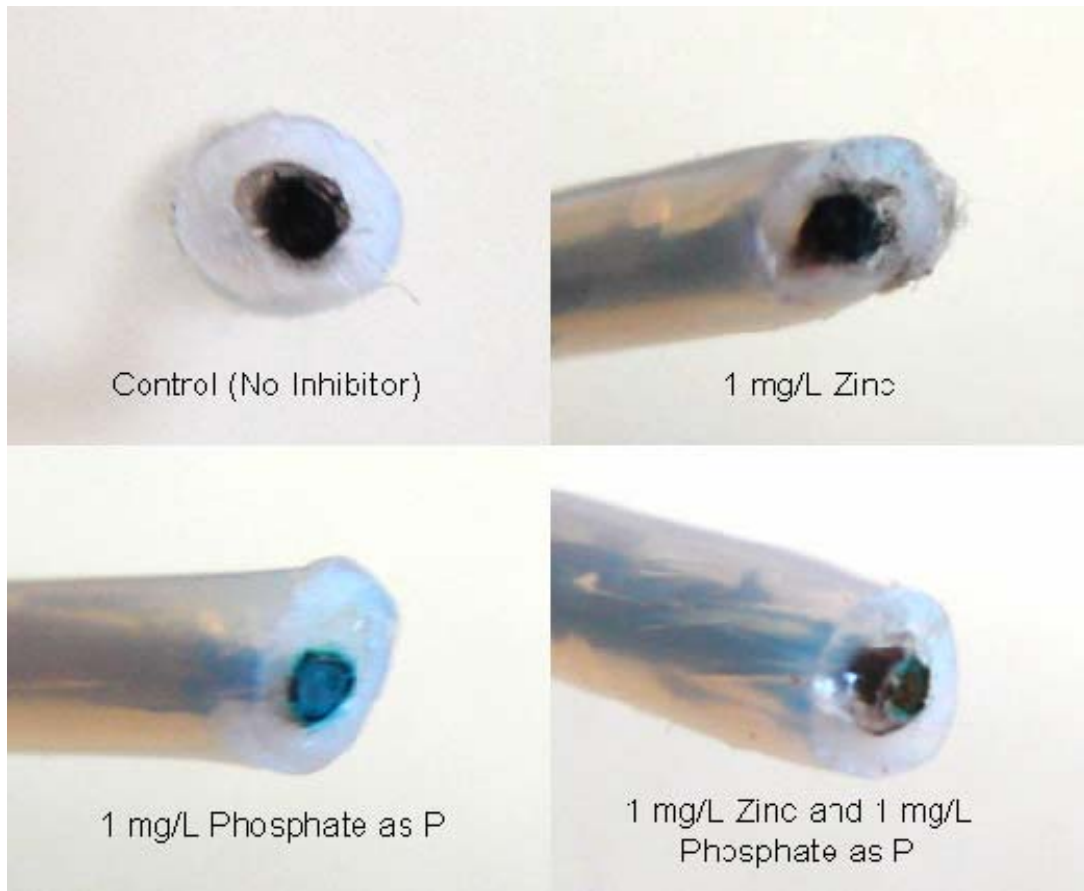


Figure 2-8: Scale on Pit Wires Removed from the Experiment

During the course of this work and in other studies, the question arose as to why pitting between the anode and cathode frequently dropped to zero in the small scale apparatus. In the Marshall study using a large scale recirculating apparatus with copper pipe sections in sequence, the first pipe section developed 8 fully penetrating pinholes within just 11 months. Clearly, something related to the bench scale apparatus, was not reproducing a critical component necessary for sustained pitting in the Marshall water.

Effects of Phosphate Concentration

In the small scale apparatus test using different levels of phosphate at pH 9.2, all three concentrations of phosphate resulted in E_{Corr} values below the control (Figure 2-9). The lowest concentration of 0.2 mg/L was only slightly below the control indicating that the concentration may be too low to produce a considerable decrease in the corrosion rate. The highest

concentration, 2.0 mg/L, had a more variable trend, but was consistently below the control. The greatest reduction in E_{Corr} arose from a dose of 0.5 mg/L $\text{PO}_4\text{-P}$.

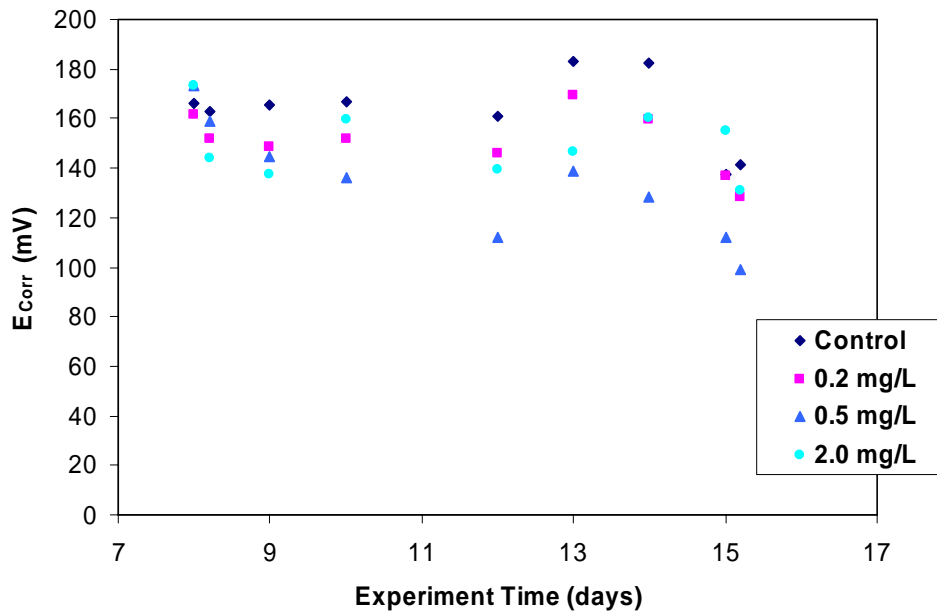


Figure 2-9: E_{Corr} Measurements for Phosphate Inhibitors at a pH of 9.2

When the pH was dropped to pH 8.2 (Figure 2-10), the same trend was observed amongst the four conditions. E_{Corr} dropped overall relative to what was observed at pH 9.2, consistent with expectations based on Rushing et al. (2004) and Marshall (2004) regarding reduced pitting at lower pH in this water.

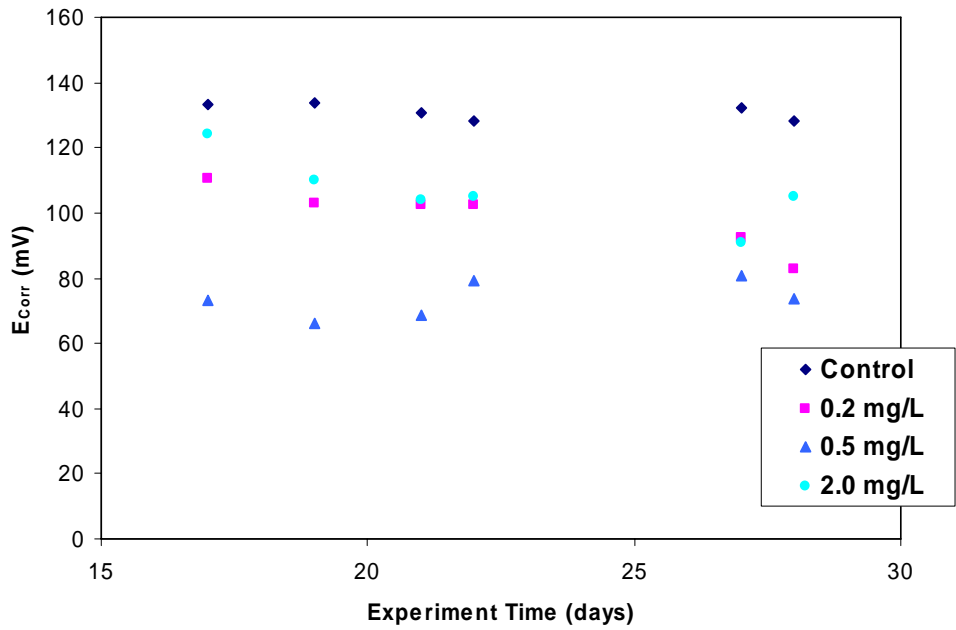


Figure 2-10: E_{corr} Measurements for Phosphate Inhibitors at a pH of 8.2

The pitting currents at pH 9.2 were always lower in the presence of phosphate (Figure 2-11), consistent with expectations based on E_{corr}. The lowest pitting currents were measured at the highest phosphate dose.

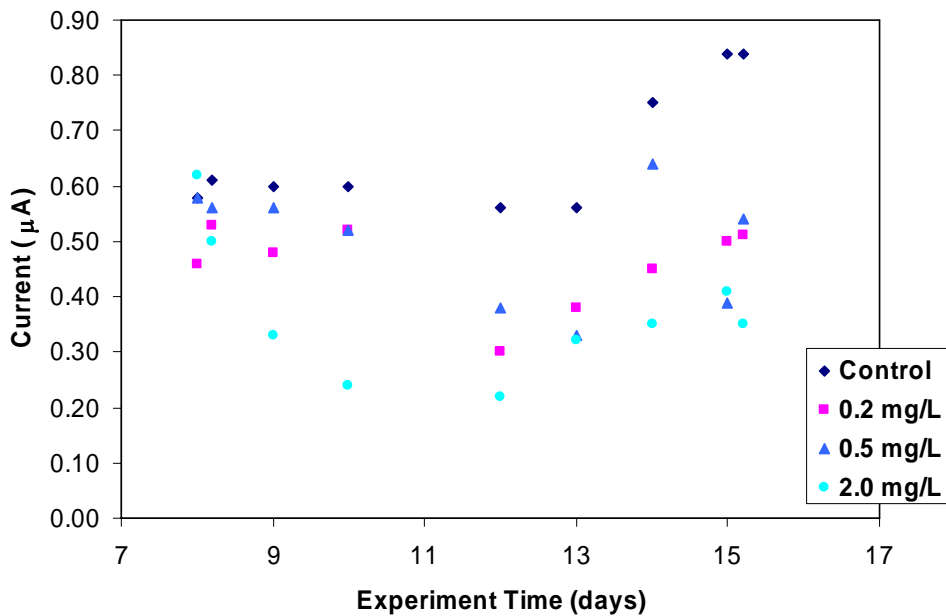


Figure 2-11: Pitting Currents for Phosphate Inhibitors at a pH of 9.2

Immediately after the pH was lowered to 8.2, the only clear trend in pitting current was a decrease observed at the lowest concentration of 0.2 mg/L (Figure 2-12). The initially large amount of scatter may have resulted from a water change which occurred on day 15 of the experiment. Once the values began to stabilize, all the concentrations resulted in values below the control with 0.5 mg/L having values closest to the control.

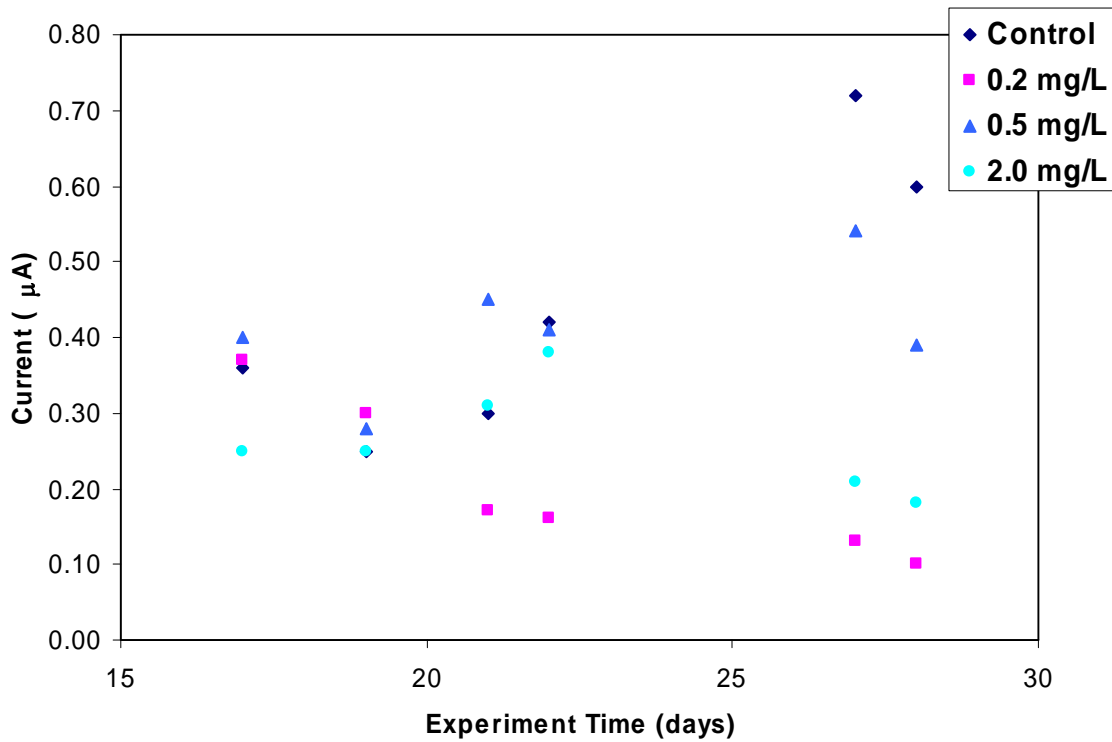


Figure 2-12: Pitting Currents for Phosphate Inhibitors at a pH of 8.2

Although average chlorine decay rates decreased at all concentrations of phosphate tested, these trends were not statistically significant (Figure 2-13). The large amount of scatter, as seen by the error bars, was due to the limited number of data points collected in this very short term test.

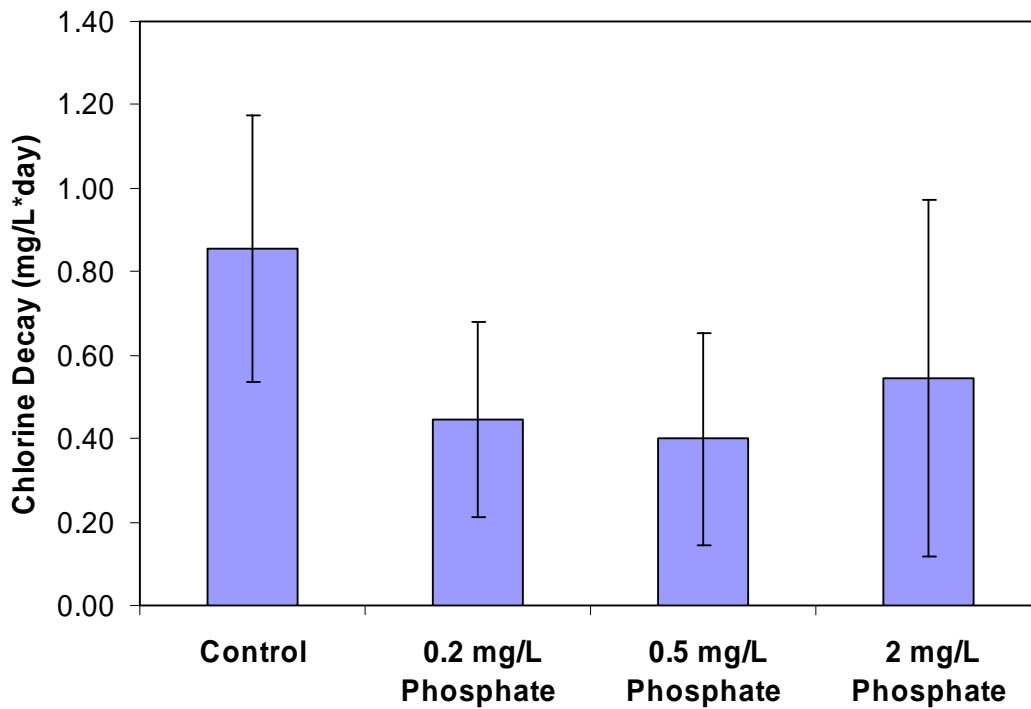


Figure 2-13: Chlorine Decay for Various Concentrations of Phosphate (in mg/L as P)

Effects of Natural Organic Matter

Although there was much scatter in the data at a pH of 9.2, the highest concentration of 3.0 mg/L NOM had E_{Corr} values consistently lower than the control or the concentrations of 0.05 and 0.3 mg/L NOM (Figure 2-14). This suggests that higher levels of NOM in the water could help reduce pitting tendencies. The lowest concentration of 0.05 mg/L followed very closely with the control signifying that this concentration was too low to obtain the desired reduction in corrosion rates. The middle concentration of 0.3 mg/L had a slight downward trend, but occasionally had E_{Corr} values above the control which implies a variable effect.

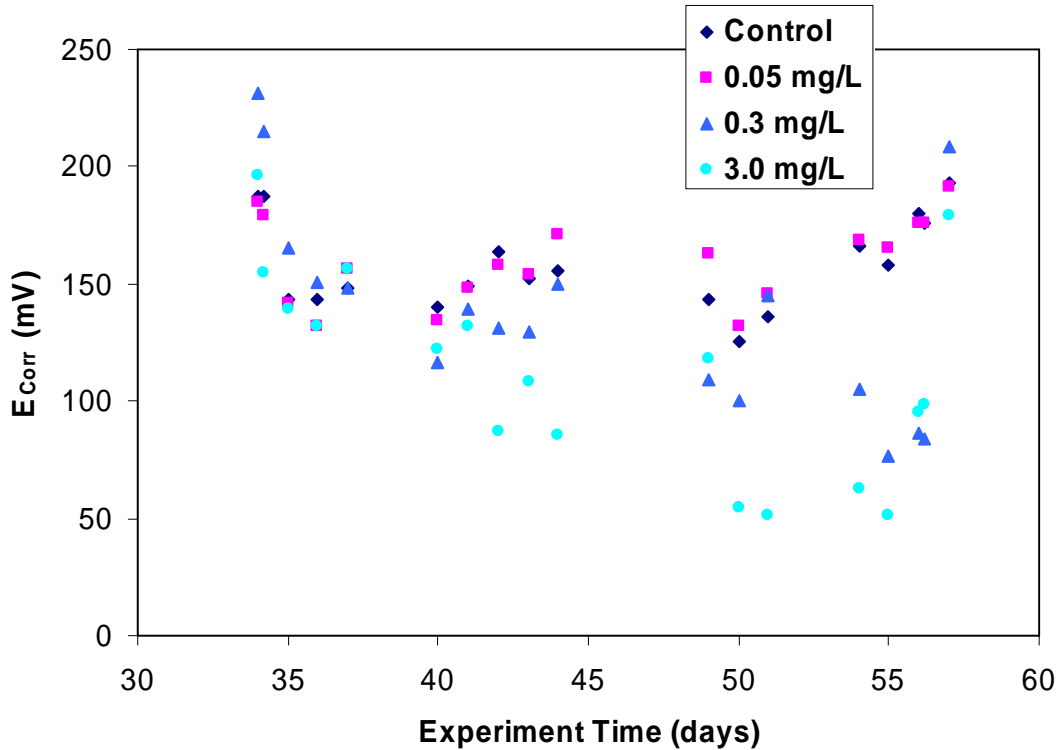


Figure 2-14: E_{Corr} Measurements for NOM Inhibitors at a pH of 9.2

A drop to a pH of 8.2 reversed some of the effects seen above (Figure 2-15). The lowest concentration still appeared to be too low to produce a significant difference from the control. However, the 3.0 mg/L had E_{Corr} values above the control in this very short term test while the 0.3 mg/L had a downward trend that fell slightly below the control. The trends continued to diverge when the pH was dropped even further to 7.2 (Figure 2-16). Here, both E_{Corr} values for the 0.3 and 3.0 mg/L, while having some scatter, were higher than the control. According to traditional interpretations of E_{Corr} , this would indicate that at a pH of 7.2 NOM does not act as an inhibitor.

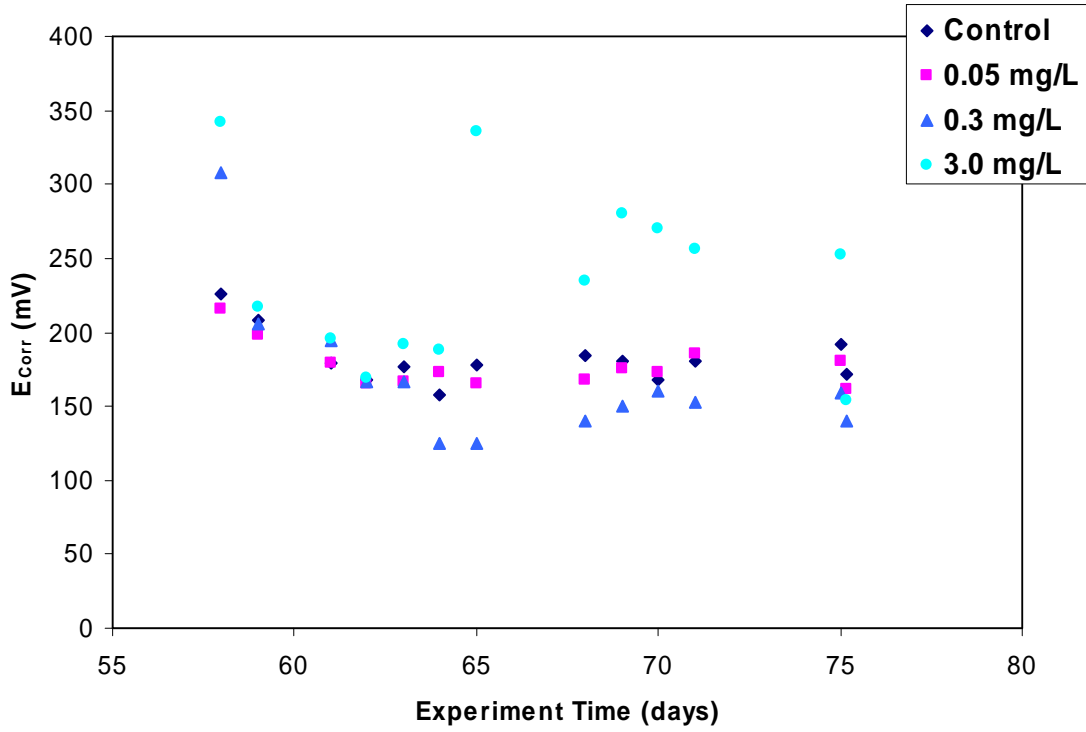


Figure 2-15: E_{Corr} Measurements for NOM Inhibitors at a pH of 8.2

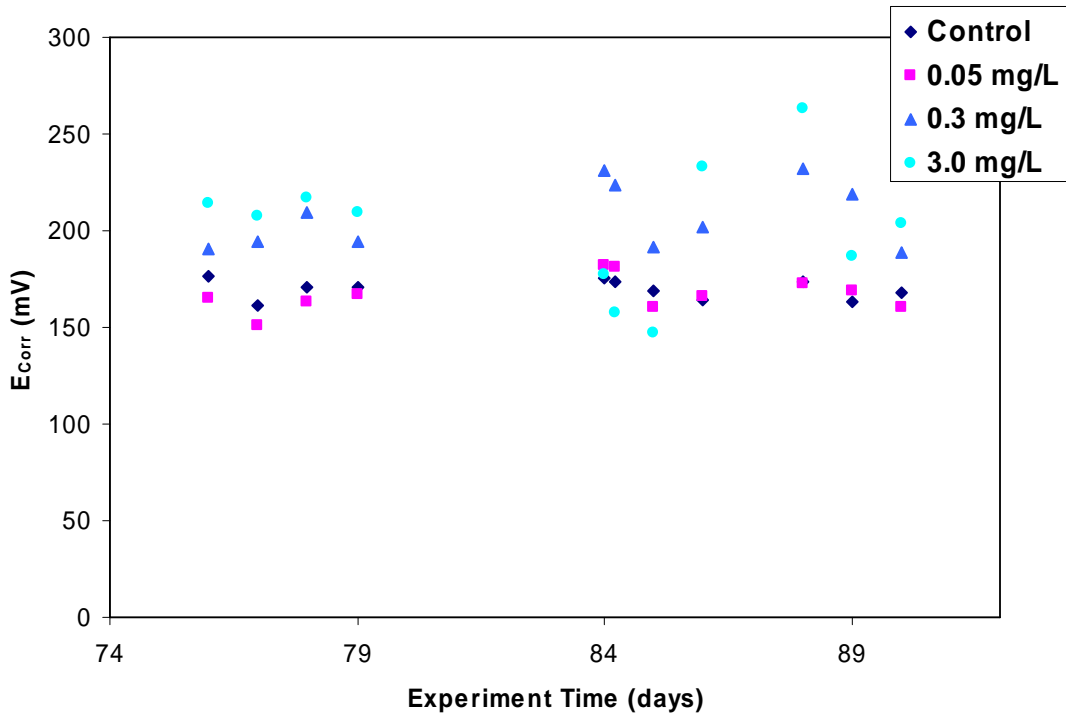


Figure 2-16: E_{Corr} Measurements for NOM Inhibitors at a pH of 7.2

Trends in the pitting current data in the presence of NOM at pH 9.2, pH 8.2 and pH 7.2 had too much scatter to allow clear conclusions to be drawn (Figure 2-17, Figure 2-18, and Figure 2-19). Overall, for this particular water, differences in NOM concentration did not have a strong influence on pitting.

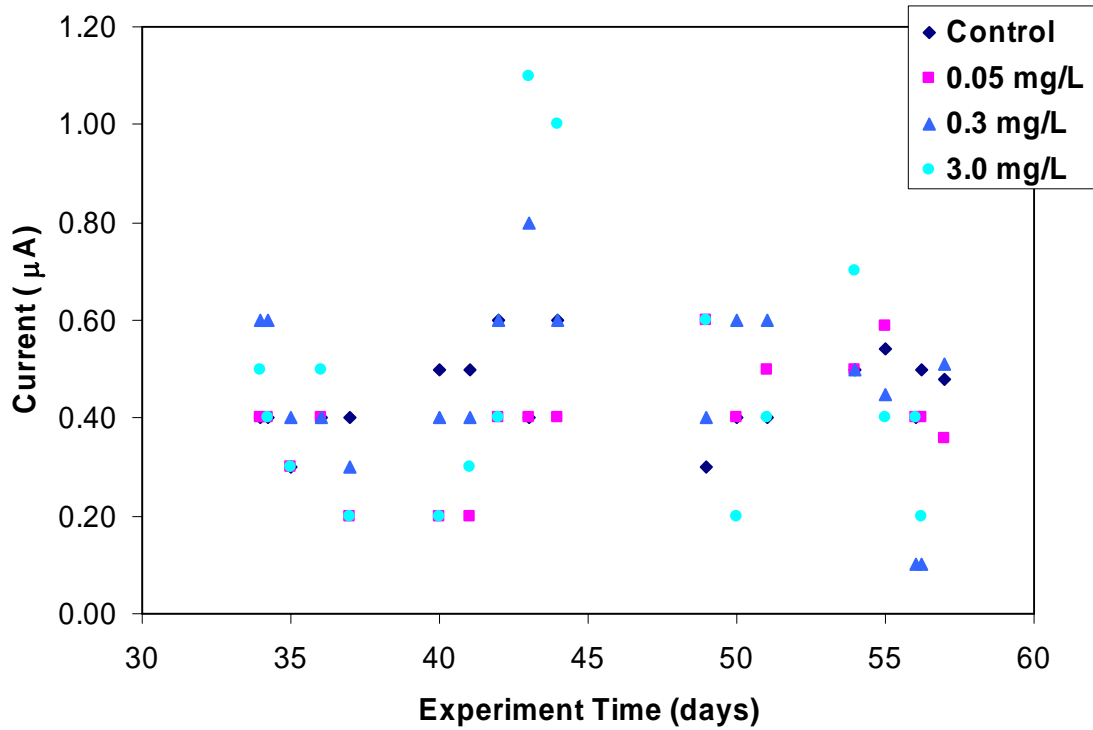


Figure 2-17: Pitting Currents for NOM Inhibitors at a pH of 9.2

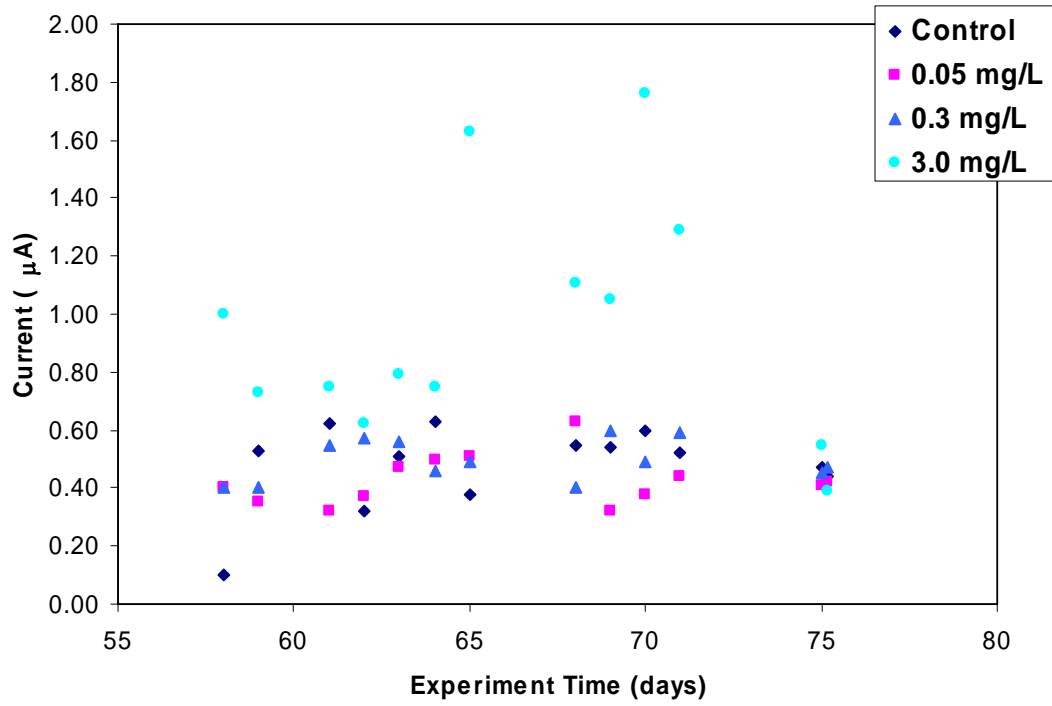


Figure 2-18: Pitting Currents for NOM Inhibitors at a pH of 8.2

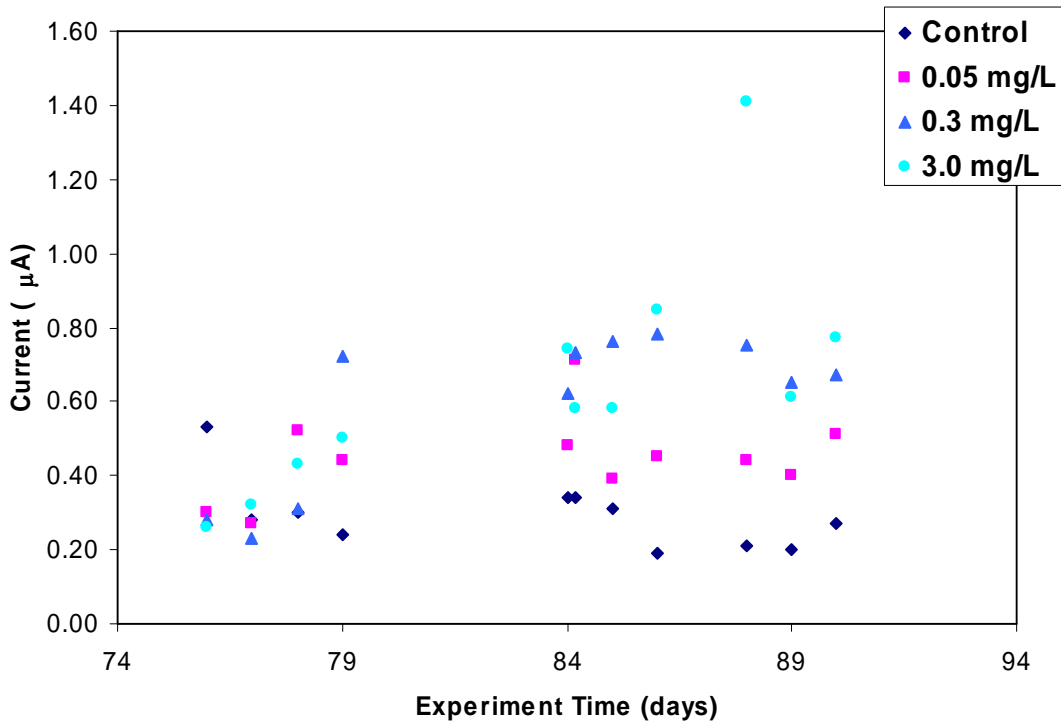


Figure 2-19: Pitting Currents for NOM Inhibitors at a pH of 7.2

Chlorine decay rates for NOM resulted in opposite trends than those observed for the zinc or phosphate conditions (Figure 2-20). The chlorine decay generally increased with concentration of NOM, perhaps because the natural organic matter itself has a chlorine demand. Therefore, the higher chlorine demand in the presence of NOM does not imply a higher rate of corrosion. Also, there is no statistical difference in chlorine decay between the lower concentrations of 0.05 and 0.3 mg/L and the control as indicated by the overlap in the error bars.

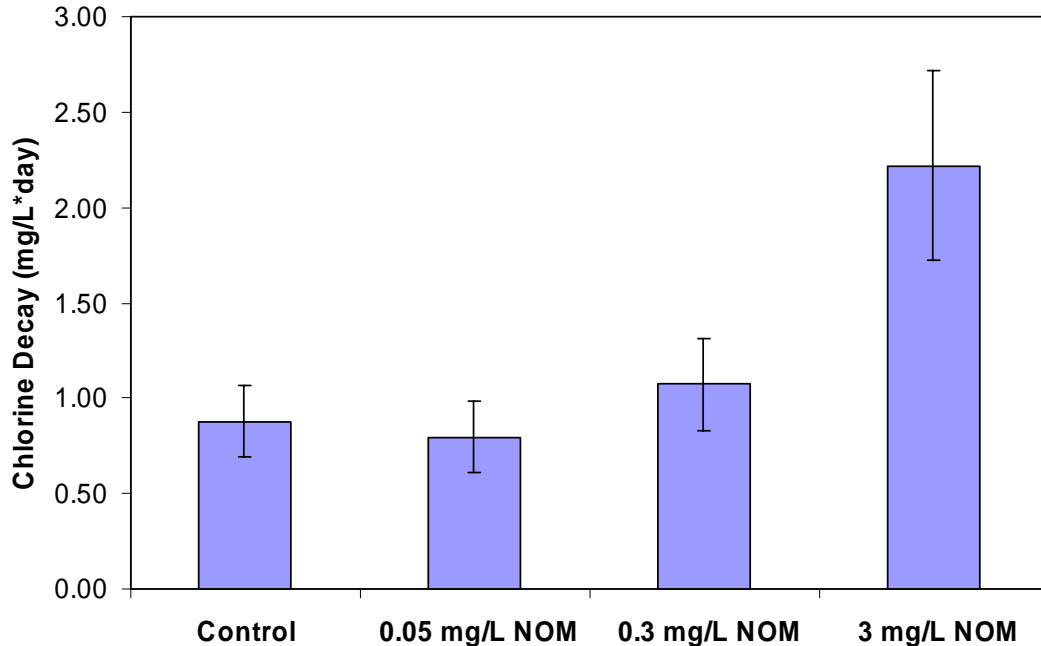


Figure 2-20: Chlorine Decay for Various Concentrations of NOM

DISCUSSION

Although the small scale divided cell experiment produced suggestive trends based on electrochemical measurements for the various inhibitors, it clearly did not replicate sustained pitting attack, even in the control water known to cause pitting. Given that numerous mechanisms and factors contribute to copper pitting (e.g., chemistry, biology, flow, installation), results of this study relative to zinc phosphate, phosphate and NOM do not necessarily apply to pitting in other water types.

CONCLUSIONS

- Results from the bench scale divided cell experiments have demonstrated that zinc in combination with phosphate provides unique and consistent reduction in non-uniform copper corrosion tendencies in the Marshall pitting water.
- Zinc phosphate dosing reduced the electrochemical potentials, pitting currents and chlorine decay rates. Phosphate also had a role in reducing non-uniform corrosion tendencies. Pitting currents were reduced at higher phosphate doses.
- The effects of NOM were weak. Most certainly, the addition of 3 mg/L NOM to this high pH water did not eliminate non-uniform corrosion tendencies over a short time period.

REFERENCES

Marshall, B. J. (2004) "Initiation, Propagation, and Mitigation of Aluminum and Chlorine Induced Pitting Corrosion." Virginia Polytechnic Institute and State University. Blacksburg, VA. **Master of Science**.

Rushing, J. C. (2002). "Advancing the Understanding of Water Distribution System Corrosion: Effects of Chlorine and Aluminum on Copper Pitting, Temperature Gradients on Copper Corrosion, and Silica on Iron Release." Environmental Engineering. Virginia Polytechnic Institute and State University. Blacksburg, Virginia. **Master of Science**.

Rushing, J.C., and M. Edwards. (2004). "Effect of Aluminum Solids and Free Cl₂ on Copper Pitting." Corrosion Science. **46** (12): 3069-3088

CHAPTER 3: FLOW ELECTRIFICATION AND NON-UNIFORM COPPER CORROSION IN POTABLE WATER SYSTEMS

Rebecca Lattyak, Marc Edwards and Chris Strock

ABSTRACT

The large scale recirculating rig experiment revealed macrogalvanic effects along a length of pipe that was not reproduced in smaller scale bench experiments. The effects were consistent with a phenomenon known as “flow electrification,” a heretofore unknown contributor to non-uniform copper corrosion occurring in water distribution systems. For copper tubing in one type of water known to cause pitting with free chlorine, some flow electrification was observed at all velocities tested between 0.9-4.9 fps and was worst at 2.8 fps. The portion of pipe first contacting flow was highly anodic relative to later pipe sections. As pH was increased from 9.2 to 11.0, reductions in flow electrification current and E_{Corr} occurred at the higher velocities (2.8 and 4.9 fps), but the opposite effect was observed at the lowest velocity of 0.9 fps. In the same water with sulfide instead of chlorine, the macrogalvanic effect was reversed, in that the portion of pipe first contacting flow was cathodic relative to later pipe sections.

INTRODUCTION

The role of water flow has emerged as an important yet under-appreciated contributor in non-uniform copper corrosion. Marshall (2004) determined that a particular recipe for high pH, high Cl_2 water with aluminum hydroxide, would cause serious pinhole leaks in copper if the water was recirculated continuously through the pipes at 2 fps. With infrequent flow in the same water, no pinholes were formed. A follow-up to the Marshall work by Nguyen observed higher E_{Corr} values at higher mixing rates or with increasing turbulence (2005), suggesting that higher velocities caused worse pitting. Taking Nguyen’s result to a logical extreme, Murray-Ramos (2006) tested water flowing through copper pipes at 8 fps, expecting to find very high rates of pitting, yet no pinhole leaks occurred using the Marshall water after 15 months. Although other factors were also changed between the Marshall study and the Murray-Ramos work such as pipe diameter, the presence of brass fittings that leached zinc into the water and the flowrates were

considered likely causes of the failure to reproduce pitting. All of the above studies were using flows or mixing rates that were classified as turbulent based on Reynolds number.

Visual observations by Marshall (2004) indicated that the scale initially formed at the entrance of the pipe, and then gradually moved down the pipe along its length. This suggested that there was a difference in corrosion for the entrance versus the exit of pipe sections, with the entrance tending to be anodic relative to the exit. This was later confirmed by much higher pit density and pit depth near of the entrance of Marshall's pipes. Likewise, Murray-Ramos reported that the entrance of pipes had a greater pit density than any other location along the surface of the pipe (2006). Given the highly variable results as measured in terms of ability to produce pinhole leaks, and the suspected and perplexing non-linear impacts of velocity on non-uniform corrosion tendencies, it was deemed desirable to examine effects of pipe water velocity systematically in one experiment for this work. Before doing so, the concept of "flow electrification," a heretofore unknown yet potentially important contributor to non-uniform corrosion in potable water systems is reviewed and developed.

BACKGROUND ON FLOW ELECTRIFICATION

The flow of fluid past a charged surface creates an imbalance in electrical charge and a voltage difference known as streaming current or streaming potential. For non-aqueous fluid flow through pipes in the petroleum industry, this phenomenon is termed "electrification" or "excitability." The concept is important because it was discovered that thousands of volts can develop along a length of pipe, with resultant creation of sparks and higher likelihood of explosions. However, no research to date has been conducted on this phenomenon in potable water applications, and indeed, the expectation from earlier work was that flow electrification was unimportant in aqueous systems.

Preliminary conceptualization of the phenomenon begins with consideration of a non-conducting pipe with a fixed negative charge at the metal-solution interface where the solution is composed of pure water (Figure 3-1). Without flow, each negative surface charge is counterbalanced by an equal number of mobile excess positive charges very close to the surface in the electrical double layer. When flow is initiated, some of these mobile excess positive charges move with the fluid,

whereas the negative surface charge is fixed. This flow of charges is termed “streaming current” and a voltage meter in electrical contact with the water can actually measure the “streaming potential” associated with this flow of positive charges along the pipe length.

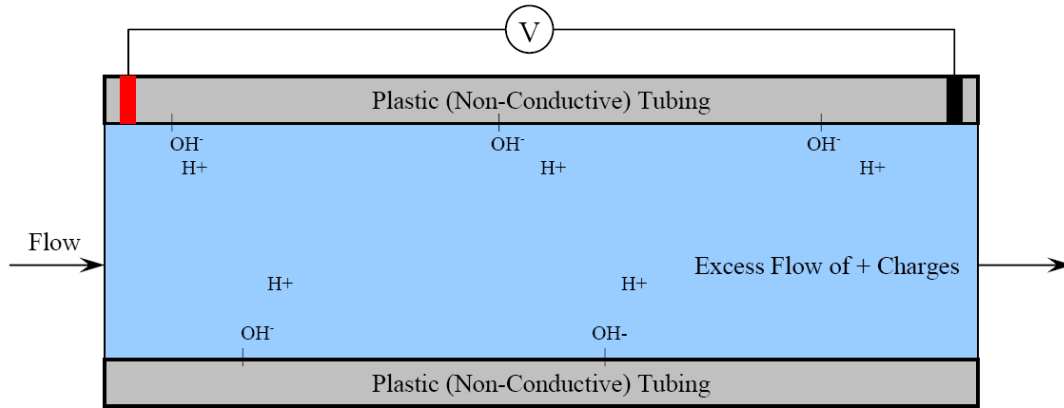


Figure 3-1: Streaming potential schematic, section through pipe along flow (no O_2 or Cu)

If an ammeter is used to connect two noble metal wires along the pipe length such as platinum or gold and if the flow and surface charge are high enough to induce sufficient potential, a current can also be measured (Figure 3-2). The electron flow through the ammeter tends to reduce the voltage drop per unit length of pipe. The upstream noble metal wire becomes the anode where O_2 is created, whereas the downstream wire becomes the cathode where H_2 gas is evolved.

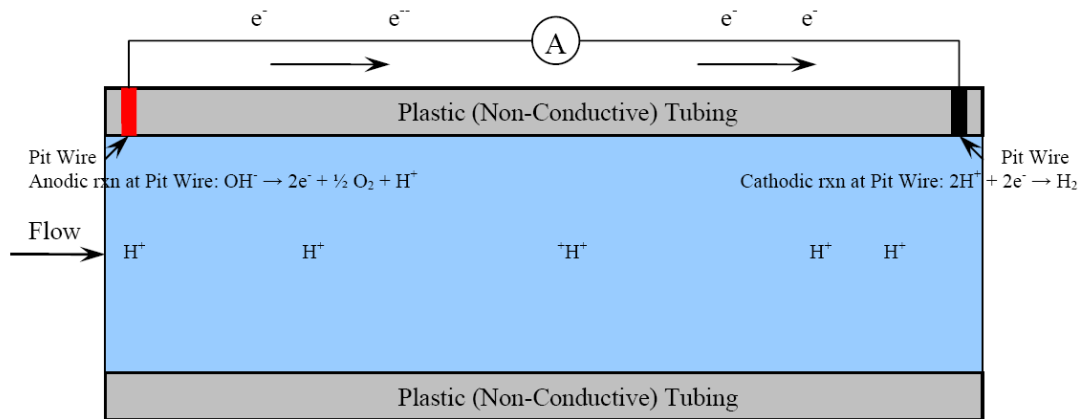


Figure 3-2: Streaming current schematic, section through pipe along flow (no O_2 or Cu)

If the downstream and upstream wires were composed of copper and the water contained dissolved oxygen, the more favorable anodic reaction would involve oxidation of copper and the cathodic reaction would involve the reduction of oxygen resulting in corrosion of the copper (Figure 3-3).

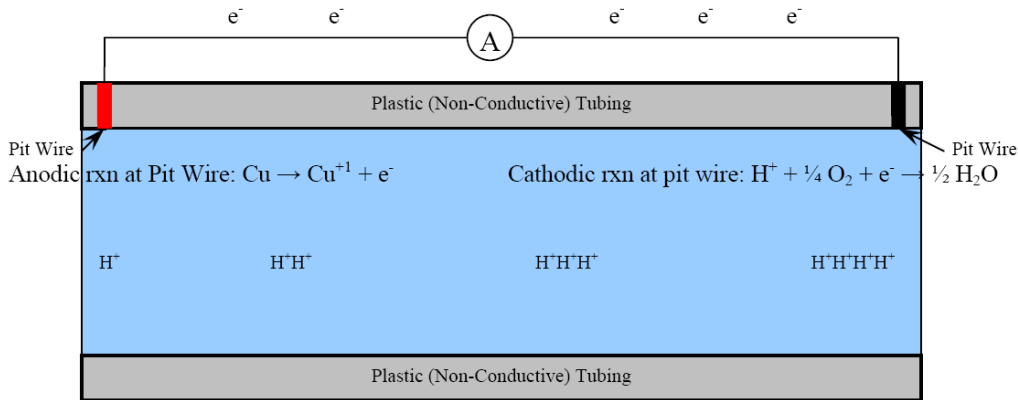


Figure 3-3: Streaming current schematic, section through pipe along flow (w/ O_2 and Cu)

Expanding this thought, if the plastic tube was replaced by a copper tube that has high conductivity, an alternative electron path exists through the metal. In such situations, the portion of the tube that first encounters flow is the site of anodic activity, whereas the downstream section of the tube becomes a site of excess cathodic activity (Figure 3-4).

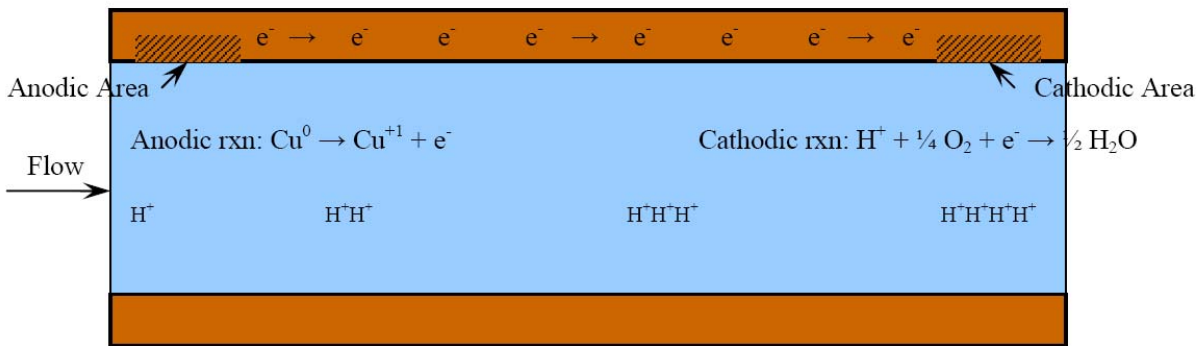


Figure 3-4: Conceptualization of electron flow through copper pipe that has a fixed negative surface charge, net excess streaming current of positive charge, and separation of anode and cathode along the pipe length.

If the direction of flow was reversed, the anodic end of the pipe would become the cathode, and the cathodic end would switch to become the anode. Thus, for a negative surface charge, the portion of pipe to last contact the flowing water would always be the anode. If the surface charge was positive, the excess mobile charges would be negative and the section of pipe that first contacts the flowing water would always be anodic.

Variouly termed electrification, excitability, streaming current and streaming potential in the petroleum industry, Dolezalek was credited with the first explanation of the problem in pipelines (1913). In his studies, Dolezalek measured potential differences of up to 1800 volts when benzene flowed through small diameter tubes and determined which pipe materials were better suited for certain hydrocarbon fluids. His work defined permissible velocity in pipes of different materials, and suggested pipe diameters, fixtures and types of pumps that could be used to reduce the possibility of self ignition of fluid via a spark caused by “electrification.”

Dolezalek also observed that the condition of the inner surface of the pipe greatly influenced electrokinetics. Specifically, a copper pipe lined with cuprous oxide scale increased electrification nearly two-fold versus a new copper pipe. This would be expected, given that different oxides or corrosion scales on pipes can have different fixed charged densities and signs. It was indicated as early as 1924 that metallic copper, cuprous oxide, cupric hydroxide and malachite all have different surface charge behaviors (Bengough and May 1924). Surface charge has also been found to be highly dependent upon pH. In general, at lower pH values, oxides have a positive charge, whereas at higher pH values, they have a negative charge. There is also an intermediate pH at which a given copper scale has a net zero surface charge. At this pH, no electrokinetic effect will occur.

Research over the intervening decades provided more insight into the concept of electrification. Bruninghaus noted that liquid hydrocarbons become electrified by flowing along a metal wall, and performed experiments demonstrating that for a liquid of given conductivity there is an optimum value for the rate of charge that is discharged, and for a given rate of discharge, there is an optimum value of conductivity (1930). Based on multiple experiments of liquid flow through pipes, Nitka recorded the following observations (1941):

- Voltage increased as velocity increased.
- Voltage decreased as diameter increased.
- Small differences of inner surface smoothness were important.
- Voltage was approximately inversely proportional to liquid viscosity.
- Pipe discharge with an outlet spraying into a vessel (as opposed to being submerged in the vessel) greatly increased the magnitude of the voltage.

Further research suggested that higher electrical conductivity was the key to reducing the problem in highly non-conductive aqueous fluids. Moreover, the problem with explosive sparks could be circumvented by grounding discharge pipes, nozzles, and receiving vessels and avoiding a high velocity, spattering, atomizing and local violent disturbances (Nitka 1941). Experimentation by Mackeown and Wouk measured electrical charges generated from the conveyance of gasoline to and from tanker trucks and into automobile fuel tanks (1942). They observed that the current produced was proportional to the rate of flow and that different brands of gasoline produced different levels of voltages per unit pipe length, hypothesizing that the different brands contained differences in certain physical and chemical properties such as detergents and other additives leading to those differences.

Other specific factors effecting electrokinetics in pipe flow include flow characteristics (laminar versus turbulent) (Rutgers et al. 1957) and oxidation properties of the fluid (Luther and Hampel 1957). Keller and Hoelscher (1957) were the first to determine that pipe length was not a factor (except in very short sections not found in practice). Gavis and Koszman further developed these early observations to better explain the applicability of electrokinetics in pipe corrosion.(1961).

In summary, fairly extensive studies have been conducted on the issue of flow electrification in the petroleum industry. The voltages that develop on copper pipe in more conductive flow are generally termed insignificant by these researchers, but this is only relative to the problem of sparking and the thousands of volts generated for non-aqueous solvents. That is, even though potentially catastrophic electrical discharges may not occur, creation of potentials of a few hundred millivolts along a pipe length could induce undesirable non-uniform corrosion.

Practical data has been obtained recently indicating that the portion of copper tubing that first contacts flow can be anodic relative to the downstream area. Specifically, Marshall (2004) recreated pitting conditions in the laboratory, and in her tests, she found that the upstream copper tube formed 8 pinholes in a one foot section, whereas no downstream pipe sections had fully penetrating holes. Likewise, measurements of pipe rigs from a utility in Florida frequently determined that the upstream section became anodic relative to the downstream section (Sheffer 2006). In that experiment, the voltage difference was recorded only around 20 mV, but it was nonetheless a consistent trend. Perhaps not coincidentally, in homes experiencing pitting in that system, the portion of copper that first contacted the flowing water (in front of the home) is most commonly the section that failed. The research that follows was designed to explicitly consider flow electrification as a contributor to copper corrosion in aqueous systems.

METHODS AND MATERIALS

Recirculating Large Scale Pipe Rig

For this test, the Marshall pitting water was placed into a 55 gallon drum and circulated through thirteen 1' long sections of $\frac{3}{4}$ " Type L copper pipe at a velocity of 4.5 fps (Figure 3-5). Chlorine and pH were maintained daily to maintain the target levels of 6.0 mg/L and 9.2 respectively. The individual pipe sections were connected together using copper wires, and the connections were interrupted only when measurements were being collected of current and voltage between the pipes.

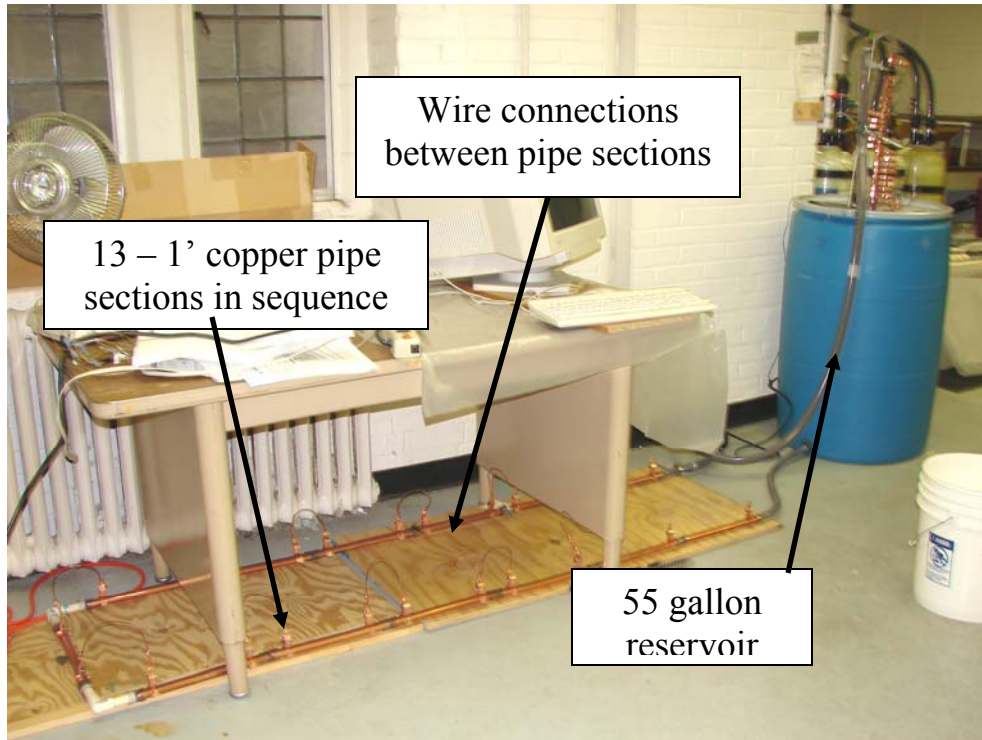


Figure 3-5: Setup of Large Scale Experiment to Test Inhibitors

Study Examining Velocity Effects

This study used a 55 gallon reservoir with water continuously circulated in five separate loops of copper piping (Figure 3-6). The water flowed through a sequence of straight sections of $\frac{3}{4}$ " Type L copper tubing that consisted of one coupon 2" in length followed by three pipe sections each 1' in length. Each section of copper was electrically separated but hydraulically connected with a dielectric made of tygon tubing. All three 1' copper sections on each rig were electrically connected to one another via an 18 gauge insulated copper wire. This connection was interrupted for short periods only to allow electrochemical measurements to be made. Each flow loop operated at a different turbulent flow as determined by Reynolds number calculation (Table 3-1). Pumps were located on the suction end of each loop where the water was then re-circulated back the reservoir.

Table 3-1: Flow Conditions for Each Test Loop

Flow Loop	Velocity (fps)	Reynolds Number	Classification of Flow
1	0.9	6267	Turbulent
2	1.6	11141	Turbulent
3	2.8	19497	Turbulent
4	4.9	34119	Turbulent
5	6.6	45957	Turbulent

The reservoir was kept covered to eliminate photochemical reactions and minimize CO₂ uptake. The Marshall pitting water (high pH, aluminum solids, high Cl₂) was circulated through the system (Marshall 2004). Chlorine and pH levels were maintained at 4.0 mg/L and 9.2 +/- 0.1, respectively, with readjustments made daily. Water was completely changed every two weeks.

Pipe Section with Viewport

An additional pipe with a viewport was temporarily inserted in each loop in the first position exposed to flow (Figure 3-6). Each pipe was constructed from a 1' section of 3/4" copper and 3/4" glass tubing. Each tube was cut in half horizontally. The interior copper surface was manually polished using ultra-fine grit, waterproof sandpaper and then rinsed with deionized water. Each copper half-tube had a matching half piece of glass tubing applied to it in order to visually examine the inside of the pipe as the copper was corroding and/or as scale formation occurred. Each viewable pipe section was covered when not actively viewed, in order to minimize photochemical reactions. Pipes were continuously examined and photographed in order to observe when the first changes in color and scale formation occurred. Electrochemical measurements were recorded periodically throughout the experiment. Once visual observations were completed, this section of tube was removed from the apparatus.

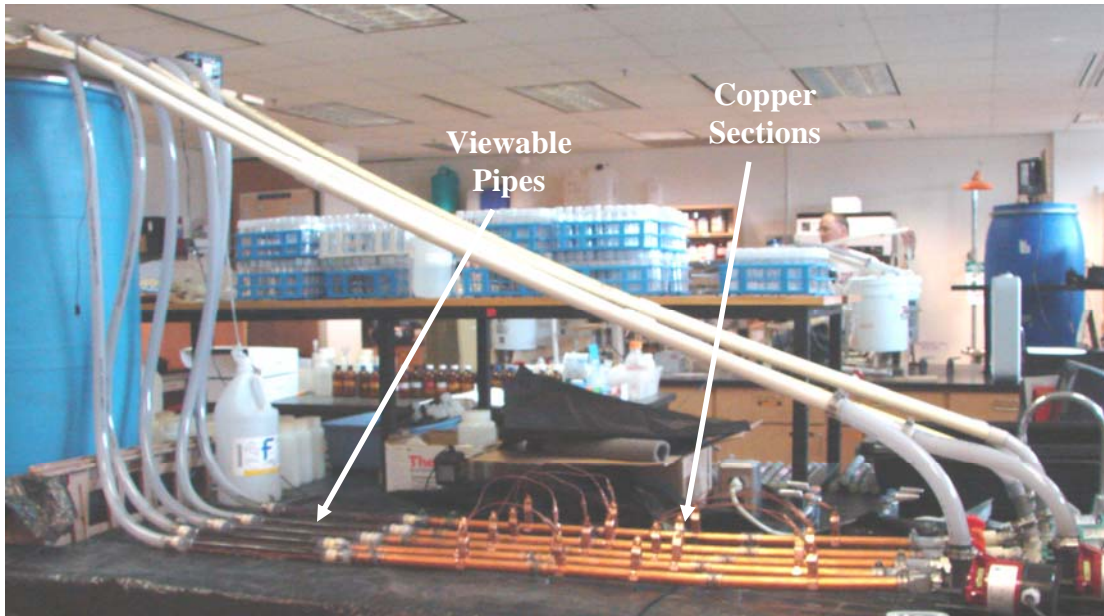


Figure 3-6: Experimental Setup

Short Term Studies on Flow and pH

After the base experiment was completed, flowrates were adjusted in three of the five loops to new values, in order to examine the short term effects of switching flowrates on flow electrification currents (Table 3-2). This test with altered flow was operated for a duration of 20 hours. Electrochemical measurements were collected periodically. Chlorine and pH were maintained at 4.0 mg/L and 9.2 +/- 0.1 respectively through the use of pump that fed a 2% sodium hypochlorite (60,000 mg/L) and a 0.1 M NaOH solution. Upon completion of the short-term test, each flow loop was restored to its original tested flowrate.

Table 3-2: Short Term Flow Changes

Flow Loop	Original Target Velocity (fps)	Short Term Velocity (fps)
1	0.9	2.8
2	1.6	1.6 (not changed)
3	2.8	0.9
4	4.9	6.6
5	6.6	6.6 (not changed)

During the final day of experimentation, the pH was increased to 10.2 for a period of four hours in order to examine short term effects of pH on flow electrification at the different velocities.

Chlorine and pH were maintained at target values of 4.0 mg/L and within 0.1 units of the target pH. Electrochemical measurements were collected for each velocity. This study was repeated at a pH of 11.0.

Evaluating Corrosion: Monitoring and Measurements

Current, Voltage, and Resistance

Corrosion measurements, which included current, voltage and resistance measurements between the pipe sections, were measured with a Fluke189 True RMS Multimeter. Data was collected daily after chlorine and pH parameters were readjusted to their target values. Current measurements were gathered at multiple locations, as specified in later text. When measurements were not being made, the pipes were electrically connected to one another, as would occur in a potable water supply.

Sign convention of the current and voltage values are important to understanding the electron flow between the copper sections. In this work, a positive current indicates that the first pipe (or coupon) in the flow sequence is anodic relative to the last pipe (or coupon). Conversely, a negative current indicates that the last section is anodic relative to the first section.

Corrosion Potential

Corrosion potential measurements were gathered using an Ag-AgCl reference electrode. Electrodes were maintained on a regular basis to ensure consistent and accurate data collection. Using the Fluke Multimeter, E_{Corr} values were obtained for every copper section immediately following the pH and chlorine adjustments.

RESULTS AND DISCUSSION

Recirculating Large Scale Rig

E_{Corr} measurements varied with adjustments made to the water quality (Figure 3-7). In particular, the higher E_{Corr} values occurred when free chlorine and pH were restored to the target value; whereas, the lower measurements occurred when pH and chlorine decreased during exposure. The adjustment of these parameters also increased the flow electrification whereby the

voltage difference observed between the front and the last pipe section jumped from +100 to +300 mV. These results indicate that E_{Corr} values are controlled primarily by the water chemistry, in addition to other factors such as the surface of the pipe, velocity and position in the flow sequence.

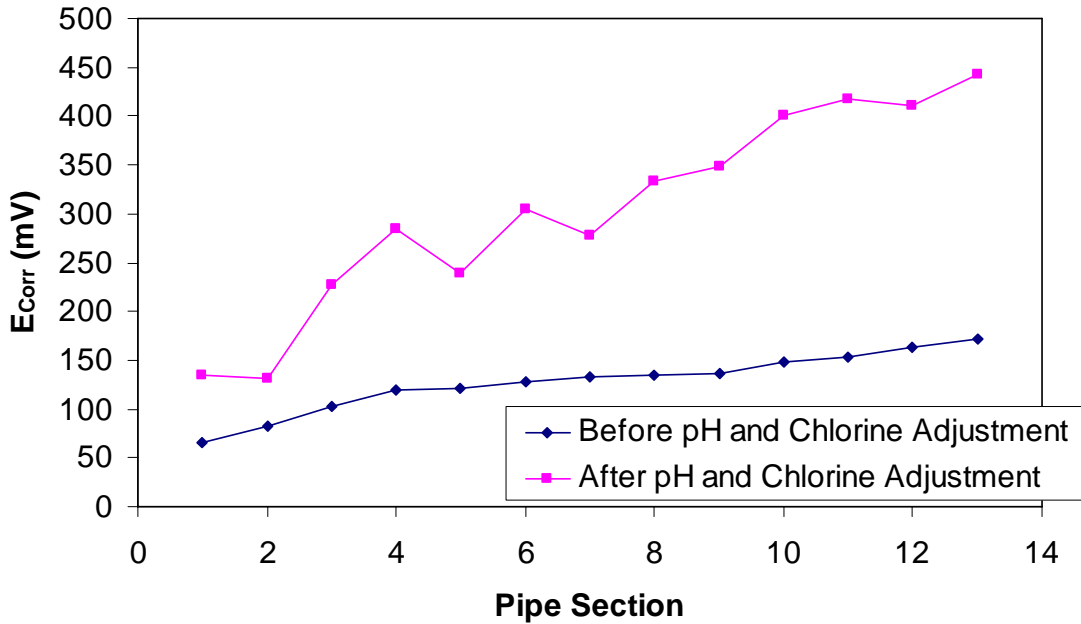


Figure 3-7: Profile of E_{Corr} Measurements before and after the Adjustment of pH and Chlorine

During the initial exposure period, the E_{Corr} of the pipe sections rose progressively from the first to the last (Figure 3-8). That is, the first pipe in the flow sequence tended to be the strongest anode and the pipe last in the sequence tended to be the strongest cathode. During this period, the potential difference between the strongest anode (the copper contacting the flowing water in the loop first) and strongest cathode (the copper contacting the flowing water in the loop last) was at times greater than 1500 mV.

It was concluded that macrogalvanic flow effects were obviously occurring during corrosion in this larger scale apparatus due to flow electrification, which made the front end of copper pipe sections highly anodic relative to the back, despite the fact that each of these copper surfaces were being exposed to essentially the same water at the same flow rate. These effects were not reproduced in the small scale apparatus discussed in Chapter 2. The overall trend is consistent

with the flow electrification phenomenon described in the background section above—this is the first time it has even been reported relative to aqueous corrosion in drinking water. In one control experiment when the pump flow direction was changed and all other factors were kept the same, copper that first contacted the flow became anodic as before, even though this pipe section occupied the position of pipe that was the strongest cathode under reversed flow.

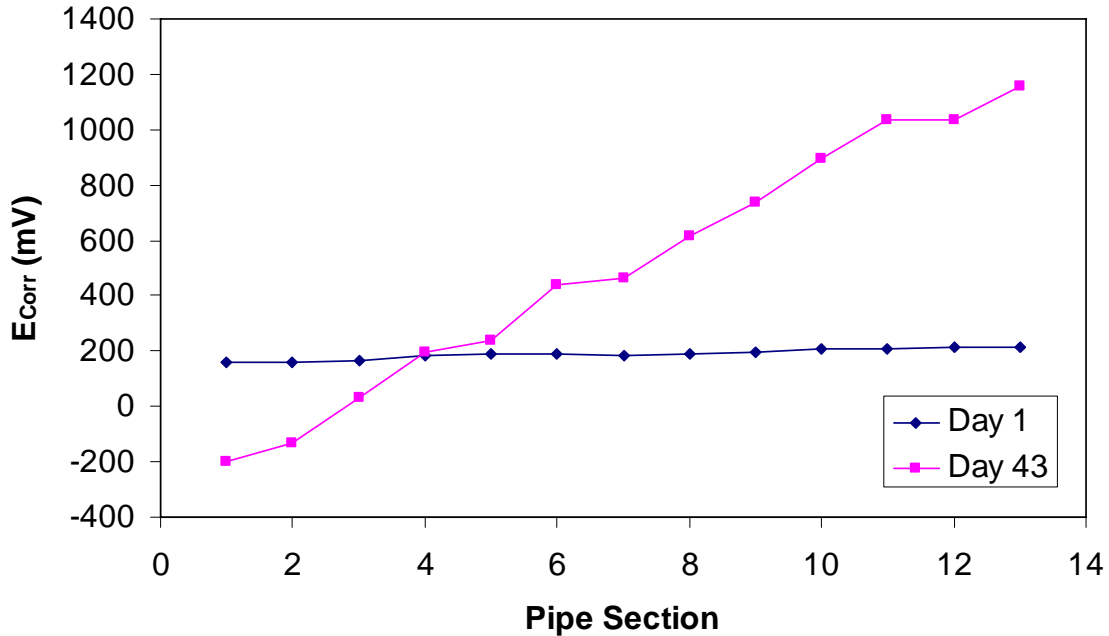


Figure 3-8: Profile of E_{Corr} Measurements on Days 1 and 43

In addition to E_{Corr} values, currents measured between a pit wire and each pipe section provided further evidence of flow electrification. This measurement was conducted for three separate pit wires. The current flowing between the pit wire and each pipe section, rose progressively when measured in succession against the first to the last pipe section (Figure 3-9). Current measured against the pipe last in the sequence produced the highest positive value indicating that the last pipe was acting as the strongest cathode. This result further confirmed that flow effects were occurring making the portion of copper pipe that first contacted flow highly anodic relative to the back. Current data was also collected between the second pipe in the flow series and pipes 3 thru 13 (these pipes were connected with copper wire). Current values on one day reach values above 88 μ A again indicating highly anodic areas in the front pipe sections.

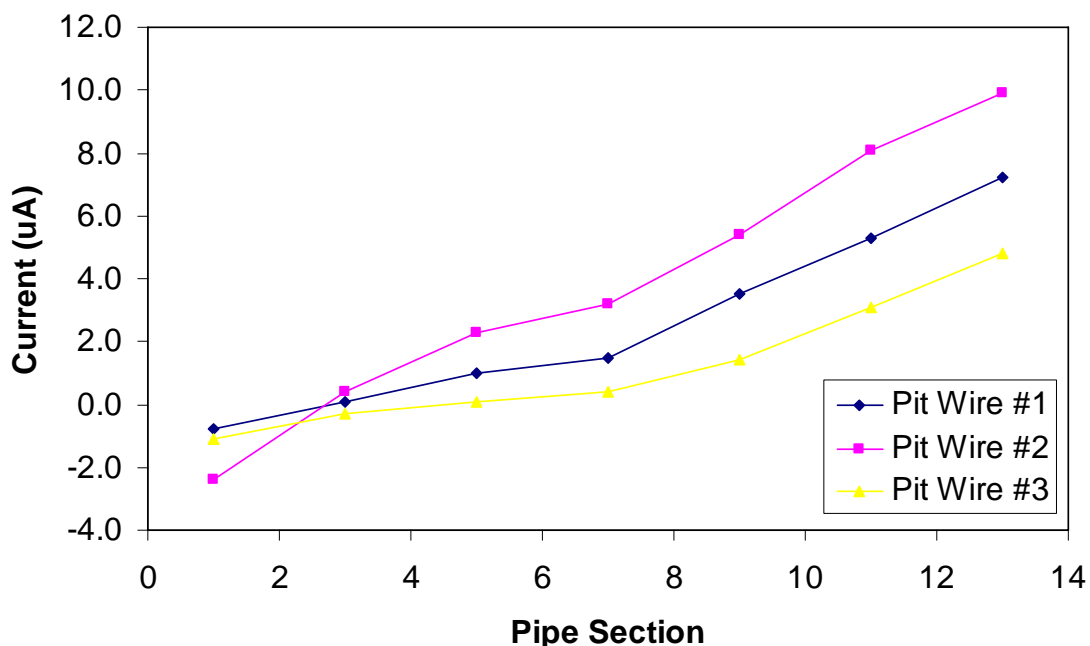


Figure 3-9: Profile of Currents between a Pit Wire and Each Successive Pipe Section

The experiment was then slightly modified in order to test the reproducibility of the phenomenon and to test effects of corrosion inhibitors. Therefore, two identical rigs were setup in the same manner as that described in the materials and methods section, with eleven 1' copper sections in each rig. Both rigs were exposed to the same water for over a month to establish flow electrification.

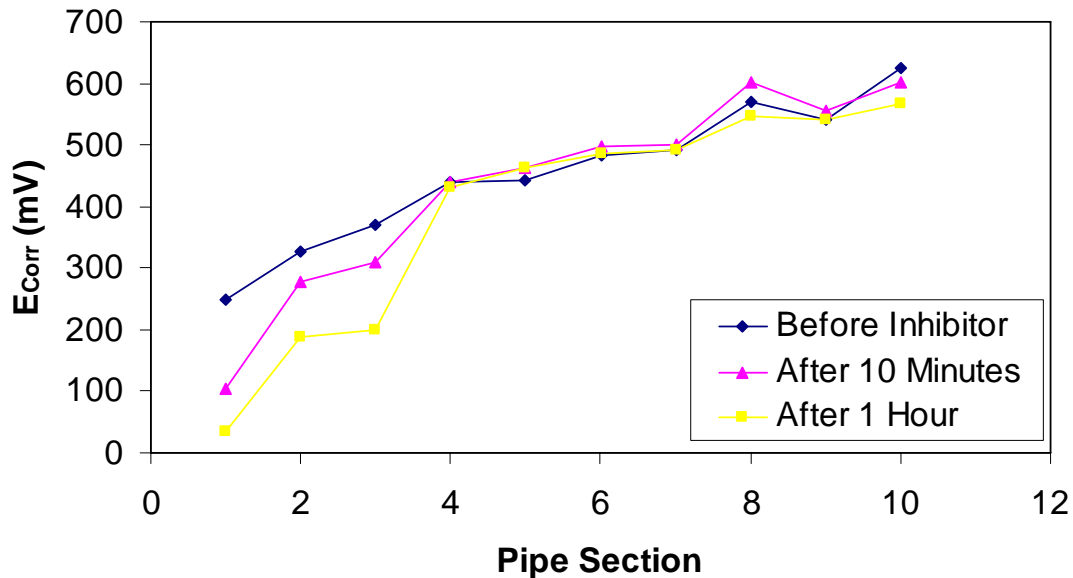
After a period in which behavior of rigs 1 and 2 were quantitatively similar, inhibitors were added to each in a series of steps. Initially, phosphate was added to rig 1 at a concentration of 1.0 mg/L as P, while phosphate and zinc were added to rig 2 at concentrations of 1.0 mg/L as P and 0.5 mg/L Zn^{+2} respectively. The voltage profile of copper pipes for each rig was measured 10 minutes and 1 hour after inhibitor addition. For the case of phosphate, one hour after the addition, the potential of the front three pipe segments dropped significantly (Figure 3-10). Since the first three pipes were effectively anodic relative to the latter section, from this perspective, phosphate was acting at the anode. The overall voltage drop between the first and last segment of copper actually increased by 41.2%. There was very little effect on the potential of the last pipe in the sequence, which was cathodic.

Conversely, one hour after the addition of 1 mg/L phosphate as phosphorous and 0.5 mg/L zinc to rig 2, the potential of the anode was almost unchanged while the potential of the cathode dropped considerably. The net result is that the potential difference between the first and last segment dropped by 42.6%. This demonstrates that the combination of the zinc and phosphate acted to strongly counter the effects of flow electrification.

The concentration of zinc in rig 2 was then increased from 0.5 to 1.0 mg/L. The higher zinc concentration did not significantly reduce the potential between the anode and cathode any further than the change caused by the addition of 0.5 mg/L zinc, implying that the decrease in the potential difference is not directly proportional to the concentration of zinc.

A key conclusion of this large scale testing is that zinc phosphate has unique advantages in controlling non-uniform corrosion in waters of this type. It also explains why the small scale apparatus discussed in Chapter 2, while still providing potentially useful insights to pitting, did not replicate the mechanism of pitting observed by Marshall.

Addition of 1.0 mg/L Phosphate



Addition of 1.0 mg/L Phosphate and 0.5 mg/L Zinc

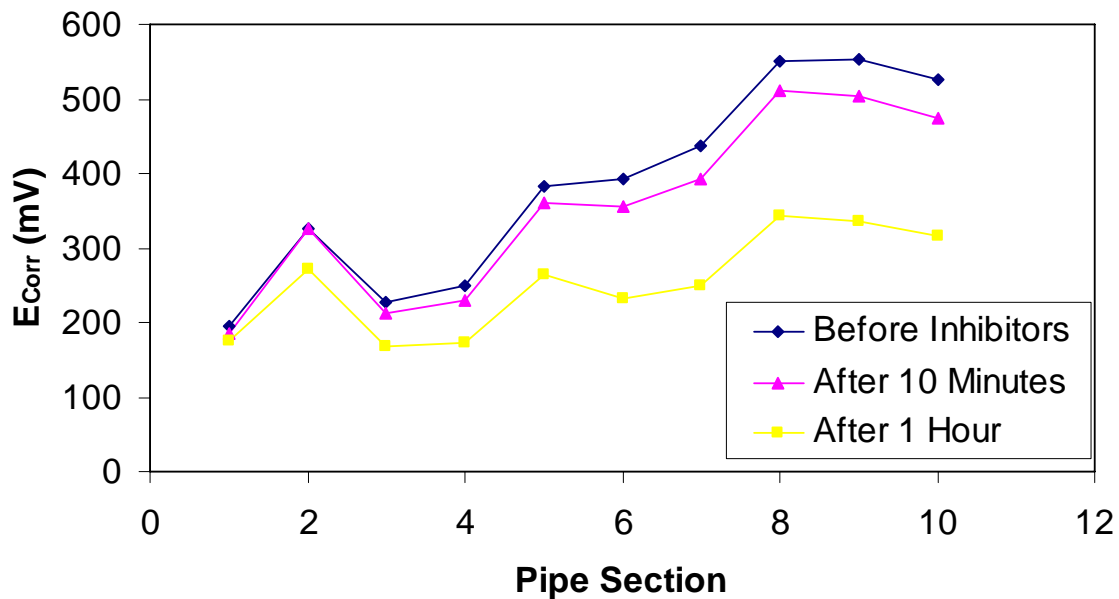


Figure 3-10: Profile of E_{Corr} Measurements before and after the Addition of Inhibitors

The large scale recirculating rig experiments verified the importance of flow through pipes, as a key contributor to non-uniform copper corrosion in this water, and the presence of macrogalvanic effects along a length of pipe that were not reproduced at smaller scale. It was previously shown that flow frequency was an important component to E_{CORR} rise, but this was never interpreted as resulting from flow electrification (i.e. Rushing 2002, Marshall 2004). This revelation led to plans for a new set of experiments in which the effects of system flowrate could be tested.

Effects of Flowrate on Pitting Corrosion and Electrification

Electrification Corrosion Potential

E_{CORR} measurements for the first and last 1' pipe sections generally increased over the testing period for all the flowrates (Figure 3-11). E_{CORR} rise is often considered an indication of pitting. While the data still exhibited a large amount of day-to-day variation, the graphical representation of the E_{CORR} values clearly illustrate the presence of flow electrification in the loops. Specifically, a divergence between the first and the last pipe sections is indicative of a larger flow electrification potential. Interestingly, at lower flows, electrification was higher during the first six days of observations, after which time electrification effects dropped slightly. But at higher flow, electrification steadily increased.

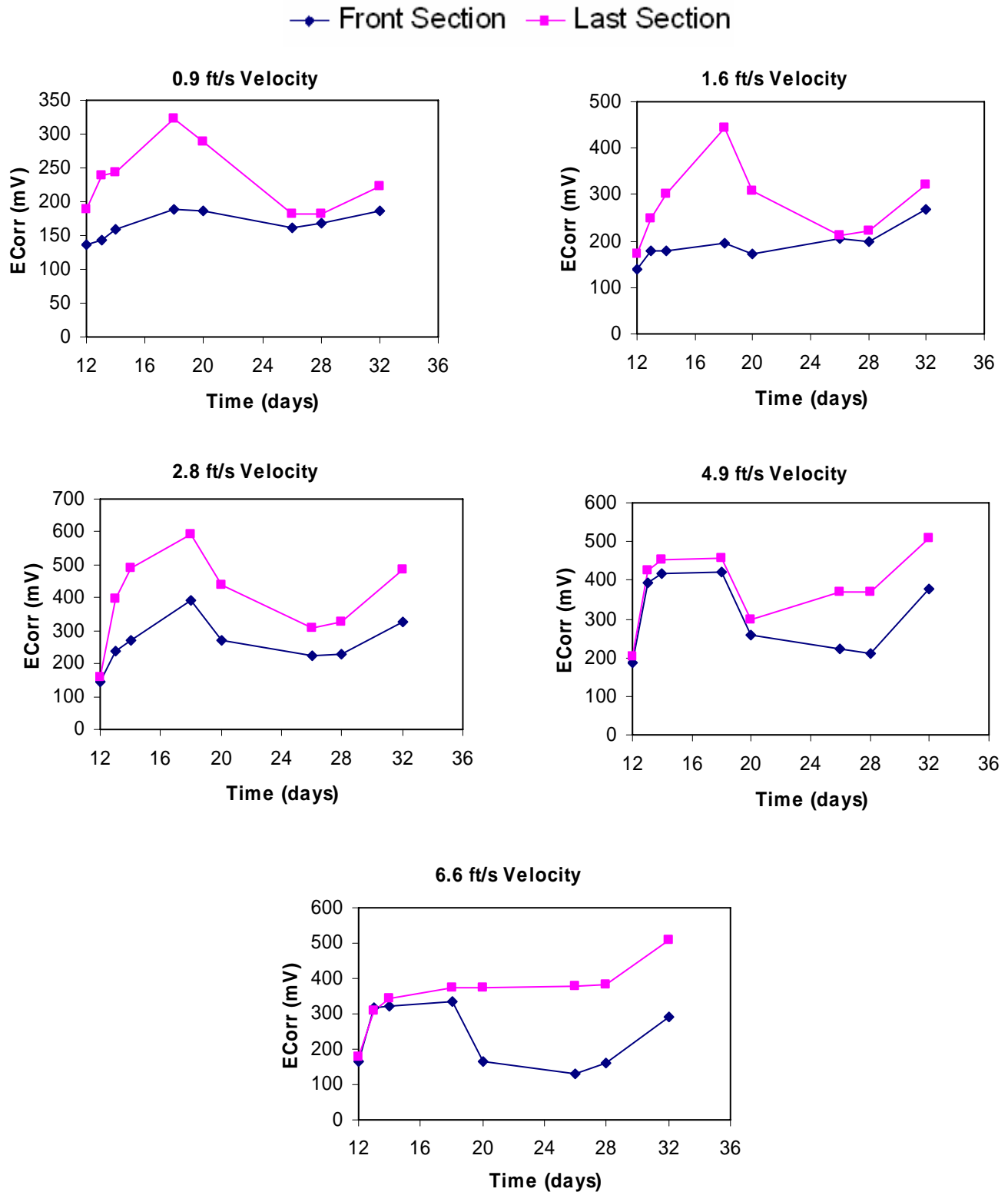


Figure 3-11: E_{Corr} Measurements for the First and Last Pipe Sections for Each Flowrate Water change occurred on day 21.

Electrification Currents

There are many ways to measure currents that flow between the different pipe sections. Each measurement can provide some different insight, relative to the normal situation for copper tube in potable water service that is not broken into sections and which has electrical continuity along its length. Currents measured between the front coupon and all three 1' pipe sections if electrically connected indicated the current flowed to the front of the pipe from the rest of the pipe. The highest electrification current occurred at a velocity of 2.8 fps (Figure 3-12). This implies that an “optimally bad” velocity exists for electrification in this water, since at 2.8 ft/s the largest current was observed, which in turn, correlates to the highest corrosion rate for the front pipe section. It is also noteworthy, that the 2.8 fps and 4.9 fps velocities consistently had larger currents sacrificing the front coupon flowing from the rest of the pipe.

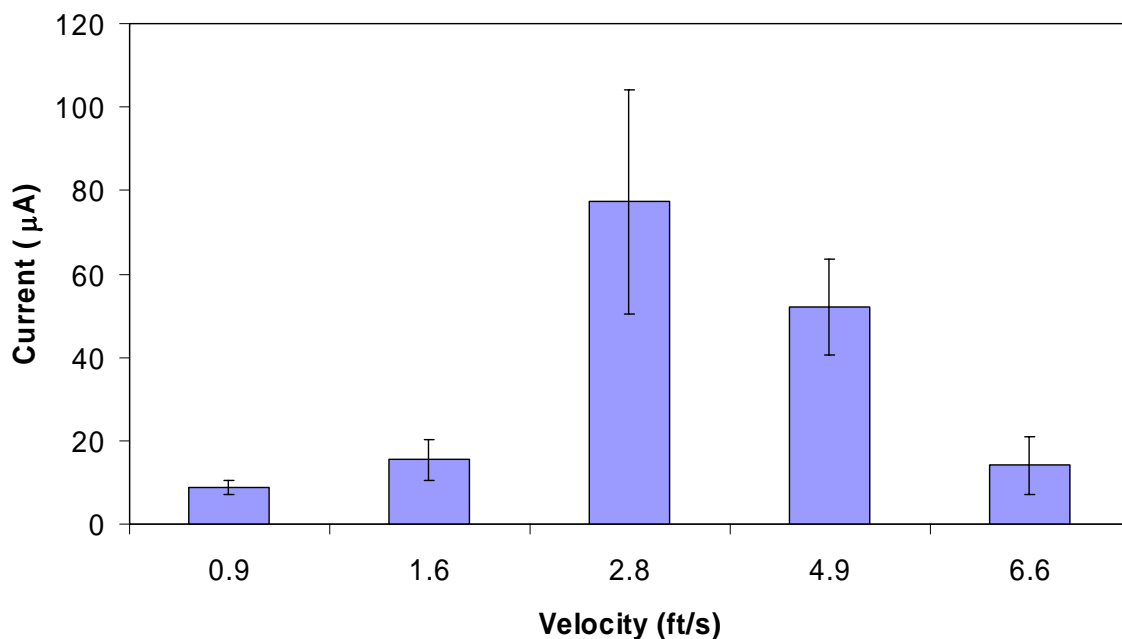


Figure 3-12: Average Currents Measured between the Coupon and Pipes A, B and C Connected

It is useful to consider the trend in Figure 3-12 relative to perplexing results from prior research regarding pitting in the Marshall water. Specifically, in the small scale divided cell experiments completed in Chapter 2, which did not reproduce pits representative of those found in practice, effective velocity was below the 0.9 fps level at which electrification was minimal. The work

by Murray (2006) tested copper pitting corrosion at a velocity of 8 fps in the Marshall water and also did not reproduce one pinhole leak in a test period of 15 months. In Figure 3-4, the expectation is that this very high velocity would give minimal electrification. Interestingly, Marshall (2004) tested copper pitting at a velocity of 2 fps and resulted in 8 pinhole leaks in the first 1' section exposed to flow in just over 11 months, which is closer to the 2.8 fps giving highest electrification in Figure 3-12. Likewise, the prior large scale test in the earlier section of this paper that gave high electrification (up to 1500 mV) was at a velocity of 4.5 fps. The key point is that the trends in Figure 3-12 explain, retrospectively, disparate results in pitting propensity noted for this water. Velocity was never previously believed to exert a primary control over pitting propensity.

Another means of testing current flowing between the pipe sections and the copper coupon that first contacted the flowing water was tested. Rather than connect the coupon to all three pipes at once, the coupon was connected to each pipe individually. The current between the coupon and each individual pipe section was as high as 30 μ A (Figure 3-13). It is interesting to note that the currents between the coupon and pipe A (the pipe immediately following the coupon) was close to that measured between the coupon and all three pipes sections (where pipe A, B and C were connected). This result implies that the rate at which the front of the pipe is sacrificed, is controlled to a large extent by the nearest portion of copper surface. Thus, electrification impacts would probably not be magnified indefinitely by increasing pipe lengths. Even though voltage differences increased between the coupon and increasingly distant pipe sections, solution resistance and other factors probably decrease the current flowing between the coupon and the more distant pipe sections.

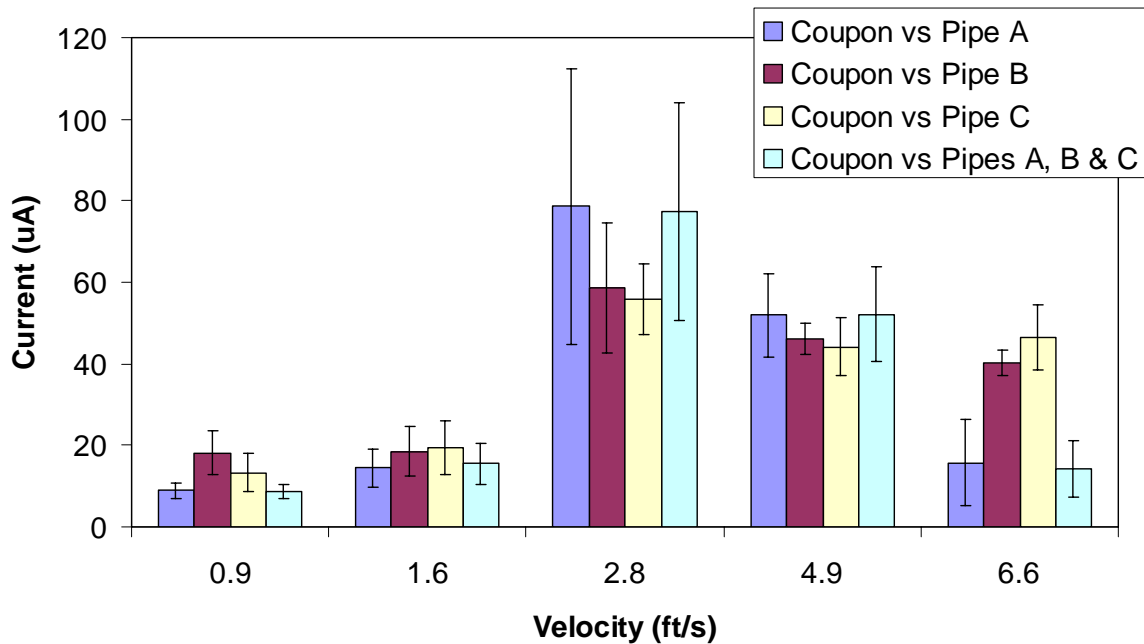


Figure 3-13: Average Currents Measured between the Coupon and Various Pipe Sections

Pipe A is next in the flow sequence after the front coupon, followed by B and C. Coupon vs. A means the front coupon was connected to only section A, for the measurement of the current.

Pipe Section with Viewport

A color change in the pipe scale was clearly observed on the viewable pipe surface. Various plots were constructed in order to determine trends relative to the time it took to achieve a certain amount of discoloration, velocity and electrification. A clear trend was identified between electrification current and the time to the first color change (Figure 3-14). As electrification current increased, the time for the new copper to appear dull was reduced, consistent with the notion that the measured currents were really accelerating corrosion. Photographs of the scale formation on the pipes at various time intervals can be viewed in Appendix A (Figure A-1).

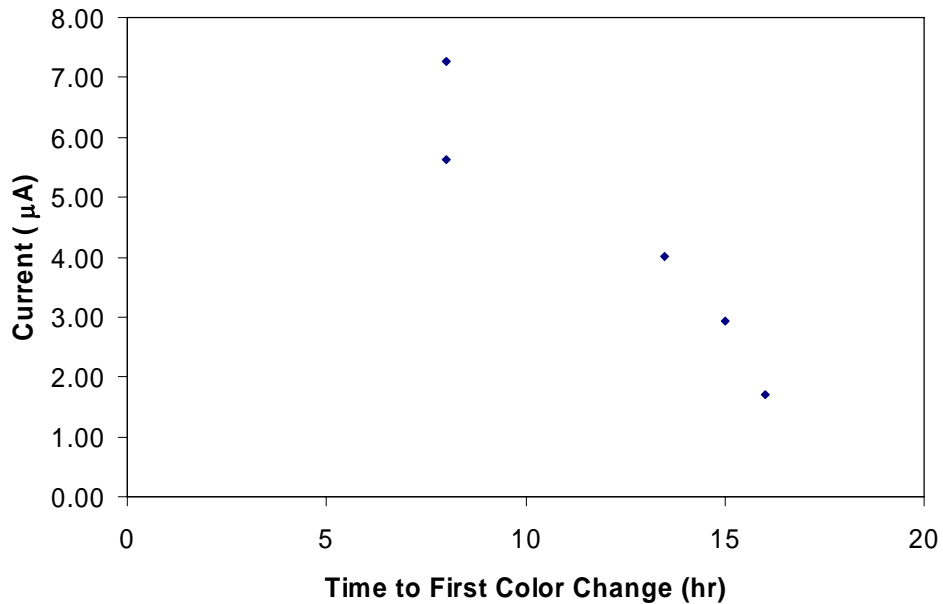


Figure 3-14: Relationship between Current (Measured between Viewable Pipe and Pipe C) and Time to First Observable Color Change in Viewable Pipe Sections

Short Term Velocity Study

It was speculated that the modification in the water velocity would quickly result in changes to the electrochemical measurements and the magnitude of electrification. For instance, when the 0.9 fps velocity was increased to 2.8 fps, it was believed that the current and E_{Corr} values would increase since the largest currents were recorded at a velocity of 2.8 fps. However, the expected changes did not occur for any flow loop that was modified within a period of hours. It may be assumed that the electrochemical measurements and the extent of electrification, both current and E_{Corr} , require a more extended period of time to adjust to the new velocity conditions. Therefore, flow electrification effects probably reflect long term changes in the nature of scale on the pipe wall as a result of velocity and not just factors from velocity alone.

Short Term pH Study

The short term pH study revealed a variety of effects at the different velocities (Figure 3-15 and Figure 3-16). For the two highest velocities tested (2.8 and 4.9 fps), the current and ΔV decreased when the pH was increased. At 2.8 fps, when the pH increased from 9.2 to 10.2, the voltage difference between the first section (coupon) and the last section decreased from +265 to

+97 mV. These results indicate that increasing pH values above 9.2 will reduce flow electrification effects, possibly by altering the surface charge on the scale that lines each pipe.

At the lowest velocity of 0.9 fps, the magnitude of the currents increased as the pH increased, consistent with the trend expected based on the change in E_{Corr} values. Interestingly, the current jumped considerably when the pH was increased from 10.2 to 11.0 at this low velocity.

At the velocity in the middle of these extremes, 1.6 fps, the increase in pH from 9.2 to 10.2 caused elevated measurements of both electrification current and E_{Corr} . However, the pH boost from 10.2 to 11.0 reduced the current to values below those measured at a pH of 9.2. The difference in E_{Corr} values between the first and least section of tubing decreased, indicative of less electrification.

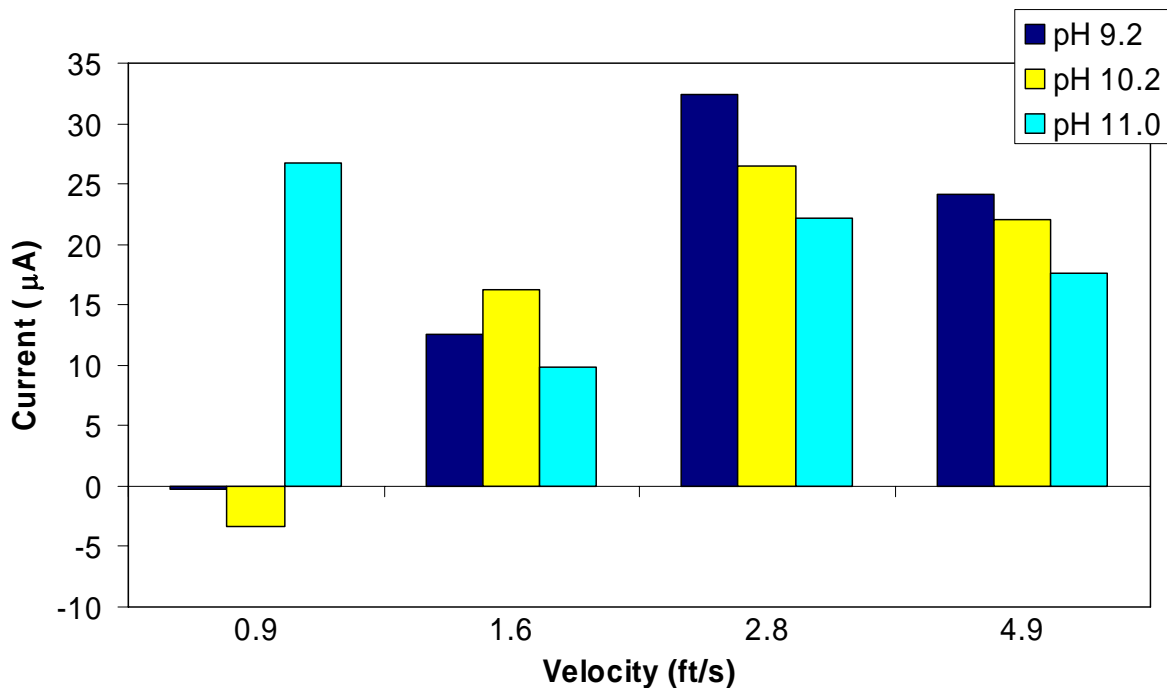


Figure 3-15: Currents Measured between the Coupon and Pipes A, B and C Connected at pH Values of 9.2, 10.2 and 11.0

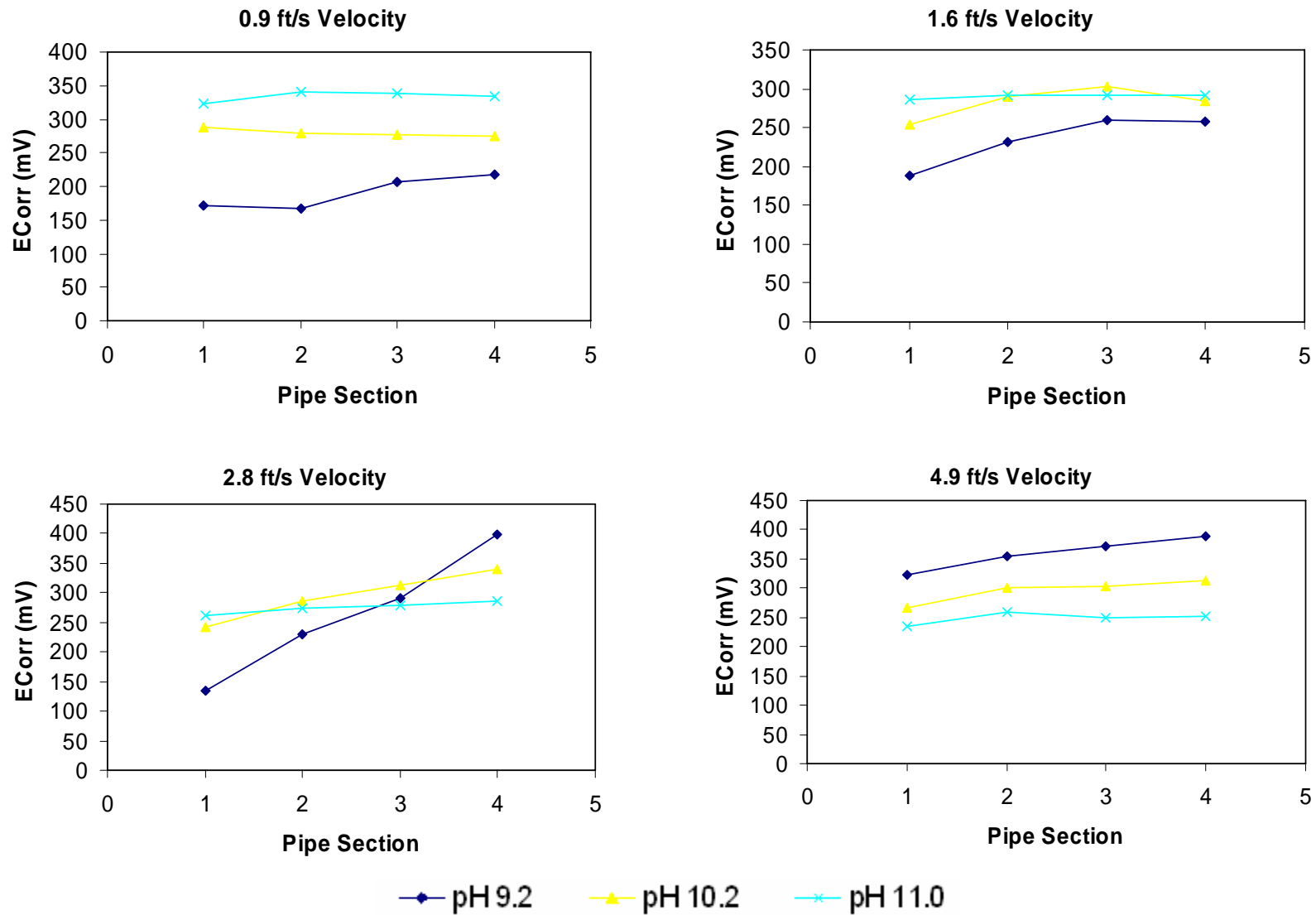


Figure 3-16: E_{Corr} Measurements of Individual Pipe Sections for Different Velocities at pH Values of 9.2, 10.2 and 11.0

Effects of Sulfides on Flow Electrification

An experiment was conducted using a large scale recirculation rig, but substituting sulfide for chlorine as the pitting agent in the Marshall water. The apparatus used a 55 gallon reservoir in which water was continuously circulated through a sequence of five straight sections of copper piping comprised of ½” Type L sections each 1’ in length (Figure 3-17). In addition to the salts in the Marshall water, the water was supplemented with 300 µg/L calcium lactate, 20 µg/L NaH₂PO₄, and 100 µg/L ammonia to eventually support sulfate reducing bacteria. During the time period of experiments reported herein, no sulfate reducing bacteria were inoculated into the system.

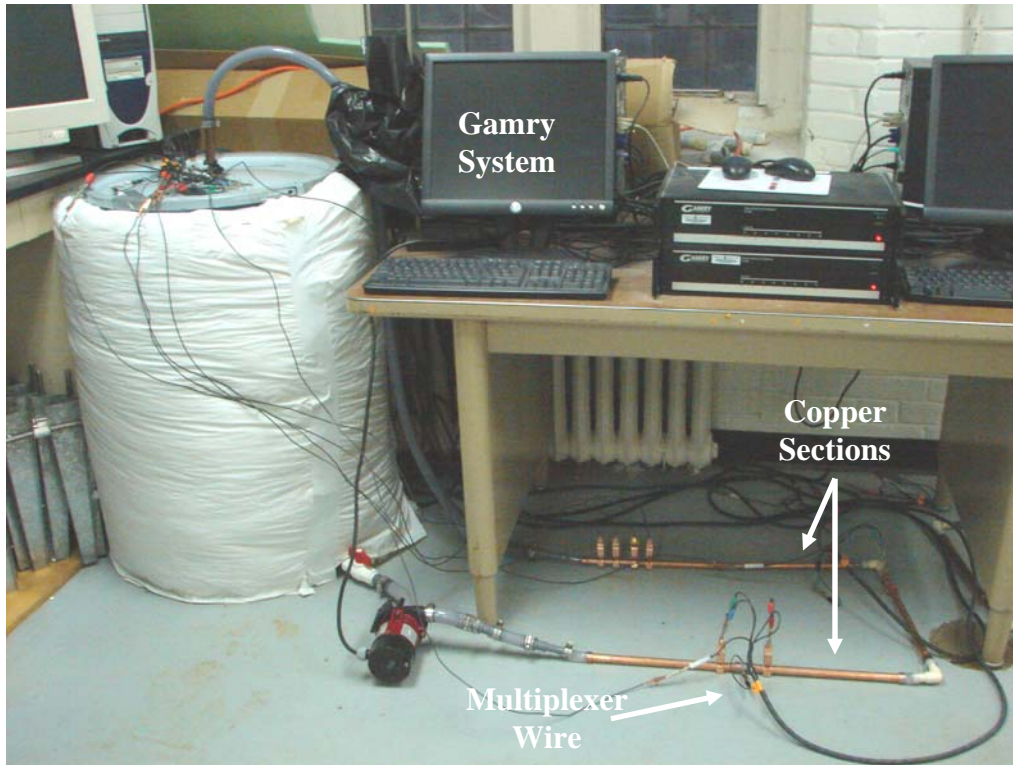


Figure 3-17: Experiment Setup

The experiment was operated for an initial time period of one month. The pH was maintained at 9.2 +/- 0.2. Sulfides of the form Na₂S * 9H₂O were supplied to the water 2-3 times per week. Target levels of the sulfide concentration ranged anywhere between 5 and 15 ppm. Sulfide concentrations were monitored intermittently using spectrophotometric analysis. Complete water changes were conducted every two to three weeks.

Four pit wires were placed in areas of low flow and electrically connected to the largest cathode, in this case, the last 1' section of copper pipe. Pitting wires were made by inserting 18 gage electrical grade bare copper wire into Teflon sleeving (ID = 1/16", OD = 1/8") and sealing both ends with silicone sealant. One end of the pitting wire was placed flush with the sleeving and sanded to a smooth, circular copper surface using a small handheld sanding tool with a 60 grit sanding band. This surface area (1 mm²) represents the pit and was the only portion in direct contact with the water. The pit wires have approximately the same cross sectional area (1 mm²) as real pits found in the distribution system.

Corrosion potential (E_{Corr}), flow electrification current between adjacent pipe sections, and pitting current measurements between the pit wires and pipes, were continuously collected using a Gamry ECM-8 multiplexer in a zero resistance ammeter (ZRA) mode. This type of galvanic corrosion program was operated for the duration of one week. E_{Corr} measurements were gathered using an Ag-AgCl reference electrode. Electrodes were maintained on a regular basis to ensure consistent and accurate data collection. Other aspects of the testing were as before.

E_{Corr} and electrification currents between pipes were highly dependent upon the presence of sulfides (Figure 3-18). When sulfides were added to the system, the E_{Corr} values became increasingly negative. During one testing period, when sulfides were dosed to a concentration of 14.4 ppm, E_{Corr} values recorded a drastic drop to -530 mV. As the sulfides disappeared, the E_{Corr} values steadily increased in the positive direction, to a level more commonly associated with copper in aerated drinking water (0-100 mV). This is the mirror image of results obtained for chlorine.

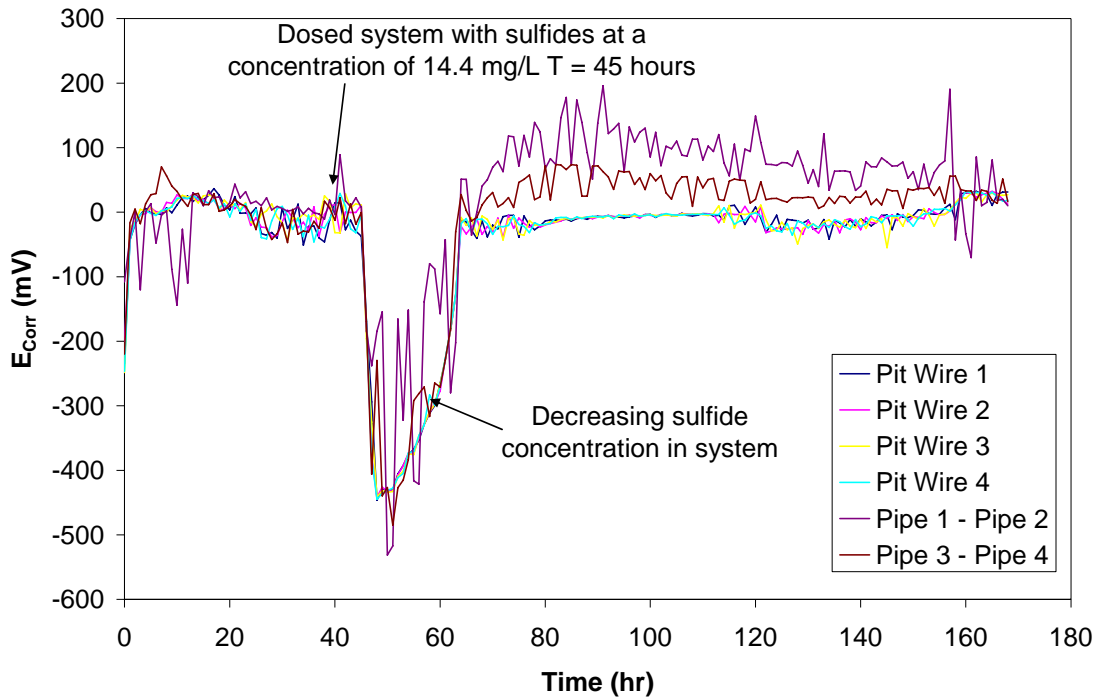


Figure 3-18: Real-time E_{Corr}

The impacts of sulfides on electrification were interesting. When sulfides were present at high levels in water, flow electrification made the portion of copper that first contacted the recirculating flow cathodic relative to later pipe sections (Figure 3-19). As the sulfides decayed, the intensification of the flow electrification lessened, evident from the flatter slopes of the data points at the intermediate sulfide concentrations. At the lowest concentration of 0.6 mg/L, the electrification reversed, whereby the upstream sections of piping became anodic relative to the downstream sections. According to theory presented in the literature review, when the surface charge of the scale lining the copper pipe is negative, the front section of pipe should be anodic, whereas the opposite effect should be observed when the surface charge is positive. Thus, while sulfides reversed the electrification trend, it was in a manner inconsistent with theory, assuming that the sulfide would make the surface negative in charge. Nonetheless, it is clear that the electrification can be reversed dependent on water chemistry, which is consistent with theory.

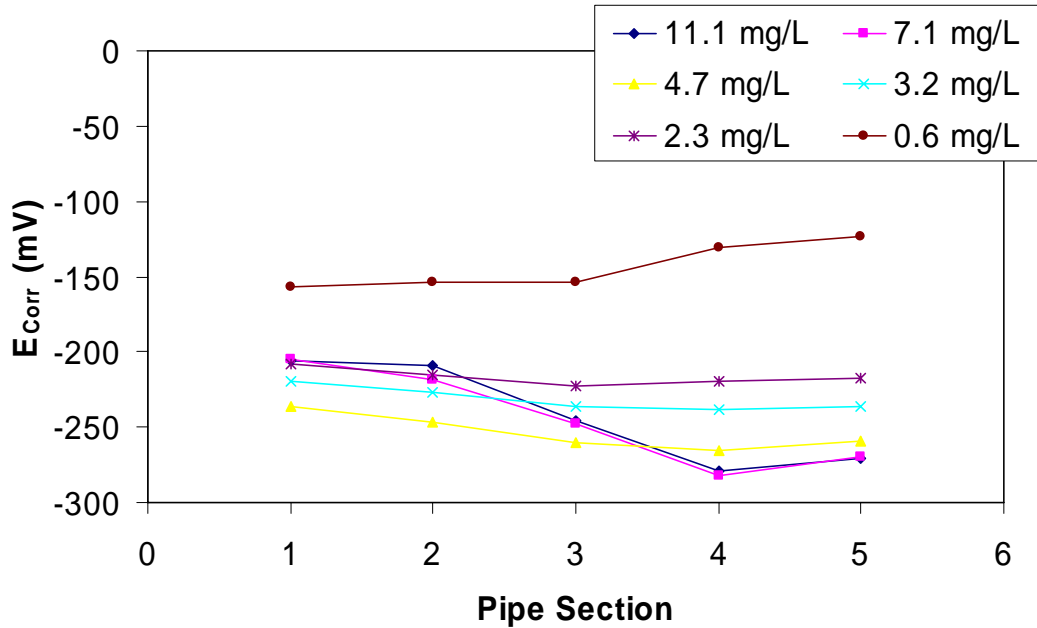


Figure 3-19: E_{Corr} Dependence on Sulfide Concentration

If it is later confirmed that sulfide is a pitting agent, and that pitting propensity worsens with higher sulfide concentration, the application of electrochemical rise as a method used to detect pitting corrosion cannot be accurate in all cases. Clearly, higher sulfides caused a drop in E_{corr} in this set of experiments. We speculate that the waters with high pitting propensity, for which E_{corr} rise method of tracking pitting was established, were a subset which always contained free chlorine. In other words, it might very well be that rising E_{corr} was correlated with the onset of pitting in those waters, but based on this result, E_{corr} rise is cannot be a universally indicator of pitting. It may eventually be proven that E_{Corr} drop is a better indicator of pitting in systems with sulfides. Sulfides also had impacts contrary to chlorine in terms of electrification. These trends deserve additional research.

CONCLUSIONS

- This is the first work to demonstrate that flow electrification is an important phenomenon in water distribution systems. One experiment produced a voltage difference between the front and the back sections of copper tubing at greater than 1500 mV, which sacrificed the front section of copper tube.

- Flow electrification currents were worst at about 2.8 fps, relative to either lower or higher velocities tested.
- Visual analysis of scale formation exhibited a clear trend between electrification current, and the time to the first observable tarnishing of the copper surface. Higher electrification currents indicated higher corrosion rates, which in turn, produced more rapid tarnishing and overall corrosion in the first coupons to contact the water.
- A short term change in velocity did not alter the effects of electrification after several weeks of exposure. This indicates that there is a short-term element to electrification due to fluid moving past a charged surface, but also a longer term element likely due to the type of scale formed on each pipe as a function of time.
- As pH was increased from 9.2 to 11.0, flow electrification current and E_{Corr} were reduced at the higher velocities (2.8 and 4.9 fps). The opposite effect was observed at the lowest velocity of 0.9 fps, where increasing pH increased the electrification current and E_{Corr} measurements.
- The presence of sulfides in a recirculating copper system made the portion of pipe that first contacts flow cathodic relative to later sections. When sulfides were absent, E_{Corr} measurements ranged anywhere between 0-100 mV, consistent with copper pipe corroding in the presence of oxygen. Flow electrification effects were highest when sulfide concentration was highest.

REFERENCES

Bengough, M. A. and R. May (1924). "Seventh Report to the Corrosion Research Committee of the Institute of Metals." Journal of the Institute of Metals **32**: 82-269.

Bruninghaus, L. (1930). "Electrification and Electrical Conductivity of Liquid Hydrocarbons." Journal de Physique et le Radium **7**: 11.

Dolezalek, F. (1913). "The Electrical Excitability of Liquids." Die Chemische Industrie **36**: 33-38.

Gavis, J. and I. Koszman (1961). "Development of Charge in Low Conductivity Liquids Flowing Past Surfaces: A Theory of the Phenomenon in Tubes." Journal of Colloid Science **16**: 375-391.

Keller, H. N. and H. E. Hoelscher (1957). "Development of Static Charges in a Non-Conductive System." Journal of Industrial and Engineering Chemistry **49**: 1433-1438.

Mackeown, S. S. and V. Wouk (1942). "Electrical Charges Produced by Flowing Gasoline." Journal of Industrial and Engineering Chemistry **34**: 659-664.

Marshall, B. J. (2004). Initiation, Propagation, and Mitigation of Aluminum and Chlorine Induced Pitting Corrosion. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.

Murray-Ramos, N. A. (2006). Examining Aspects of Copper and Brass Corrosion in Drinking Water. Environmental Engineering. Blacksburg, Virginia. Virginia Polytechnic Institute and State University. **Master of Science**.

Nguyen, C. K. (2005). Interactions between Copper and Chlorine Disinfectants: Chlorine Decay, Chloramine Decay and Copper Pitting. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.

Nguyen, C. K. and M. Edwards. "A Novel Method of Tracking Copper Pitting." Proceedings of the 2006 AWWA Annual Conference. San Antonio, Texas. June 2006.

Nitka, H. (1941). "The Origin, Removal and Danger of Electrostatic Charges." Chemische Fabrik **14**: 211-214.

Rutgers, A. J., M. de Smit, et al. (1957). "Influence of Turbulence Upon Electrokinetics Phenomena." Transactions of the Faraday Society **53**: 393-396.

Rushing, J. C. (2002). Advancing the Understanding of Water Distribution System Corrosion: Effects of Chlorine and Aluminum on Copper Pitting, Temperature Gradients on Copper Corrosion, and Silica on Iron Release. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.

Sheffer, G. J. A. (2006). Investigation of Copper Pitting Propensity Using Bench and Field Scale Testing. Environmental Engineering. Blacksburg, Virginia. Virginia Polytechnic Institute and State University. **Master of Science**.

CHAPTER 4: LABORATORY AND FIELD STUDIES EXAMINING THE EFFECTS OF INHIBITORS ON ASPECTS OF NON-UNIFORM PITTING CORROSION

Rebecca Lattyak, Marc Edwards and Paolo Scardina

ABSTRACT

The presence of a phosphate or zinc-phosphate corrosion inhibitor could markedly reduce flow electrification and non-uniform corrosion. Moreover, systems with an inhibitor had reduced chlorine decay rates, less weight loss, fewer pits per unit area and lower pit depths. Out of the five inhibitor combinations tested, zinc orthophosphate provided the best performance, regardless of whether the pits had been initiated or pipe was new. Flow electrification was reduced more than 90% and average weight loss was reduced more than 98% when zinc orthophosphate was used in new copper systems compared to a new system devoid of an inhibitor. Also, the zinc orthophosphate managed to slow if not completely hinder the corrosion process in a system pre-exposed to aggressive corrosion conditions. The inhibitors must be continually dosed into the system in order to maintain safe conditions, and if dosing was stopped, non-uniform corrosion tendencies rapidly returned. In particular, systems pre-treated with zinc phosphate were very prone to aggressive attack if the inhibitor was stopped. Indeed, though zinc phosphate gave the best result as long as the inhibitor was present, it gave the worst result if the inhibitor dosing was later stopped.

Practical data from one water utility provided evidence of a confirmed case of non-uniform corrosion where pitting increased as the zinc concentration in the water decreased. Additional field studies at three water utilities identified that the first coupon in a flow sequence was more heavily corroded than the later coupons exposed to flow. These results indicated that flow electrification is an important contributor to pitting corrosion in some circumstances.

INTRODUCTION

Prior work at lab scale using synthesized water established that flow electrification could be a primary control on non-uniform copper corrosion. Moreover, inhibitors could profoundly impact electrification over short time-periods. One goal of this work was to determine the effect of inhibitors on electrochemical measures of non-uniform copper pitting corrosion, and

unambiguous measures of pitting such as pits per unit surface and pit depth. Throughout this discussion, reference will be made to current densities relative to predicted times to failure for copper tubing. For example, a corrosion rate of 1 $\mu\text{A}/\text{cm}^2$ can completely consume the thickness of a Type M pipe in 60 years (Table 4-1).

Table 4-1: Classification of Corrosion Rates

Current Density ($\mu\text{A}/\text{cm}^2$)	Predicted Failure Rate (Years)	Classification of corrosion rate
$i < 0.1$	$t > 60$	Low
$0.1 < i < 1$	$6 < t < 60$	Medium
$i > 1$	$t < 6$	High

Inhibitors were selected based on their use in practice and suspected likelihood of mitigating copper pitting corrosion. Inhibitors included phosphate, zinc, zinc orthophosphate, and NOM. An extensive review of each can be found in Chapter 1. For this study, two forms of phosphates were tested: polyphosphate and orthophosphate. Although polyphosphate is a blend of orthophosphate and polyphosphate, polyphosphate inhibitors have a greater ability to disperse particles and complex metals than does a comparable does of orthophosphate, and they possibly have a lower likelihood of forming copper phosphate solids on pipes. Both inhibitors are commonly used in practice.

The second objective of this study was to examine pitting propensity from water produced at two water utilities operated by the Washington Suburban Sanitary Commission (WSSC) in Maryland in field tests. The Patuxent and Potomac Water Treatment Plants are conventional treatment plants which use different surface water sources. At both treatment plants, the water is first disinfected with potassium permanganate and then coagulated and flocculated using polyaluminum chloride (PACl). Once the water has settled, it passes through dual media filters consisting of sand and granular activated carbon (GAC). The target effluent pH of 7.5 is achieved through the addition of lime. Free chlorine is used as a secondary disinfectant with a target chlorine concentration is 2.0 and 1.5 mg/L Cl_2 at the Potomac and Patuxent utilities, respectively. Finally, before discharge into the distribution system, fluoride and orthophosphate are currently added to the water. Total average water production is 140 MGD at the Potomac

plant and 50-60 MGD at the Patuxent plant, collectively serving approximately 1.6 million people.

Beginning in 1998, customers served by the WSSC began experiencing an outbreak of pinhole or pitting leaks in copper pipes. At the time, polyaluminum chloride, alum or ferric chloride was used as a coagulant depending on the season. Research conducted by Virginia Tech in 2003 determined that dosing orthophosphate might alleviate copper pitting (Marshall 2004). Beginning in 2003, both utilities began adding orthophosphate to the water, and the reported pitting problems decreased soon thereafter (Nguyen 2005).

Specifically in this case study, experiments were erected in order to investigate the effects of chlorination, chloramination and enhanced coagulation on the pitting propensity. These conditions were chosen since they are potential methods to comply with the Stage 1 and Stage 2 Disinfectants/Disinfection By-Product (D/DBP) Rules. In addition, the effectiveness of orthophosphate as a corrosion inhibitor to decrease the pitting propensity was considered for each scenario tested. Pitting propensity was evaluated using a variety of analytical methods including copper pipe coupon testing, chlorine decay kinetics, and electrochemical measurements.

METHODS AND MATERIALS

Laboratory Inhibitor Study

This study used seven 100 L reservoirs with water continuously circulated in a sequence of straight sections of Type L copper tubing at 1.85 gpm (velocity of 1.2 and 2.5 fps in $\frac{3}{4}$ " and $\frac{1}{2}$ ", respectively). In each loop, water flowed through a sequence of six copper coupons. The first three were $\frac{3}{4}$ " coupons followed by three $\frac{1}{2}$ " coupons each 2" in length (Figure 4-1). Each section of copper was electrically separated but hydraulically connected with a dielectric made of tygon tubing.

The reservoirs were kept covered to eliminate photochemical reactions and minimize CO₂ uptake. The Marshall pitting water (high pH, aluminum solids, high Cl₂) was circulated through the system (Marshall 2004). Chlorine and pH levels were maintained at 4.0 mg/L and 9.2 +/-

0.1, respectively, with readjustments made daily. Water was completely changed every two weeks. The experiment was separated into two phases described below.

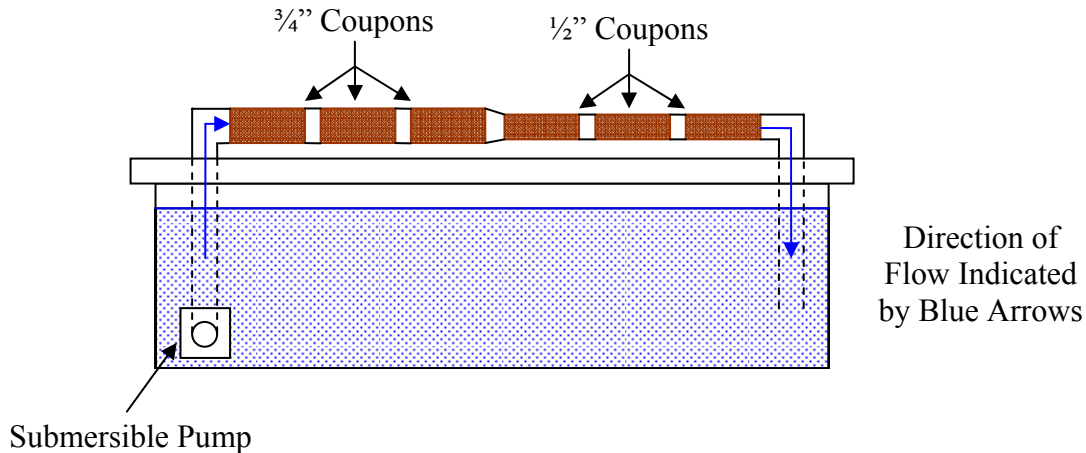


Figure 4-1: Schematic of Experimental Setup

Phase I Testing

The first phase of this experiment tested the effects of five different inhibitors relative to a control without inhibitor. The conditions selected for evaluation were tested for a total of 45 days (Table 4-2). Ion chromatography testing of the standard solution revealed that the fraction of orthophosphate in the polyphosphate used for this experiment was 0.34.

Table 4-2: Phase I Experimental Conditions for Each Container

Container	Condition Tested
1	Control 1 (No Inhibitor)
2	1.0 mg/L Polyphosphate as P (from Sodium Hexametaphosphate)
3	1.0 mg/L Orthophosphate as P (from NaH ₂ PO ₄)
4	1.0 mg/L Zinc (from ZnCl ₂)
5	0.5 mg/L Zinc (from ZnCl ₂)
6	1.0 mg/L Orthophosphate as P (from NaH ₂ PO ₄)
7	Control 2 (No Inhibitor)

The control was run in duplicate. The second control was identical to the first control except that all six coupons were 3/4" instead of containing a combination of 3/4" and 1/2" coupons. Since both

controls produced nearly identical results throughout the entire study, the data for the second control will not be presented in detail in this report.

Total chlorine concentrations were recorded daily to determine chlorine decay kinetics. Inhibitors were dosed immediately after water changes and then again one week later. Therefore, actual levels of inhibitors may have been up to twice the amounts listed in Table 4-2.

Phase II Testing

Phase II testing was to determine the effects, if any, of stopping inhibitor dosing, relative to electrification and non-uniform copper corrosion. Additionally, based on the results from Phase I, the inhibitor that prevented pitting corrosion most efficiently based on weight loss, chlorine decay and electrochemical measurements was introduced into the control, which had not been previously exposed to any inhibitor. The goal was to determine whether this inhibitor could stop non-uniform corrosion once it was well underway. Aluminum solids were no longer added to any of the containers for the duration of the experiment. All other conditions were kept identical to those in Phase I, including pH and chlorine levels. Phase II was operated for a total of 90 days.

Current, Voltage, and Resistance

Corrosion measurements, which included current, voltage and resistance, were measured with a Fluke189 True RMS Multimeter. Data was collected daily after chlorine and pH parameters were re-adjusted to their target values. The measurements were collected between the first and last coupon.

Sign convention of the current and voltage values are important to understanding the electron flow between the copper sections. In this work, a positive current indicates that the first pipe (or coupon) in the flow sequence is anodic relative to the last pipe (or coupon). Conversely, a negative current indicates that the last section is anodic relative to the first section.

Corrosion Potential

Corrosion potential was measured relative to an Ag-AgCl reference electrode. Electrodes were maintained on a regular basis to ensure consistent and accurate data collection. Using the Fluke Multimeter, E_{Corr} values were obtained for every copper section immediately following the pH and chlorine adjustments.

Analysis of Copper Coupons

Precise weight and length measurements were gathered prior to the experiment for each copper section used in both studies. For the inhibitor study, coupons were briefly removed from the containers and photographed periodically in order to visually examine the corrosion and scale formation. After 45 days of experimentation, the first and last coupons were permanently removed from containers 1 through 6 and destructively tested.

Once each experiment was terminated, each copper section was allowed to dry and then weighed to determine any preliminary weight loss, as well as to quantify the weight of scale formed. Sections were measured before and after mechanical cleaning which was completed with the use of a handheld Dremel tool with 428 carbon and 530 stainless steel brushes. In some cases for the inhibitor study, scale was captured and analyzed using electron dispersive spectroscopy (EDS) to determine the elemental composition. Once weight loss analysis was completed, coupons were cut in half lengthwise in order to measure pit depth and density, if applicable. The visible depressions per unit area, or pit density, were determined macroscopically using the naked eye. Pit depths were calculated from the following equation:

$$\text{Pit Depth} = \text{Initial Wall Thickness} - \text{Remaining Wall Thickness}$$

Remaining wall thicknesses were measured using a point micrometer. The depths of pits were determined by measuring the wall thickness at those points, and subtracting from the normal wall thickness. The estimated detection limit for pit depth with this method was 0.05 mm.

Case Studies at Florida and Maryland Utilities

These studies used 55 gallon reservoirs with water continuously circulated in a loop of copper piping at 2 gpm (Figure 4-2**Error! Reference source not found.**). Water flowed in a sequence, first through four $\frac{3}{4}$ " soft Type L copper coupons 2" in length, then through 3' of $\frac{3}{4}$ " soft Type L soft copper pipe (bent), and finally through a 3' section of $\frac{3}{4}$ " soft Type L. The two 3' sections of copper pipe were electrically separated by a plastic 90° bend and were electrically connected to one another with 18 gauge copper wire. Finished water (post filtration prior to secondary disinfection) was taken from each treatment plant and then adjusted to pre-selected target conditions.

Electrochemical measurements were collected using a Gamry ECM-8 multiplexer in a zero resistance ammeter mode for the duration of the test periods. Coupons were weighed both before and after the experiment to quantify any initial scale formation and/or weight loss due to corrosion.

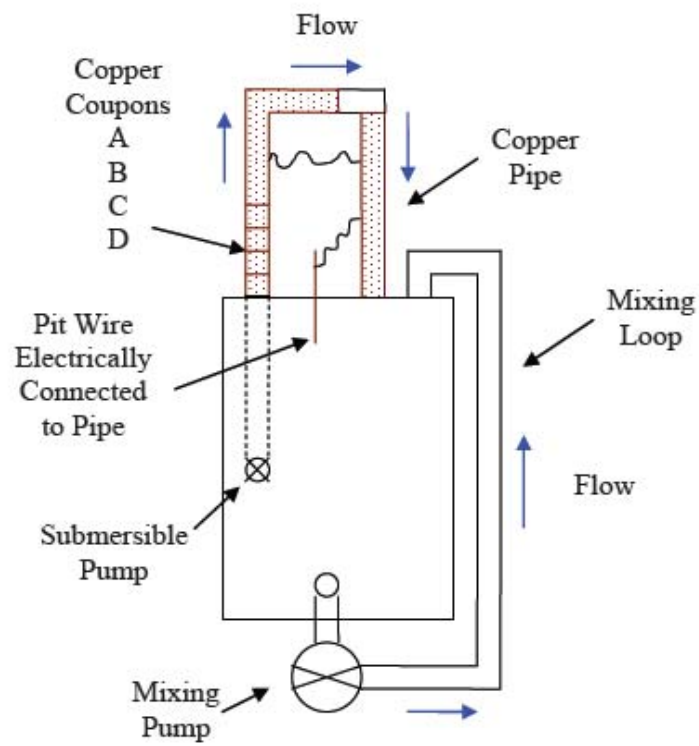


Figure 4-2: Experimental Setup and Pit Wire (Top Right)

RESULTS AND DISCUSSION

Effects of Inhibitors on Pitting Corrosion and Electrification: Phase I Testing

Current, Voltage, and Resistance

Strong electrification currents were quickly established in the control system, confirming that the apparatus reproduced the flow electrification observed in the large scale rig (Figure 4-3). The pipes exposed to the control water had the highest average currents, with values reaching 7.6 μA flowing from the front section to the back sections. All five inhibitors decreased the average current compared to the control, but some inhibitors were much more effective than others. Overall, the zinc orthophosphate inhibitor maintained the lowest current values (independent of sign) with a reduction of over 97% when compared to the average electrification current for the control. Interestingly, both phosphate compounds, polyphosphate and orthophosphate, reversed the effect of electrification, in that the front of the pipe became slightly cathodic relative to the latter pipe sections. While the presence of zinc lowered the current below values recorded in the control, the measurements were still relatively high, reaching values above 3.00 μA . Although zinc is supposed to be a cathodic inhibitor in which case no concentration is expected to intensify the corrosion, the results of this study clearly show that zinc, by itself, plays little role in reducing flow electrification effects.

Trends in average ΔV measurements between the first and last coupons followed expected trends for electrification currents in all six containers (Figure 4-4). The control easily exhibited the highest average voltage value at 333 mV and peaked at a value slightly above 550 mV. While voltages equal or greater to 500 mV were reported in other experiments herein, the 333 mV accumulated over only twelve inches of copper pipe length, and a larger voltage difference would be expected if there were more sections of tube and of greater length. Reductions in voltage of over 50% were observed in all cases where an inhibitor was added, with a 96% reduction in the system dosed with zinc orthophosphate.

Resistance trends were somewhat contrary to expectations. That is, given simplistic understanding of D.C. circuits, a higher resistance scale would be expected to have the lowest current for a give voltage. But for flow electrification, the highest resistance measured between

two pipe samples, occurred in the situations with the highest electrification current (Figure 4-5). Resistance measured between two pipes reflects the resistance of the water path between them, as well as resistance of the scale on the pipe surface. It seems possible that formation of a high resistance scale may co-occur with whatever scale properties cause worsened flow electrification.

While all the inhibitors (zinc orthophosphate, polyphosphate, orthophosphate and NOM) tested reduced flow electrification current, voltage and resistance, the inhibitor that proved to be most effective was zinc orthophosphate.

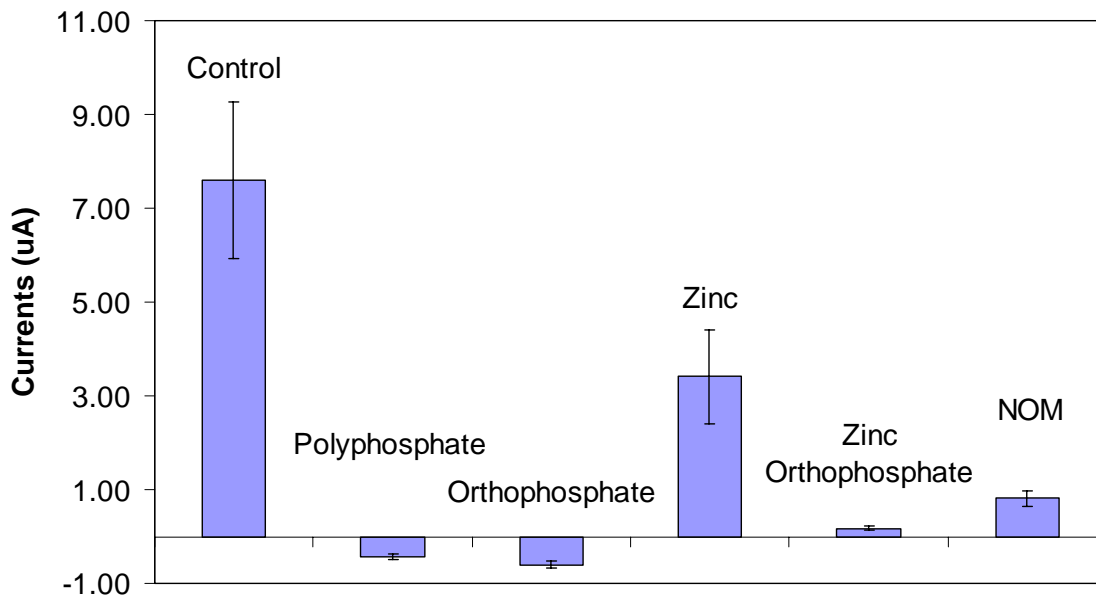


Figure 4-3: Average Currents from Phase I Testing
Error bars represent the 95% confidence interval.

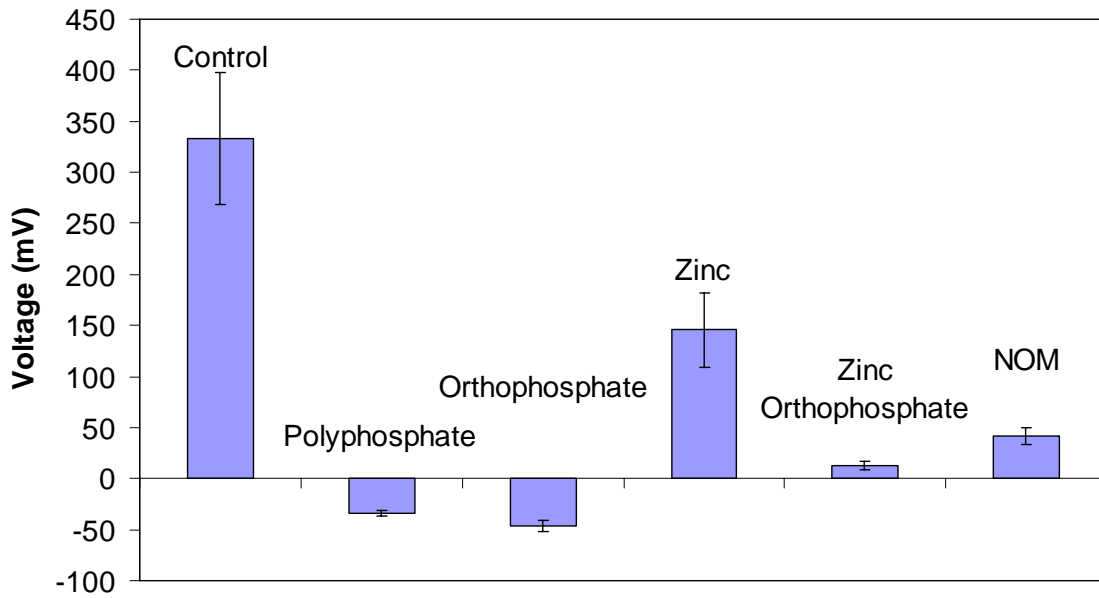


Figure 4-4: Average Voltage Differences from Phase I Testing
Error bars represent the 95% confidence interval.

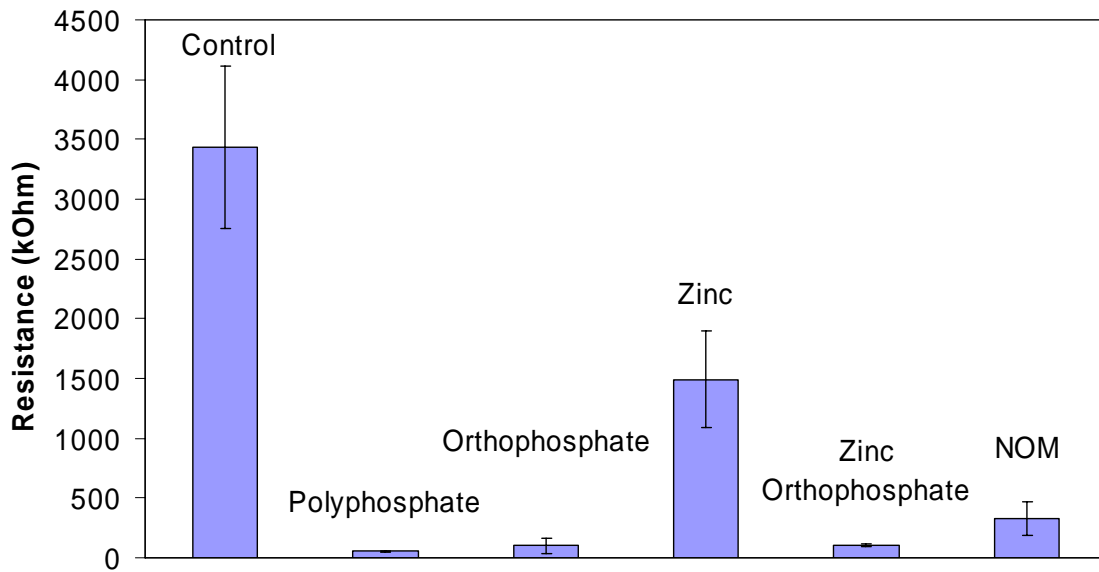


Figure 4-5: Average Resistance from Phase I Testing
Error bars represent the 95% confidence interval.

Corrosion Potential

The E_{Corr} measurements can be used to illustrate changes in flow electrification with time. From measurements gathered both prior to and following chlorine adjustments, it was determined that E_{Corr} measurements are highly dependent upon chlorine concentration (Figure 4-6). As the concentration increases, the magnitudes of the E_{Corr} values generally increase, and in cases where flow electrification is occurring, the electrification intensifies. For example, prior to re-adjusting chlorine to the target value, E_{Corr} measured in the control ranged from an average of 100-175 mV between the first and last coupons. However, after the chlorine was adjusted, E_{Corr} for those same coupons ranged from -80 to 430 mV. For all the containers testing an inhibitor, the values increased with chlorine level, except for the rig dosed with polyphosphate. Due to differences in chlorine decay rates, absolute chlorine concentrations before adjustment to the target value differed from rig to rig.

Every inhibitor reduced the E_{Corr} values, as well as the intensity of the flow electrification, when compared to the control at the target chlorine level. The addition of zinc orthophosphate resulted in virtually no electrification, identified by the flatter slope of E_{Corr} measured sequentially along copper coupons along the pipe length, as well as the overall lowest E_{Corr} values. As previously mentioned both orthophosphate and polyphosphate reversed the flow electrification trend, since the first copper coupons to contact the water were slightly cathodic relative to the last coupons. Both orthophosphate and polyphosphate reduced E_{Corr} values to below 100 mV. The water dosed with zinc only had the second highest E_{Corr} values, consistent with trends noted above.

◆ Prior to Chlorine Adjustment ■ Following Chlorine Adjustment

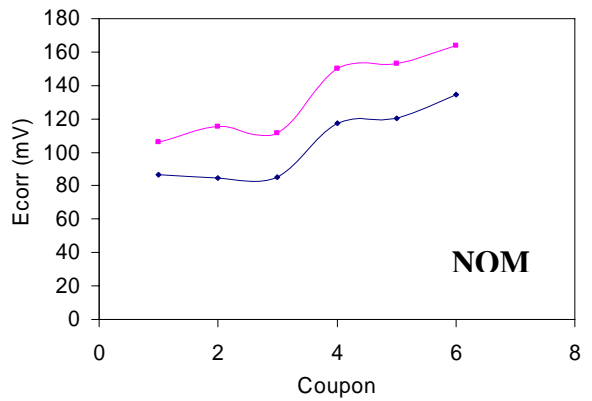
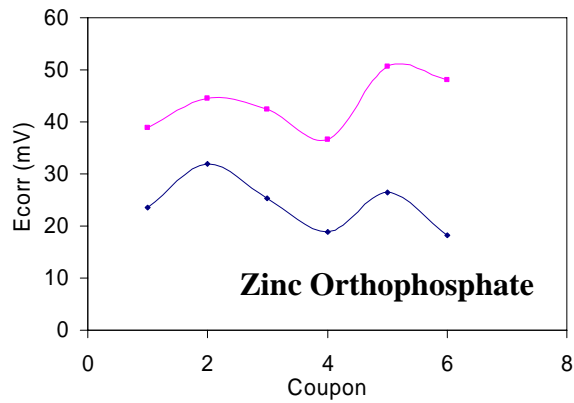
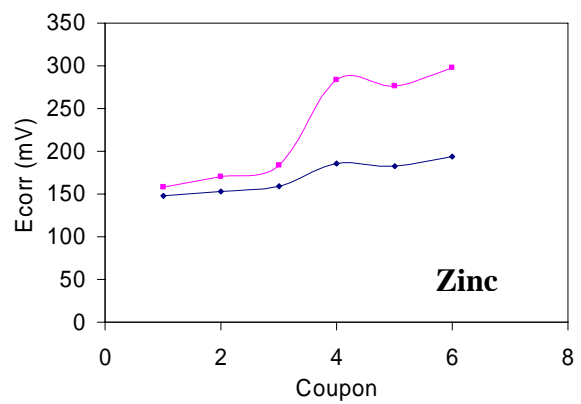
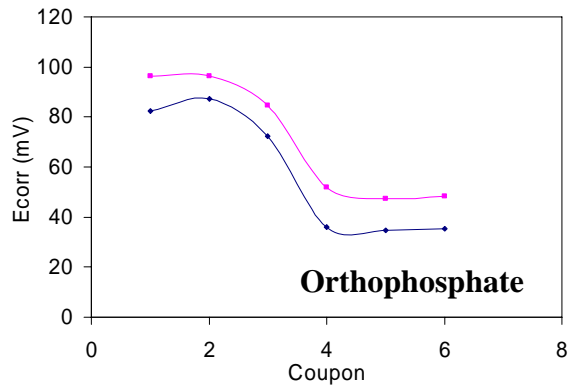
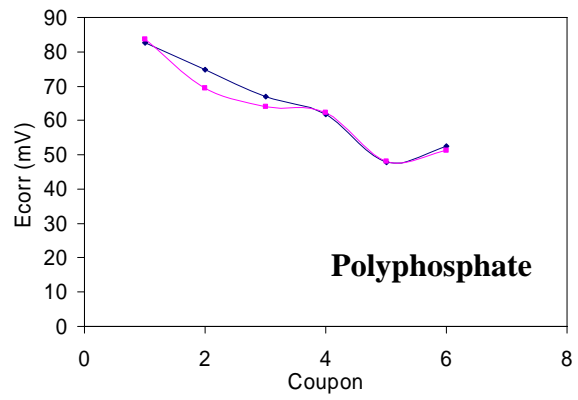
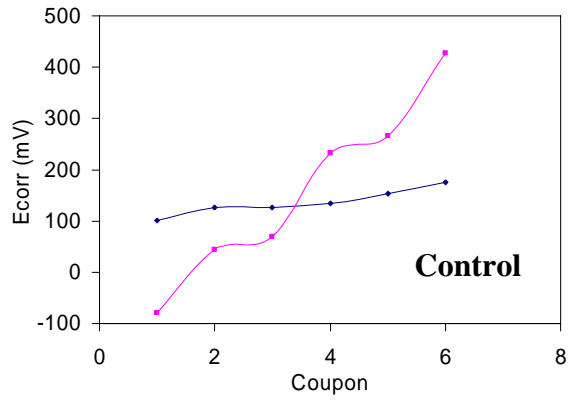


Figure 4-6: E_{Corr} Profiles during Phase I

Chlorine Decay

Since a key cathodic reaction in electrification is chlorine reduction, and the cathodic reaction is often rate limiting in corrosion, the rate at which chlorine is consumed may be an indirect indicator of corrosion. If chlorine losses from auto-decomposition and other reactions are negligible, the rate of chlorine decay would be directly related to the rate of corrosion. The rate of chlorine decay agreed with expectations based on the electrochemical measurements (Figure 4-7). In the control with any inhibitor, the average chlorine decay rate was 0.90 mg/(L*day).

The addition of all inhibitors decreased the average rate of chlorine decay. Addition of zinc alone resulted in a 17% reduction in average rate, although this is not significant at 95% confidence. But the other inhibitors including orthophosphate (69% reduction), polyphosphate (72% reduction) and zinc orthophosphate (79% reduction) reduced the rate of chlorine decay with > 95% confidence. Interestingly, the presence of NOM reduced the chlorine decay by half. When it is considered that chlorine reacts relatively rapidly with NOM itself, and NOM addition would therefore be expected to increase chlorine decay, the inhibiting action of NOM on the reaction between chlorine and copper is quite dramatic.

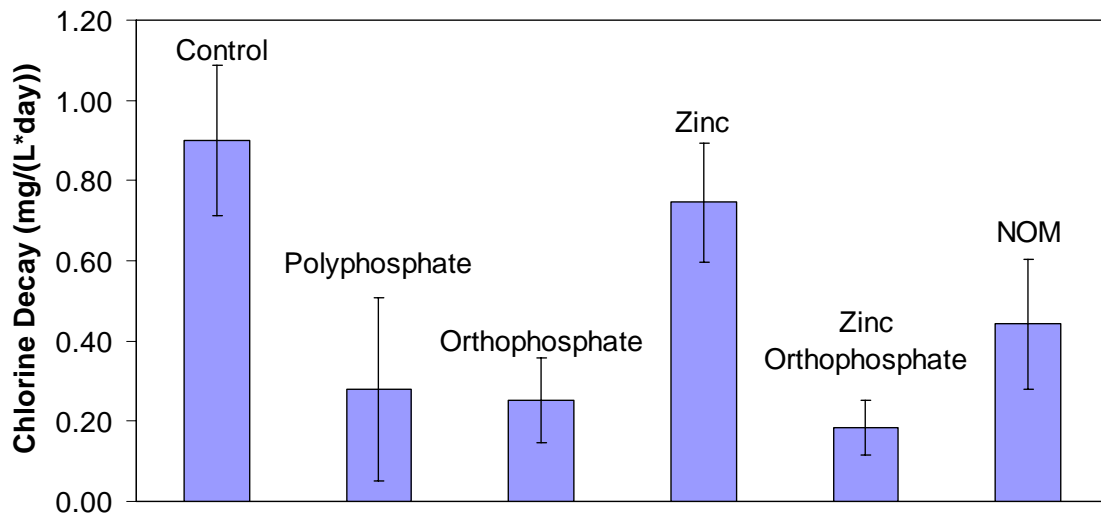


Figure 4-7: Average Chlorine Decay from Phase I Testing
Error bars represent the 95% confidence interval.

Analysis of Copper Coupons

The first ($\frac{3}{4}$ "") and last ($\frac{1}{2}$ "") coupon in each container were removed and photographed at days 0, 4, 11, 25, and 45 (Figure A-2 and Figure A-3). Additional photographs were taken once the coupons were permanently removed from the system and dried in order to more accurately document tubercle formation and variations in scale texture and color.

Scale formed in morphologies and thicknesses that are fairly consistent with expectations based on results presented earlier in this report. Intense localized corrosion was observed on the coupons exposed to the control zinc inhibitor. Only minor amounts of deposits were noticeable on coupons removed from the polyphosphate, orthophosphate and NOM containers. Finally, the coupon exposed to zinc orthophosphate was devoid of visible scale or corrosion, and looked like a new piece of copper piping. If it is considered that chlorine is corrosive, and the levels of chlorine tended to be lowest in the system with the control or zinc inhibitor, the benefits of the inhibitor are more significant.

Exposure to aluminum solids undoubtedly played an integral part in the progression of the corrosion of the coupons. Most likely, the solids increased the propensity of pit propagation and tubercle formation on the pipe surface.

After all the necessary photographs were collected, at the end of this first part of the experiment, each coupon was weighed to determine scale formation and weight loss. Coupons removed from the control and the zinc container had an average of 21 and 19 mg/cm² of scale, respectively, while coupons removed from the remaining containers formed on average less than 0.7 mg/cm². Once the scale was removed from the polyphosphate, orthophosphate, zinc orthophosphate and NOM coupons, a clean, smooth pipe surface remained. However, the control and zinc coupons were extremely rough, and a small portion of the scale was extremely difficult to remove using soft brushes.

Weight loss was normalized per unit of surface area (Figure 4-8). Consistent with their high corrosivity, the control and the coupon from the system with zinc had the two highest weight losses, averaging 10.8 mg/cm² and 8.4 mg/in², respectively. Coupons from the four remaining

containers averaged weight loss values below 0.6 mg/in² and zinc orthophosphate lost only 0.1 mg/in². Compared to the control, therefore, the zinc orthophosphate reduced the loss of metal due to corrosion by nearly 99%. The theory of electrification would suggest that if the pipe sections contacting the water first are anodic, that greater weight loss should occur in those samples. Indeed, somewhat greater weight loss was measured in the first 3/4" coupon for the control and the zinc (per unit area), relative to the last 1/2" coupon. No difference, or the opposite trend, was observed for the polyphosphate, orthophosphate, zinc orthophosphate and NOM. At this phase of testing, however, there was not a large difference in weight loss between the first and last coupon on a per unit area basis.

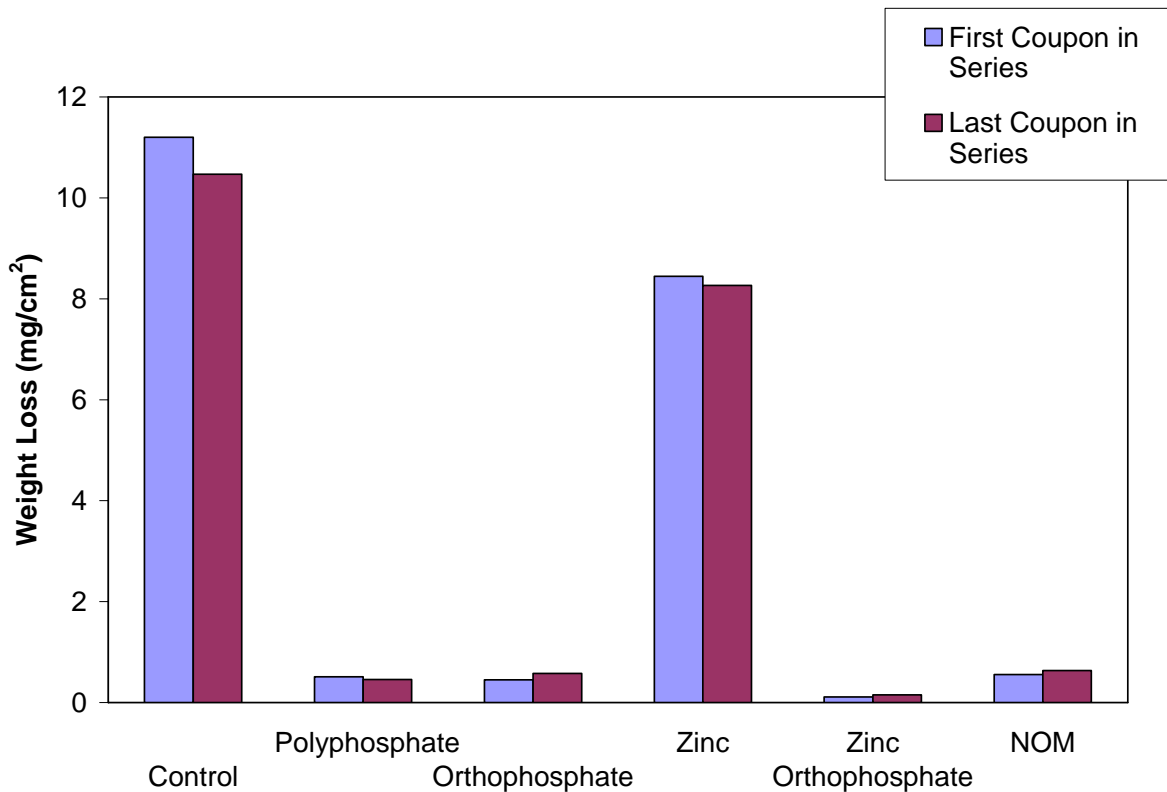


Figure 4-8: Coupon Weight Loss from Phase I Testing

Effects of Inhibitors on Pitting Corrosion and Electrification: Phase II Testing

There are two phases of pitting: pit initiation and pit propagation. As is the case with cancer, the factors that may cure the problem once it is started, can be very different from the factors that could have prevented the problem from occurring in the first place. The earlier section described

the benefits of inhibitors, if they were present continuously from the instant the pipes were contacted with a highly corrosive water. This phase of experiments was designed to examine two other key considerations:

- 1) If inhibitors were dosed to a system once the problem was started, could it stop it?
- 2) If inhibitors were dosed to a system at the start, but the inhibitor was later removed, how long would the protective effects last?

For this test, all conditions previously dosed with inhibitors, were now exposed to the control water which has a high pitting propensity. For labeling purposes in this section, these pipe samples are referred to by the inhibitor that they were initially exposed to. The condition that was the control and which had initiated the most serious corrosive attack, was dosed with the best inhibitor (zinc phosphate), to determine if zinc phosphate could stop the problem once it started.

Current, Voltage, and Resistance

Within an hour after the changes in conditions were made, electrification had already started to revert to the trend observed in the earlier section (Figure 4-9, Figure 4-10, and Figure 4-11). Specifically, within the first hour that zinc orthophosphate had been added to the loop that had been the control, current, voltage and resistance measurements decreased dramatically. With 24 hours the electrification current had become virtually nonexistent, dropping to 0.08 μA . Electrochemical measurements for the loops that had been dosed with inhibitors started to rise steadily within one to two days of starting exposure to the control water without inhibitor, and continued to change throughout the experiment. As a result of these temporal changes, error bars for the pooled data are quite large.

Amongst the conditions that had previously been exposed to inhibitors, corrosion was worst for the container previously containing zinc orthophosphate. Flow electrification current peaked at about 12 μA for the container previously containing zinc orthophosphate, which is significantly higher than the maximum current of 0.4 μA recorded during Phase I. In the meantime, the average current, voltage and resistance measurements for the container converted from zinc to a

control lessened. Discontinuing the addition of aluminum solids may have also influenced this decline in pitting propensity. The system previously dosed with polyphosphate retained less electrification effect, for a longer time period, than did the system with orthophosphate. NOM has the slowest reversion from an inhibited state when converted to control water.

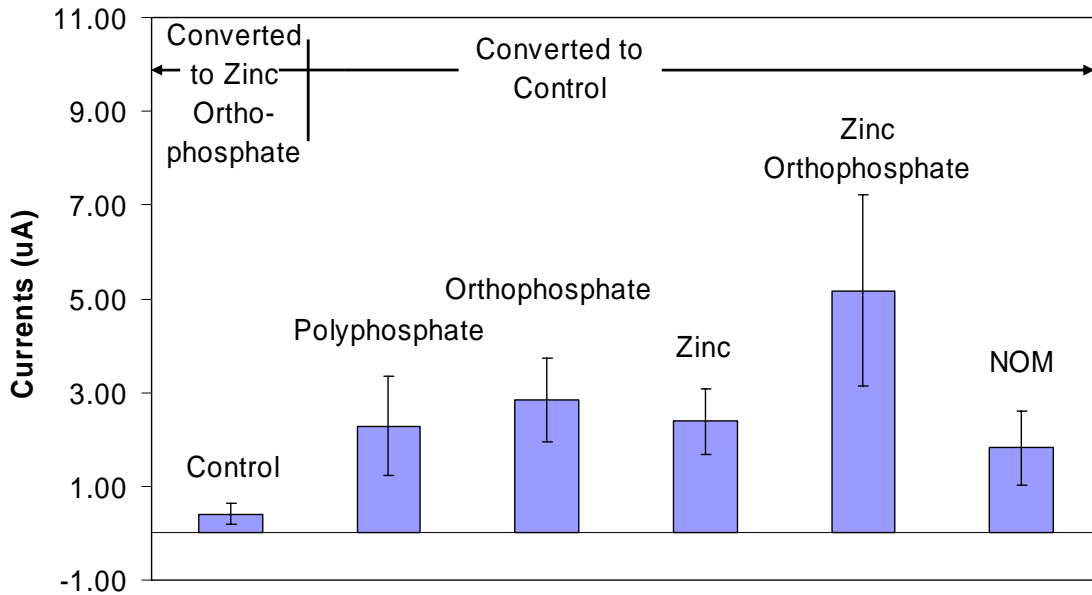


Figure 4-9: Average Currents from Phase II Testing

Error bars represent the 95% confidence interval. Labels above the bars represent previous conditions while labels along arrows indicate final condition.

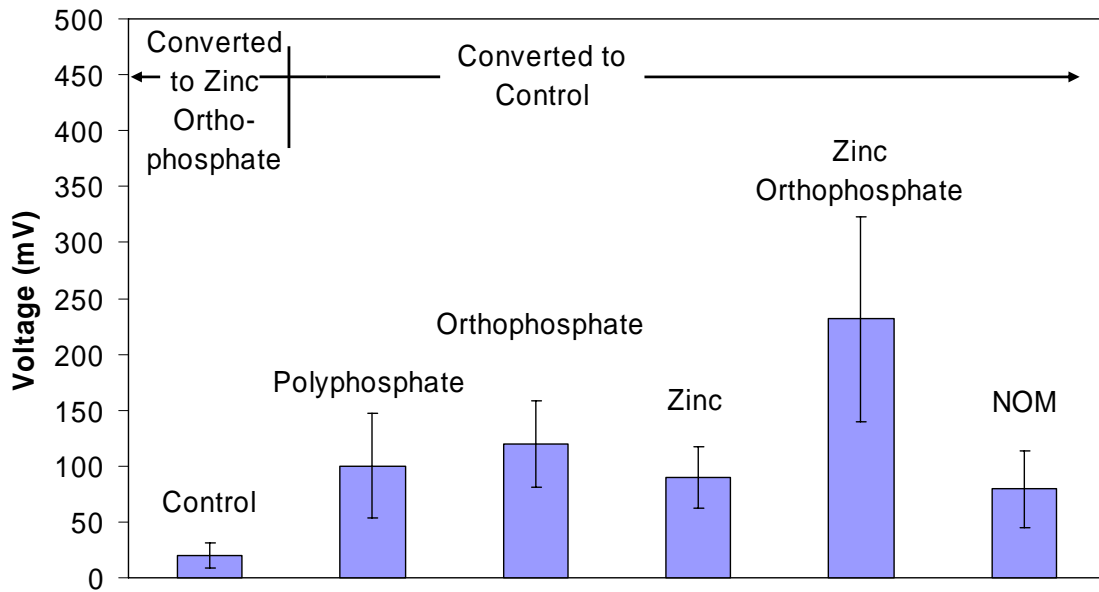


Figure 4-10: Average Voltage Differences from Phase II Testing

Error bars represent the 95% confidence interval. Labels above the bars represent previous conditions while labels along arrows indicate final condition.

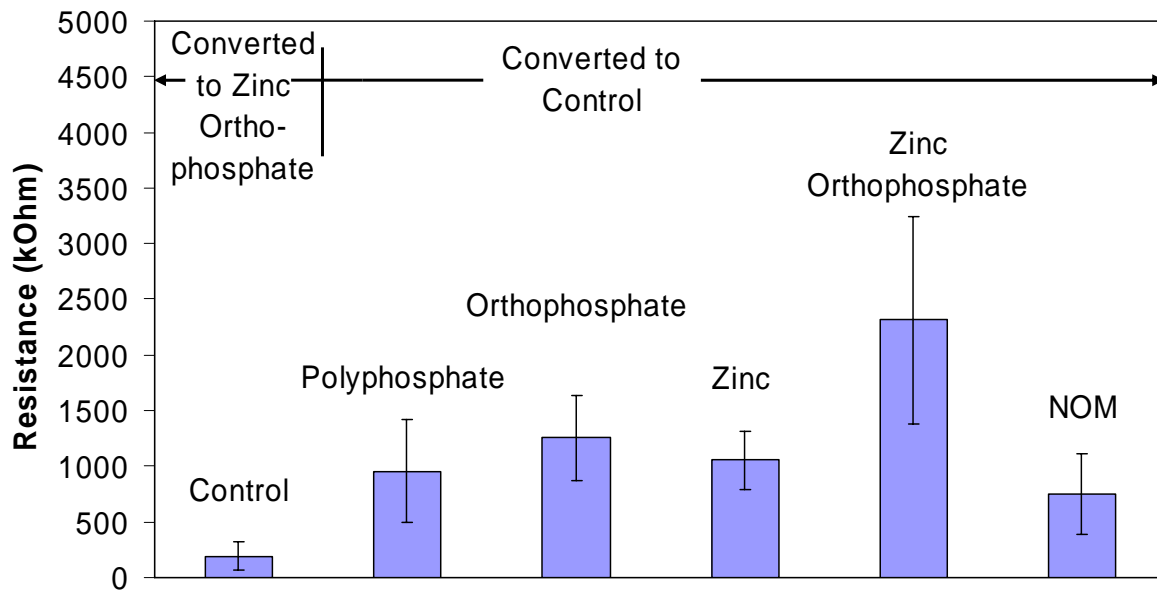


Figure 4-11: Average Resistance from Phase II Testing

Error bars represent the 95% confidence interval. Labels above the bars represent previous conditions while labels along arrows indicate final condition.

Corrosion Potential

Measurements recorded on day 46 were taken immediately before modifications to Phase II occurred (Figure 4-12). E_{Corr} measurements were then taken periodically as the experiment progressed in order to quantify transitions. Unmistakably, the flow electrification that was being recorded for the control during Phase I weakened within one day of being treated with zinc orthophosphate, evident from the flattening of the slope. Additionally, the high E_{Corr} values lowered with each passing day, leveling off in the range of 55 to 75 mV.

The opposite effect was observed in E_{Corr} values recorded for all loops in which inhibitor dosing was stopped. The largest impact occurred in the container previously treated with zinc orthophosphate. Limited changes were observed within the first seven days. However, by day 114, E_{Corr} values ranged between 43 and 608 mV increasing in the direction of flow in the four coupon sequence. Similar rises were observed in containers previously dosed with orthophosphate, zinc, and NOM. While this result was also detected in the container previously dosed with polyphosphate, it did not occur to the extent seen in the other containers. One final observation showed that the flow electrification reversed in sign after discontinuing the use of polyphosphate and orthophosphate. During Phase I, E_{Corr} values decreased through the sequential sections of copper. However, once these containers were converted to controls during Phase II, the measurements began to reverse, whereby the front section was anodic relative to the downstream coupons. This was indicative of more intense flow electrification and aggressive corrosion.

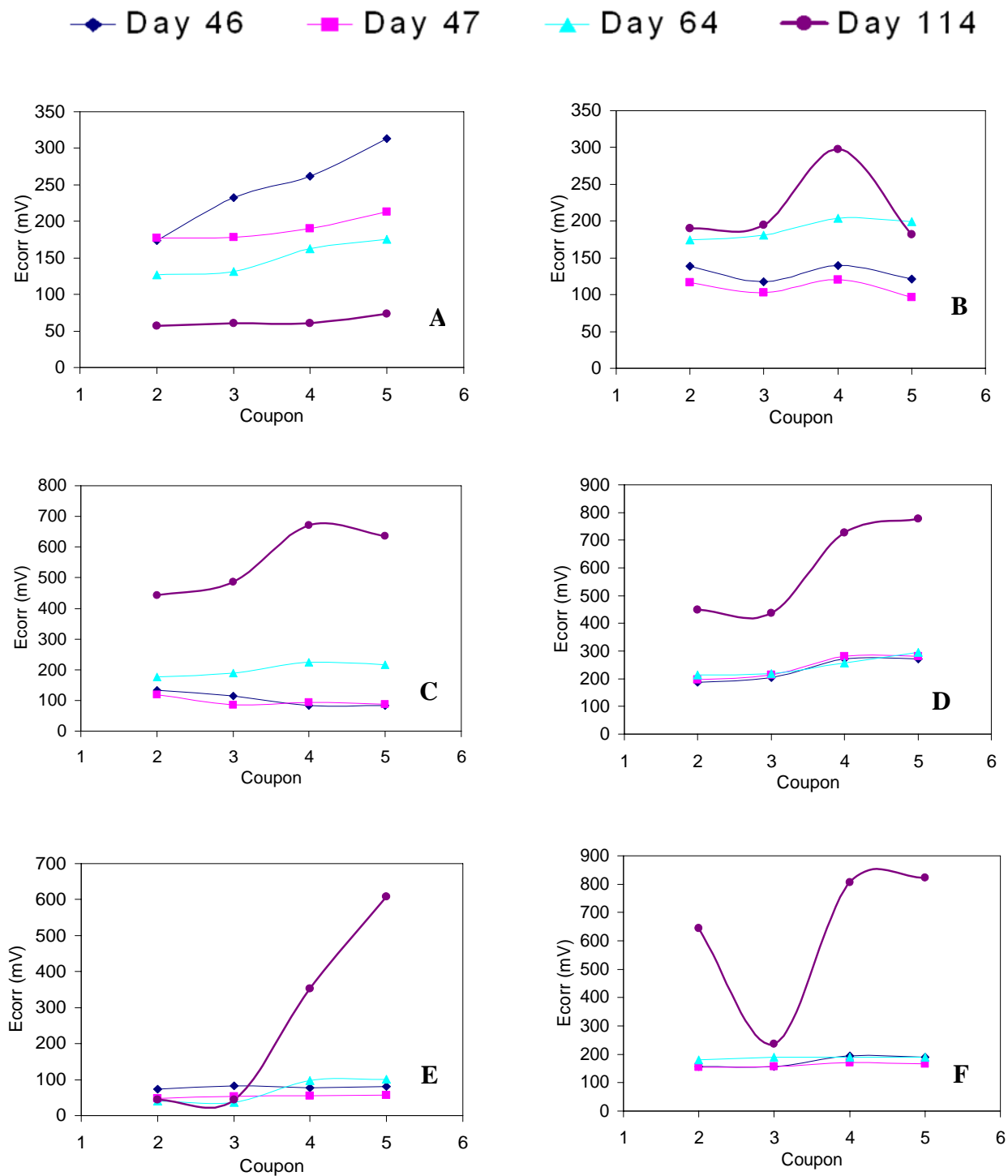


Figure 4-12: E_{Corr} Profiles from Phase II

A) Zinc Orthophosphate- Previously Control, B) Control- Previously Polyphosphate, C) Control- Previously Orthophosphate, D) Control- Previously Zinc, E) Control- Previously Zinc Orthophosphate, F) Control- Previously NOM

Chlorine Decay

As the experiment progressed, the chlorine decay rates increased for all the containers converted to controls with the exception of the container that previously contained NOM (Figure 4-13). The NOM maintained an average chlorine decay of 0.41 mg/(L*day), which is comparable to the 0.44 mg/(L*day) average calculated during Phase I. The greatest increases in decay rates were observed in the containers previously dosed with polyphosphate, orthophosphate, and zinc orthophosphate, and chlorine decay rates increased by a factor of at least 2.3. Since these coupons visually appeared to have the least scale formation on the pipes before modifications to Phase II occurred, it might be that these coupons also had the highest percentage of readily active copper surface available to react with chlorine.

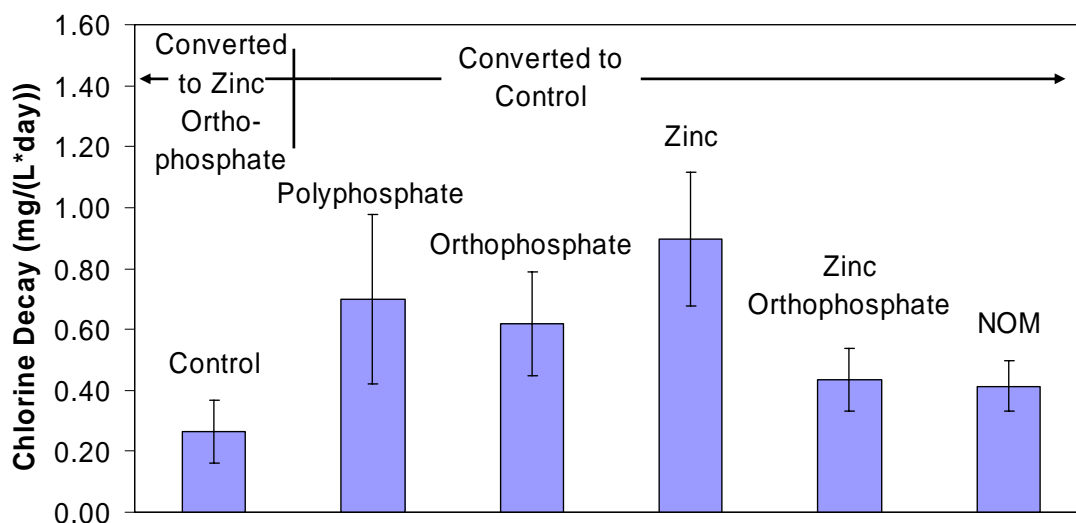


Figure 4-13: Average Chlorine Decay from Phase II Testing

Error bars represent the 95% confidence interval. Labels above the bars represent previous conditions while labels along arrows indicate final condition.

The addition of zinc orthophosphate to the control reduced the chlorine decay rate by approximately 70%, which was the lowest chlorine decay rate when comparing the rates calculated only during Phase II. The largest decay rate was calculated for the container previously dosed with zinc. Paired t-tests, however, revealed that there were no statistical differences between the average chlorine decay rates for the containers previously dosed with polyphosphate, orthophosphate and zinc, over the duration of this phase of testing, at 95% confidence.

Analysis of Copper Coupons

In order to observe the time it took for aggressive corrosion to occur in the systems previously dosed with inhibitors, coupon #2 ($\frac{3}{4}$ "") and coupon #5 ($\frac{1}{2}$ "") coupons in each container were removed and photographed periodically throughout the experiment. It is important to remember that coupons #1 and #6 were removed at the end of Phase I. Therefore, coupons #2 and #6 were the first and last coupon in the flow during Phase II. The coupons were photographed at days 64, 103, and they were dried once permanently removed from the system in order to more accurately identify tubercle formation and variations in scale texture and color (Figure A- 4).

By day 64, scale was visually apparent on all the coupon surfaces, but the surfaces that had been protected during the first part of the experiment had relatively thin scale, especially the containers treated with phosphates and with NOM. Visual differences in scale were slight between containers previously dosed with zinc or with zinc orthophosphate, and then exposed to control water, as both had relatively thick scale. At day 103, all of the coupons looked very similar with respect to scale color and texture. Tubercles were easily identifiable in each coupon and appeared to be heavily concentrated in the coupon removed from the container previously dosed with zinc. The final set of pictures, taken after the coupons were dried, looked very similar to the pictures from day 103 and was not included herein. Interestingly, the mounds of scale in the containers previously treated with orthophosphate and zinc orthophosphate formed lines of tubercles parallel to the direction of flow. For the container that previously contained zinc, the mounds were concentrated on the lower half of the coupon, whereas the other coupons had mounds scattered over the entire surface.

Weight loss was normalized per unit surface area for each coupon and then averaged for each container (Figure 4-14). Comparing only the containers converted to controls, the lowest average weight loss was observed in the control previously treated with polyphosphate followed by the containers dosed previously with orthophosphate, zinc orthophosphate, NOM and finally zinc. The majority of fell within the weight loss range of 8.1 to 11.2 mg/cm². The exception is the container previously treated with zinc, for which weight loss averaged 19.2 mg/cm². Also, for zinc, the weight loss per unit area was higher in the $\frac{1}{2}$ " coupons rather than the front two coupons which were $\frac{3}{4}$ " in diameter. Weight loss for the control converted to zinc

orthophosphate averaged 10.2 mg/cm². Although this was not the lowest average weight loss recorded during Phase II, the average was actually slightly lower than the 10.8 mg/in² calculated for the control during Phase I (Figure 4-15). Clearly, the dosing of zinc orthophosphate virtually stopped all weight loss, even in a sample in which severe localized attack had been initiated previously.

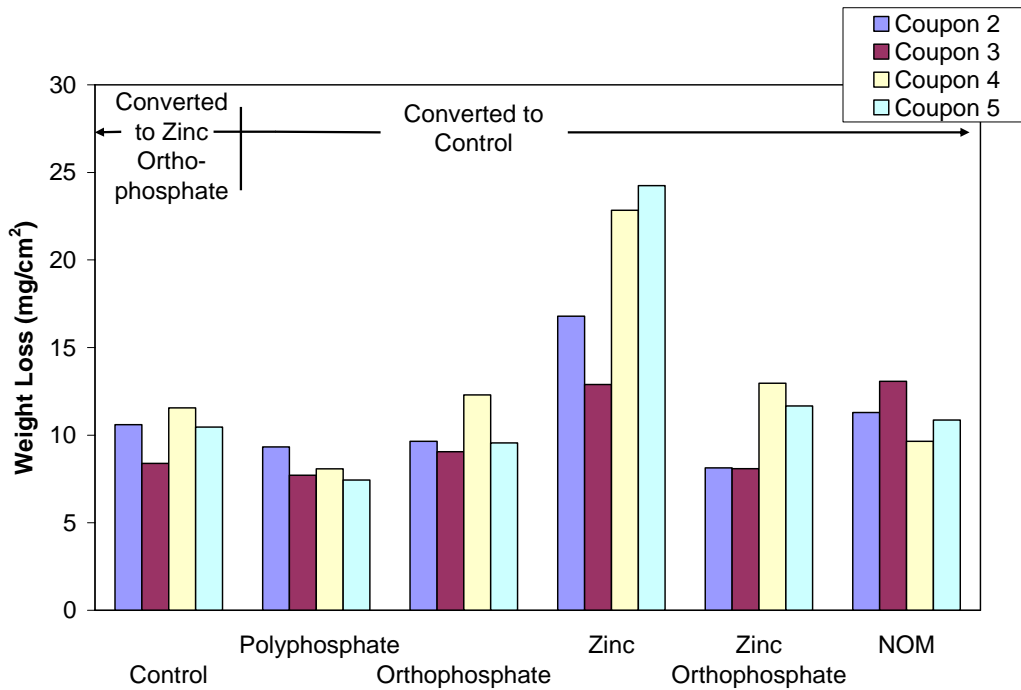


Figure 4-14: Weight Loss Data for Each Coupon from Phase II Testing
Labels along x-axis represent initial conditions while labels along arrows indicate final condition.

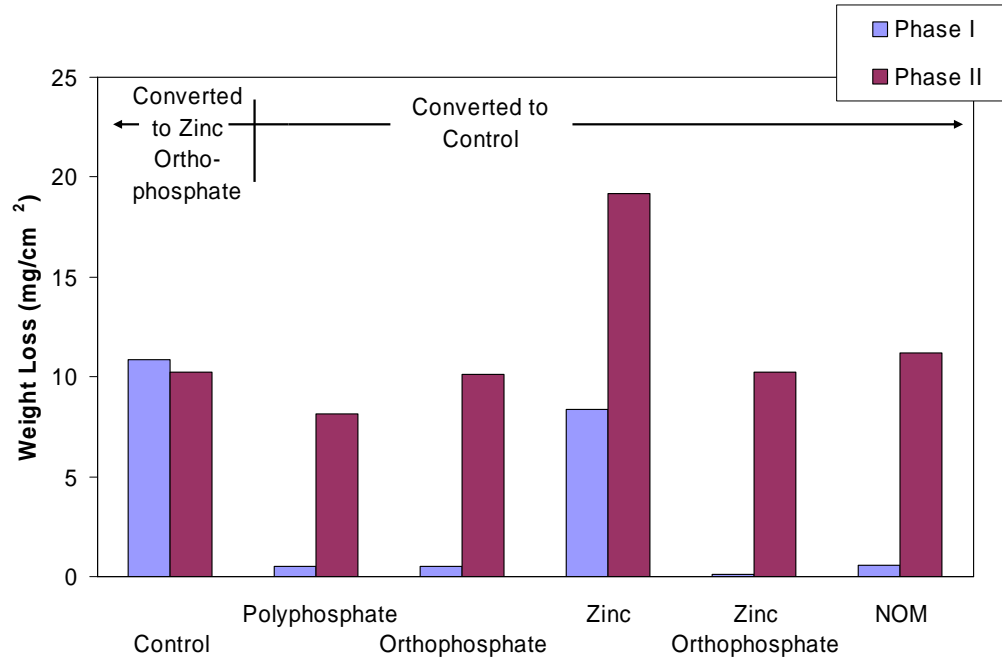


Figure 4-15: Weight Loss Data Comparing Phase I and Phase II Averages
Labels along x-axis represent initial conditions while labels along arrows indicate final condition.

Determination of pit depth, areal density and location was based on a number of physical and chemical parameters. In general, the electrochemical measures had predicted that all of the inhibitors had acted to reduce the extent of non-uniform copper corrosion relative to the control. Although deep pit formation was not observed in coupons removed from the control during Phase I, the time period may have been too constrained for significant pit propagation to occur (Table 4-3). However, formation of very significant pits occurred during the second phase of the experiment (Table 4-4). Large pits were detected in all but three coupons, two of which were in the condition that was the control in Phase I and then dosed with zinc orthophosphate in Phase II. Pit depth was consistent with findings based on chlorine decay and electrochemical measurements. Although the container previously containing polyphosphate did not exhibit signs of significant electrification, coupon #3 removed from this container had the largest pit density of 2.2 pits per square centimeter of surface area.

As notes to the table, flow electrification was considered insignificant if the slope of the E_{Corr} measurements for the pipe sections was below 30. Results from both testing phases correlated

cases where the front section was anodic with typically higher E_{Corr} values when compared to cases where electrification was not significant. Although no pits were visually detected in the coupons removed at the end of Phase I, at the end of Phase II the average pit depths were higher for the first coupons when compared to the last coupon removed from each container. Additionally, average pit depths from Phase II were highest for one of the first two coupons exposed to flow for every condition tested. These results agree with previous work by Marshall that identified deeper pits in the first sections exposed to flow. There seemed to be a complete randomness associated with the relationship between pit areal density and coupon position; thus, no conclusions could be drawn.

Important to note, the control reported in Phase II was the duplicate control which was operated for a total of 105 days. This control was never exposed to an inhibitor. Also, like the other containers aluminum solids were initially added to the water during Phase I and then discontinued during Phase II. Unlike the other six containers, this control did not have any coupons removed at the end of Phase I.

Overall, the presence of orthophosphate combined with zinc in a new or existing pitting system prevented and/or alleviated pit propagation and growth in systems disinfected with chlorine at a high pH. The reduction in electrochemical measurements and the nearly complete (99%) reduction in weight loss compared to the control is strong evidence that the inhibitor works to mitigate both the anodic and cathodic reactions. On the other hand, pre-exposure to zinc may have formed deposits that seemed to strongly intensify the attack if the inhibitor was removed. Specifically, an average of 2% of the total coupon weight was lost by the conclusion of the study of the case of zinc, which surpassed the weight loss of the control. For all the conditions tested, the deepest pits were measured in the control with a maximum depth of 0.57 mm in the second coupon in the flow sequence after only three months. Based on a typical wall thickness of 1.1430 mm (0.045") and the assumption that the corrosion would continue at a linear rate, pinhole leaks would be observed in just over 6 months.

Table 4-3: Summary of Results from Phase I

Container	Coupon	Initial Weight	Total Inner Surface Area	Total Coupon Weight Loss	Pit Density	Pit Depth #1	Pit Depth #2	Pit Depth #3	Pit Depth #4	Pit Depth #5	Average Pit Depth	Electrification	E _{Corr} Slope	Highest E _{Corr} at Day 43
		g	cm ²	%	# of Pits/cm ²	mm	mm	mm	mm	mm	mm		mV	mV
Control	1	30.99	31.81	1.15	0	0.15	0.15	0.14	0.13	0.10	0.13	Front section anodic	96	428
	6	20.01	22.06	1.16	0	0.08	0.08	0.06	0.06	0.06	0.07			
Polyphosphate	1	30.52	31.35	0.05	0	0.13	0.13	0.12	0.12	0.11	0.12	Not significant electrification	-7	84
	6	19.91	21.74	0.05	0	0.11	0.09	0.04	0.04	0.02	0.06			
Orthophosphate	1	30.93	31.81	0.05	0	0.15	0.14	0.13	0.10	0.05	0.11	Not significant electrification	-12	96
	6	20.06	21.74	0.06	0	0.10	0.10	0.08	0.03	0.02	0.07			
Zinc	1	30.44	30.84	0.86	0	0.16	0.14	0.14	0.14	0.13	0.14	Front section anodic	32	298
	6	19.30	21.03	0.90	0	0.10	0.08	0.06	0.06	0.05	0.07			
Zinc Orthophosphate	1	30.83	31.81	0.01	0	0.13	0.12	0.12	0.10	0.10	0.12	Not significant electrification	2	51
	6	19.54	21.74	0.02	0	0.09	0.09	0.08	0.06	0.05	0.07			
NOM	1	30.59	31.35	0.06	0	0.11	0.11	0.10	0.10	0.10	0.11	Not significant electrification	13	64
	6	19.74	21.74	0.07	0	0.09	0.09	0.08	0.07	0.07	0.08			

Table 4-4: Summary of Results from Phase II

Container	Coupon	Initial Weight	Coupon Interior Diameter	Total Coupon Weight Loss	Pit Density	Pit Depth #1	Pit Depth #2	Pit Depth #3	Pit Depth #4	Pit Depth #5	Average Pit Depth	Electrification	E _{Corr} Slope	Highest E _{Corr} at Day 114
		g	in	%	# of Pits/cm ²	mm	mm	mm	mm	mm	mm		mV	mV
Control	1	31.38	0.785	1.57	1.3	0.46	0.45	0.44	0.42	0.39	0.43	Front section anodic	115	651
	2	31.63	0.785	1.88	1.1	0.57	0.54	0.51	0.49	0.55	0.53			
	3	32.26	0.785	1.47	1.1	0.48	0.46	0.45	0.44	0.41	0.45			
	4	31.38	0.785	1.41	1.2	0.47	0.46	0.43	0.42	0.41	0.44			
	5	31.83	0.785	1.08	0.4	0.36	0.32	0.23	0.21	0.20	0.26			
	6	32.70	0.79	1.28	0.8	0.52	0.49	0.46	0.45	0.38	0.46			
Zinc Orthophosphate (Control)	2	30.79	0.785	1.10	0.0	0.21	0.21	0.21	0.19	0.18	0.20	Not significant electrification	5	74
	3	30.60	0.785	0.86	0.0	0.23	0.18	0.14	0.13	0.12	0.16			
	4	19.91	0.545	1.26	1.2	0.27	0.19	0.17	0.17	0.17	0.19			
	5	20.27	0.545	1.14	0.9	0.23	0.22	0.18	0.18	0.15	0.19			
Control (Polyphosphate)	2	30.82	0.785	0.95	0.8	0.28	0.25	0.24	0.24	0.23	0.25	Not significant electrification	8	298
	3	31.16	0.785	0.79	1.2	0.28	0.27	0.26	0.26	0.22	0.26			
	4	20.02	0.545	0.88	2.2	0.36	0.22	0.19	0.19	0.19	0.23			
	5	20.11	0.545	0.82	1.7	0.27	0.20	0.18	0.17	0.16	0.20			
Control (Orthophosphate)	2	30.63	0.785	0.97	1.2	0.30	0.29	0.29	0.21	0.21	0.26	Front section anodic	76	670
	3	30.80	0.785	0.92	0.4	0.39	0.35	0.34	0.33	0.27	0.34			
	4	19.90	0.545	1.34	1.2	0.26	0.23	0.23	0.22	0.21	0.23			
	5	19.61	0.545	1.04	1.5	0.27	0.21	0.20	0.20	0.19	0.21			
Control (Zinc)	2	30.62	0.785	1.72	0.2	0.44	0.41	0.40	0.37	0.36	0.40	Front section anodic	128	778
	3	30.76	0.785	1.33	0.5	0.43	0.28	0.22	0.22	0.21	0.27			
	4	19.84	0.545	2.50	0.9	0.27	0.23	0.22	0.18	0.17	0.21			
	5	19.75	0.545	2.67	0.6	0.33	0.33	0.22	0.21	0.17	0.25			

Table 4-4 Continued: Summary of Results from Phase II

Container	Coupon	Initial Weight	Coupon Interior Diameter	Total Coupon Weight Loss	Pit Density	Pit Depth #1	Pit Depth #2	Pit Depth #3	Pit Depth #4	Pit Depth #5	Average Pit Depth	Electrification	E _{Corr} Slope	Highest E _{Corr} at Day 114
		g	in	%	# of Pits/cm ²	mm	mm	mm	mm	mm	mm		mV	mV
Control (Zinc Orthophosphate)	2	31.13	0.785	0.83	1.4	0.31	0.29	0.27	0.26	0.25	0.28	Front section anodic	200	608
	3	30.95	0.785	0.83	0.0	0.20	0.18	0.17	0.16	0.13	0.17			
	4	20.01	0.545	1.43	1.8	0.32	0.22	0.21	0.21	0.18	0.23			
	5	19.96	0.545	1.29	1.2	0.25	0.23	0.22	0.21	0.21	0.22			
Control (NOM)	2	31.01	0.785	1.16	1.3	0.46	0.43	0.43	0.39	0.38	0.42	Front section anodic	110	822
	3	31.10	0.785	1.34	1.2	0.39	0.37	0.32	0.30	0.26	0.33			
	4	19.65	0.545	1.05	1.7	0.41	0.39	0.34	0.31	0.29	0.35			
	5	20.04	0.545	1.18	1.3	0.39	0.37	0.37	0.33	0.33	0.36			

Field Studies at Utilities with Pitting Problems

Studies conducted at the two water utilities in Maryland provided similar results. Although no macro-pits formed on pipes in the studies, the portion of the copper pipe first exposed to flowing water tended to be anodic relative to pipe sections downstream. Coupon weights were recorded prior to the start of the experiments, at the end of the experimentation, and following removal of the corrosion scale (Table B-1 and Table B-2). Significant weight losses occurred only in coupons removed from the control rigs at both utilities. Initial weight loss was greatest in the first coupon exposed to the flowing water and decreased in consecutive coupon. Thus, the data support the notion that electrification was occurring, and that the portion of copper first contacting the flowing water was being sacrificed. The lack of detectable weight loss or flow electrification in the systems dosed with inhibitor, supports the findings of the previously described bench scale experiments.

Orthophosphate performed well as a corrosion inhibitor. In general, the extent of corrosion was less in the systems dosed with orthophosphate. The benefits of orthophosphate were the most dramatic in the enhanced coagulation systems. Phosphate was found to be precipitating on the interior pipe surface. This may have inhibited any adverse effects of the aluminum solids. Likewise, since 1) the cathode was the limiting the corrosion reaction and 2) no pits were found on the coupons, the phosphate was probably functioning as a cathodic corrosion inhibitor in these systems.

The addition of zinc has appeared to improve deposition and performance of phosphate corrosion inhibitors in other recent studies, but there was no apparent benefit following dosing zinc to these waters. Zinc addition was very short term herein, and longer testing might be needed to observe any potential improvements. A summary of the key findings from both utilities is provided in the table below.

Table 4-5: Summary of Methods Used WSSC Study

Measurement	Results for Corrosion	Key Findings at Patuxent and Potomac
Water Quality/Chemistry Measurements		
Chlorine Decay	Rates of chlorine decay can be correlated to copper corrosion	Copper corrosion was directly controlled by the chlorine cathodic half reaction. Chlorine decay rates were statistically similar in all 4 waters.
Aluminum	Aluminum linked to copper pitting	Higher [Al] in enhanced coagulation rigs where higher initial corrosion rates were observed
Zinc	Zinc could enhance precipitation of phosphate corrosion inhibitors	Short term tests only, but no immediate benefits observed
Electrochemical Measurements		
E_{Corr} (mV)	Rising E _{Corr} thought to be indicative of pitting corrosion. Larger E _{Corr} reflective of higher corrosion rates.	E _{Corr} trend for all waters dosed with phosphate corrosion inhibitor was less than control water without inhibitor.
Pit Wires and Pitting Currents	Currents and potentials on pit wires are a direct and real time measure of copper pitting corrosion.	Some activity on wires in free chlorine with phosphate, but all other pit wires died. Thus, pitting was not sustainable or reproducible on pit wires.
Current and Potential between Pipe Sections	Measure of corrosion activity	Water quality (pH and disinfectant concentration) was driving corrosion in these systems.
Flow Electrification and Streaming Current Exp.	Measure electrification or streaming current along pipe sections with flow	Flow electrification observed in small extent, but not deemed significant

Table 4-5 Continued: Summary of Methods Used in WSSC Study

Measurement	Results for Corrosion	Key Findings at Patuxent and Potomac
Physical and Surface Analyses		
Visual Inspection and Scale Formation	Inspect pipe interior for pits/tubercles and type and degree of corrosion scale formation	Little to no scale formation on control coupons, and all three waters containing orthophosphate had thick scale almost completely covering pipe interior
Weight Loss	Indication of pipe loss due to corrosion	Initial weight loss was only in control coupons and was greatest in the first coupons receiving flow. All weight losses were similar after completely removing corrosion scale.
Pit Identification	Identify, confirm, and measure pit depth	No pit formation on coupons or pipe sections in any of the waters
Elemental Surface Analysis	Identify elements present on pipe surface on/within corrosion scale	Aluminum solids present on coupons from enhanced coagulation rigs and all Potomac rigs. Phosphorus was found on coupon surfaces from systems dosed with phosphate corrosion inhibitor.

Interestingly, the results from the Maryland studies correlate to conclusions from two additional field studies conducted by Sheffer at utilities in Florida and Iowa (2006). Comparisons between the three studies are summarized in Table 4-6. All three studies determined that the portion of the copper pipe first exposed to flowing water tended to be anodic relative to pipe sections downstream in the control water without inhibitor. As expected based on this result, the highest weight loss was observed in the first coupon exposed to flow. While the studies conducted by Sheffer examined a greater number of various inhibitors, all three studies tested the results of using zinc in combination with a form of phosphate. Overall, it was determined that zinc polyphosphate acted as the best inhibitor for the Florida and Iowa utilities, and orthophosphate provided effective corrosion reduction at the WSSC utilities.

Table 4-6: Summary of Field Studies Conducted at Three Water Utilities

Utility	Electrification in Control Water	Inhibitor that Provided the Best Results	Comments
Florida (serves south area of the city)	Yes	Zinc Polyphosphate	First pipe in the system before inhibitor addition was anodic relative to later pipe sections. Blend of orthophosphate-polyphosphate decreased pitting currents, but not to the extent that zinc polyphosphate did. Addition of the zinc polyphosphate inhibitor also reversed the electrification, whereby the first pipe section became cathodic relative to the second pipe section after inhibitor addition. Significant reductions in E_{Corr} were observed following the addition of zinc polyphosphate at pH values of 8.5 and 7.5 when compared to the less significant reductions in the blended ortho-polyphosphate, orthophosphate, and control rigs. Corrosion was also highest in the first coupon exposed to flow and gradually decreased with each successive coupon in the flow sequence.
Iowa	Yes	Zinc Polyphosphate	The addition of orthophosphate did not result in any benefits based on various electrochemical measurements. Zinc polyphosphate provided the best results, but due to the short period of testing, more extensive studies with the inhibitor should be examined. Corrosion was also highest in the first coupon exposed to flow and gradually decreased with each successive coupon in the flow sequence in the control.
Maryland (WSSC)	Yes	Orthophosphate	Significant weight loss was occurred only in control coupons. Also, the first copper sample exposed to flow had greatest weight loss. Flow electrification observed to a small extent. E_{Corr} trend for all waters dosed with orthophosphate corrosion inhibitor was less than control water without inhibitor. No benefits were observed by adding zinc into the system in very short term testing.

Other data from the collected utilities supported the conclusions from the bench scale work. At the Florida utility, there was a significant pinhole leak problem in the south part of the city which developed when the water had no inhibitor. But the north part of this city is served by a different water source which doses with zinc orthophosphate and has had relatively little pinhole leak activity. Our field testing using water from the south part of the city suggested strong benefits from zinc orthophosphate in terms of stopping flow electrification.

In early 2006, the authors started to receive inquiries from consumers in the north part of the system, requesting information regarding pinhole leaks that started to occur in their homes and apartments. An inquiry to the utility supplying this water revealed that in January of 2006, they had suddenly stopped feeding the zinc orthophosphate to the water due to concerns over turbidity created by the inhibitor (Figure 4-16). Further investigation revealed that as the zinc and phosphate concentrations in the water decreased, the number of replumb permits for the north part of the city began to rise, eventually reaching more than 75 in one month. When the utility began re-dosing the zinc orthophosphate inhibitor the number of replumb permits dropped to a low level. Not only does this practical data provide strong confirmation of the benefits of zinc orthophosphate in stopping pitting, but also supports our finding that if this inhibitor is suddenly stopped, very rapid deterioration in performance may be observed..

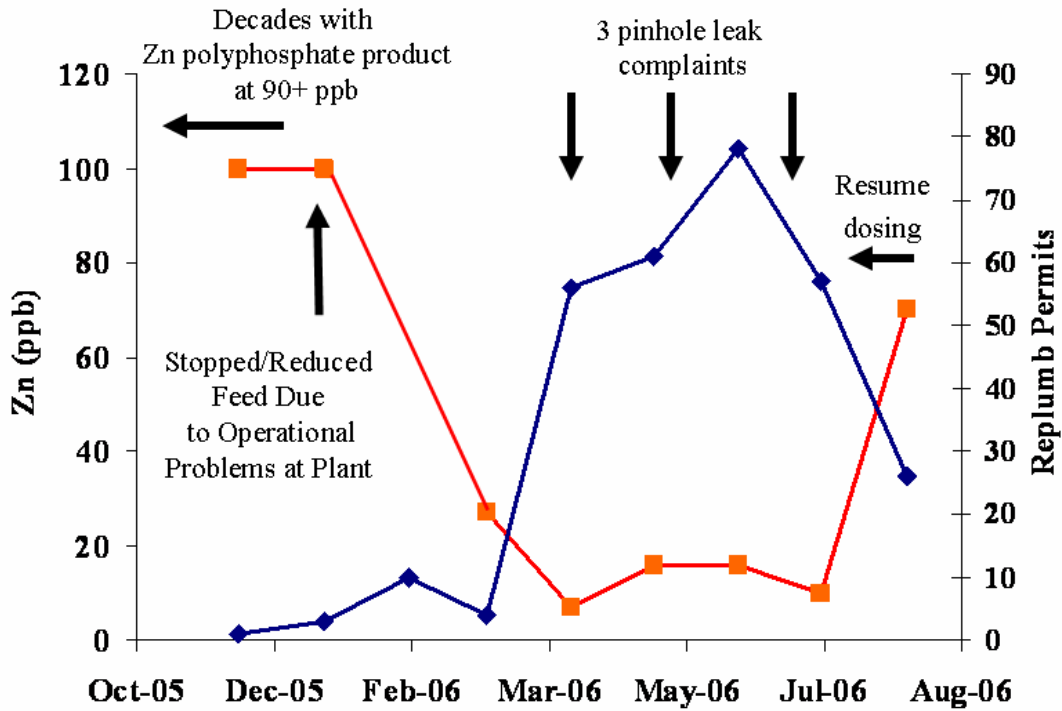


Figure 4-16: Zinc Concentration and Replumb Permits from a Water Utility Case Study in Florida

CONCLUSIONS

- The presence of an inhibitor did not completely eliminate the occurrence of corrosion. However, containers dosed with an inhibitor experienced lower flow electrification currents, electrification voltages, resistances, and E_{Corr} measurements when compared to the control (no inhibitor). Additionally, systems with inhibitor had reduced chlorine decay rates, less weight loss and reduced formation of live pits.
- Out of the five inhibitors tested, the lowest corrosion rate was observed in the system treated with zinc orthophosphate independent of the state of the copper. The system reduced electrochemical indicators of flow electrification by greater than 90% and an average weight loss of less than 0.02% (less than 0.1 mg/cm^2) when used in new copper systems. Also, the zinc orthophosphate managed to slow if not completely hinder the corrosion process in a system pre-exposed to aggressive corrosion conditions.
- Polyphosphate performed extremely well as a non-pitting inhibitor during Phase I resulting in a total coupon weight loss of 0.05%, only behind zinc orthophosphate. Polyphosphate also did not exhibit significant signs of electrification in both Phase I and

Phase II. However, the largest pit density for a single coupon was calculated in the control system previously containing polyphosphate which resulted in a maximum number of pits at 2.2 per square centimeter of surface area.

- Similar outcomes were observed for the duplicate control conditions examined. It was concluded that waters of this type can result in dangerous corrosive conditions when not treated with an inhibitor, either anodic or cathodic.
- It appears that the inhibitor must be dosed continuously into the system in order to maintain corrosion control. Once stopped, pit initiation occurred in all systems, regardless of initial inhibitor type that was dosed.
- Copper systems that are pre-exposed to water containing zinc, can produce extremely aggressive corrosion if the zinc is no longer dosed to the system. Based on weight loss data, this condition may be worse than systems where the water was never treated with an inhibitor. Data provided by a utility in Florida provided evidence of a confirmed case where pitting increased as the zinc concentration in the water decreased.
- Coupon analysis from experiments at three different field studies confirmed that the first coupon was more heavily corroded than the later coupons exposed to flow. This evidence further identified the presence of flow electrification in systems exhibiting pitting corrosion.

ACKNOWLEDGEMENTS

The American Water Works Association Research Foundation (AWWARF) provided generous funding for this work through project 3109. Additionally, thanks are given to Greg Sheffer, students from Howard University, and the staff at WSSC who assisted in this project.

REFERENCES

Marshall, B. J. (2004). Initiation, Propagation, and Mitigation of Aluminum and Chlorine Induced Pitting Corrosion. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.

Nguyen, C. K. (2005). Interactions between Copper and Chlorine Disinfectants: Chlorine Decay, Chloramine Decay and Copper Pitting. Environmental Engineering. Blacksburg, Virginia, Virginia Polytechnic Institute and State University. **Master of Science**.

Nguyen, C. K. and M. Edwards. "A Novel Method of Tracking Copper Pitting." Proceedings of the 2006 AWWA Annual Conference. San Antonio, Texas. June 2006.

Sheffer, G. J. A. (2006). Investigation of Copper Pitting Propensity Using Bench and Field Scale Testing. Environmental Engineering. Blacksburg, Virginia. Virginia Polytechnic Institute and State University. **Master of Science**.

CHAPTER 5: SUMMARY OF KEY CONCLUSIONS

- Conclusions resulting from high flow experiments demonstrated the severity of flow electrification occurring when water was continuously circulated through copper tubing. A voltage increase from the first to the last section reached values over 1.0 V in thirteen 1' sections of pipe.
- Based on current measurements in a continuous flow system, an optimally bad velocity existed at 2.8 fps when compared to the other velocities tested. Higher current values also indicated higher reaction rates, which in turn, resulted in shorter time periods until scale deposition was observed.
- A separate cell study and two experiments testing inhibitors in continuous flow at different flowrates all concluded that zinc in combination with phosphate provided unique and consistent reduction in non-uniform copper corrosion in waters characteristic of high pH, high chlorine and aluminum solids. The zinc phosphate acted as a mixed inhibitor resulting in reductions in the potentials, currents and chlorine decay.
- Other inhibitors tested (polyphosphate, orthophosphate, zinc, and NOM) lessened the occurrence of corrosion at different rates. All the containers dosed with an inhibitor experienced lower current, voltage, resistance, and E_{Corr} measurements when compared to the control water (no inhibitor). Additionally, systems with inhibitor resulted in reduced chlorine decay rates, less weight loss and fewer formations of live pits.
- Copper systems pre-exposed to water containing zinc can result in extremely harmful conditions if zinc is no longer supplemented into the system. Based on weight loss data, this condition may be worse than systems where the water was never treated with an inhibitor.
- The presence of sulfides in copper systems increased the E_{Corr} in the negative direction. The system demonstrated electrification, however, in a direction opposite to that observed in high chlorine systems. In this sulfide system, the upstream sections of pipe acted cathodically compared to the downstream pipe sections.
- When sulfides were absent, E_{Corr} measurements ranged anywhere between 0-100 mV in the positive direction as commonly seen in chlorine systems. Like corrosion potential, currents were relatively nonexistent when sulfides were not present in the system.

However, once sulfides were added, the currents significantly increased in the negative direction. .

- Electrochemical noise programs were successfully used to differentiate between systems of low and high pitting propensity. Amplitudes of potential and current noise measurements drastically increased with the presence of sulfides, implying a higher pitting propensity. However, the values could not be used to deduce any information regarding the occurrence of flow electrification.
- From the case study completed with WSSC, waters dosed with a phosphate corrosion inhibitor had lower E_{Corr} trends than control waters without inhibitors, suggesting that corrosion was more active in the control pipes. Short term testing did not find immediate benefits to dosing zinc with the phosphate corrosion inhibitor, and flow electrification was not occurring at a large extent in these experiments.

APPENDIX A

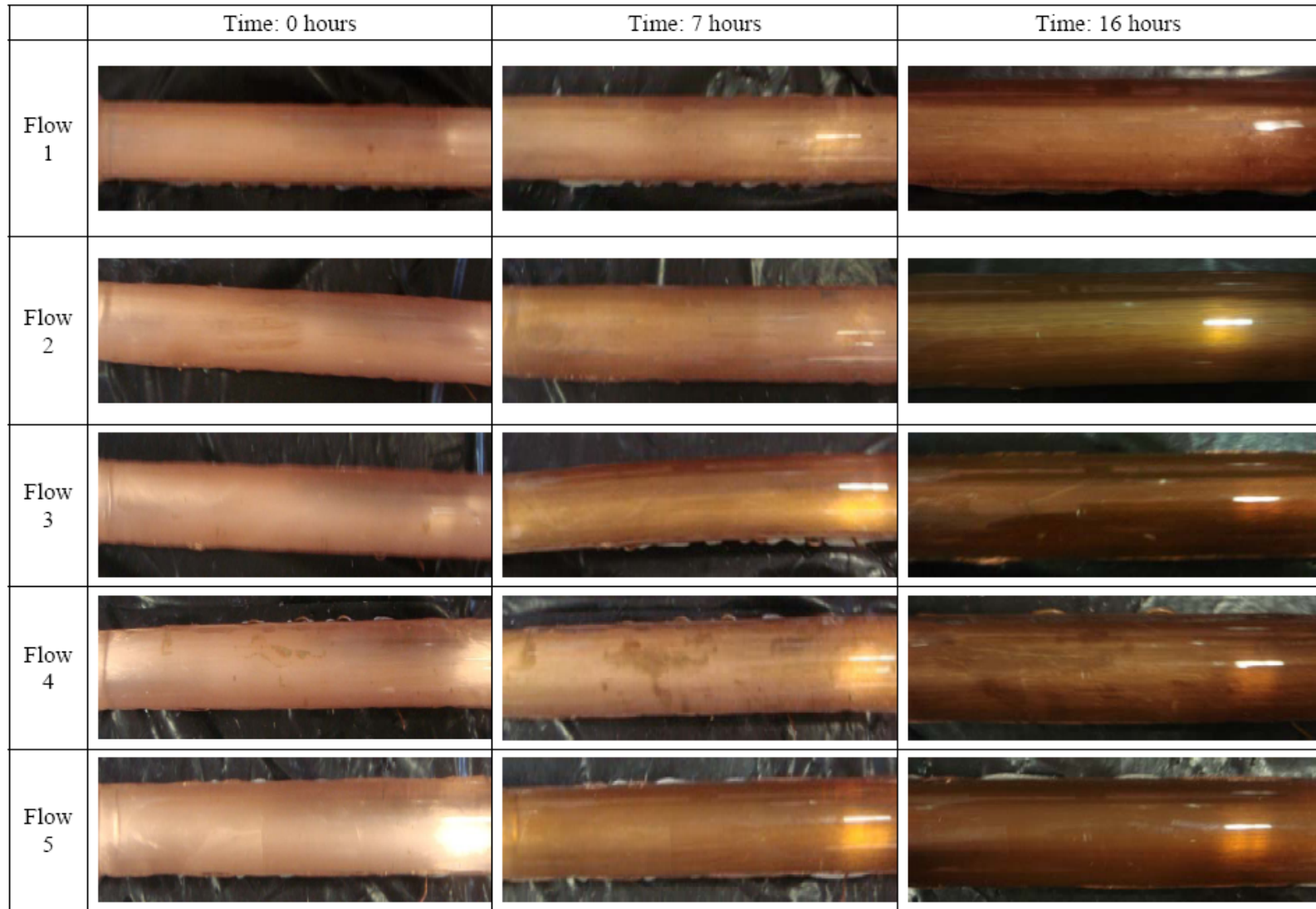


Figure A- 1: Scale Deposition on Viewable Pipe Sections







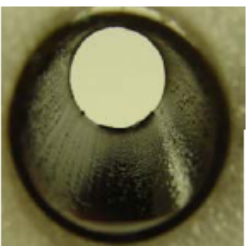
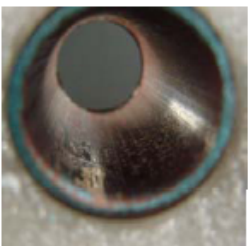
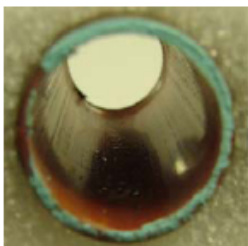
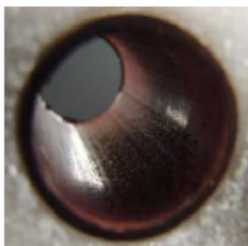



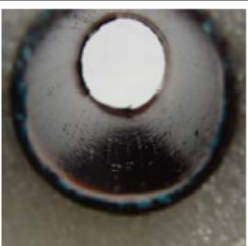


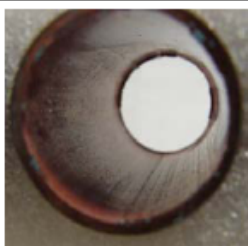

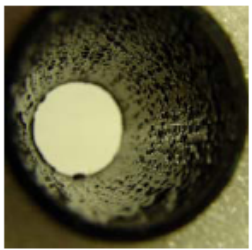
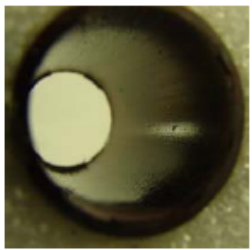
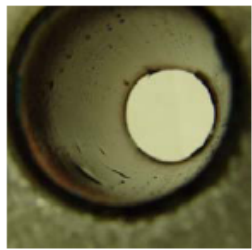
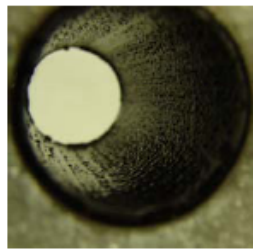
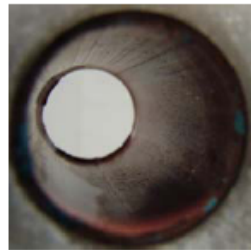
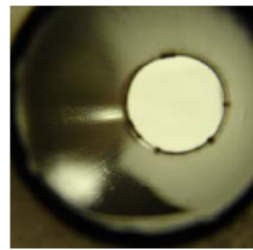
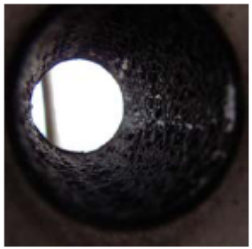

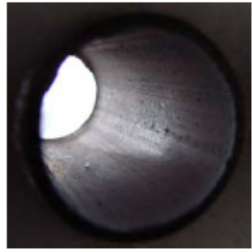

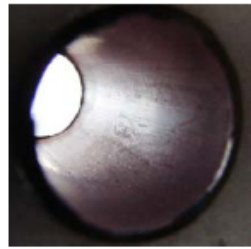
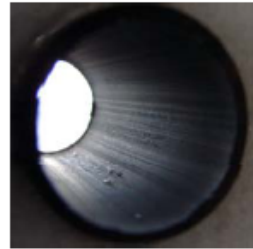
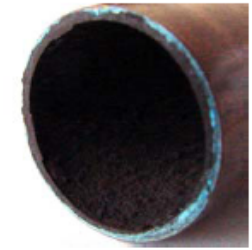

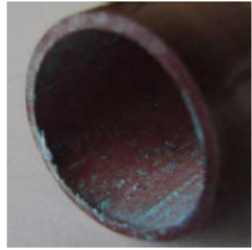

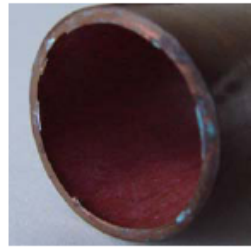

Day	Control	Polyphosphate	Orthophosphate	Zinc	Zinc Orthophosphate	NOM
0						
4						
11						

Figure A- 2: First (3/4") Coupon from Each Container during Phase I Testing

Day	Control	Polyphosphate	Orthophosphate	Zinc	Zinc Orthophosphate	NOM
25						
45						
AR*						

**Figure A-2 Continued: First (3/4") Coupon from Each Container during Phase I Testing
AR* - After Removed and Dried**



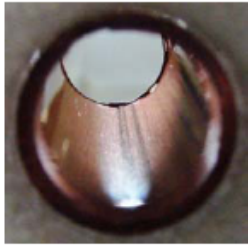





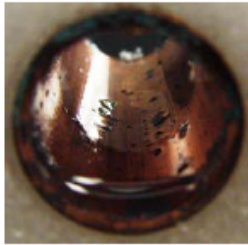
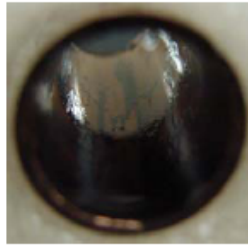


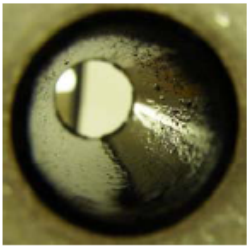
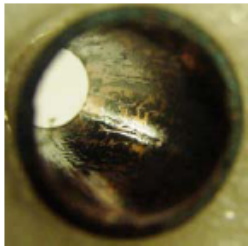
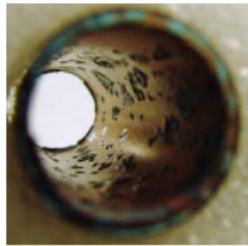
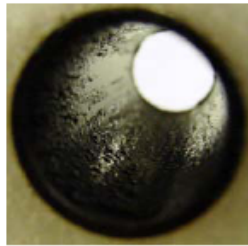
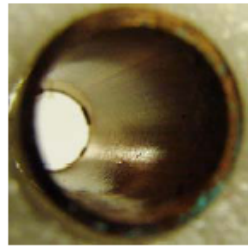
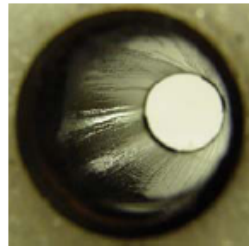

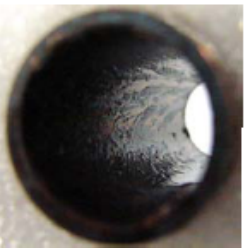
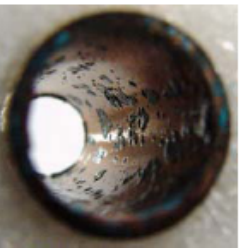
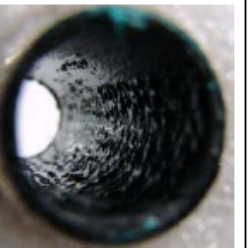
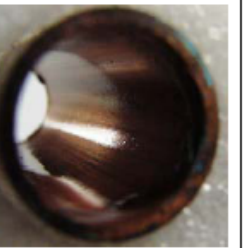

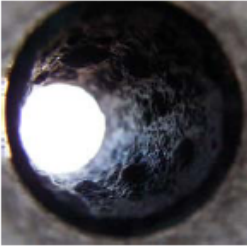
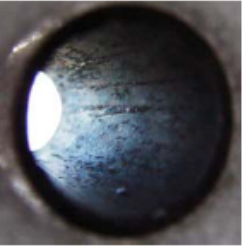
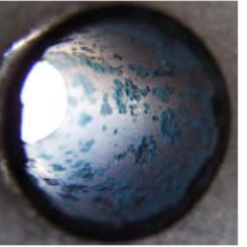
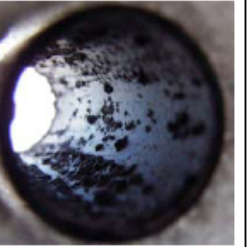
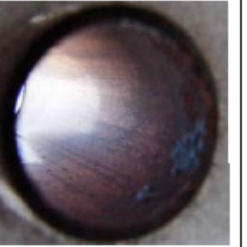
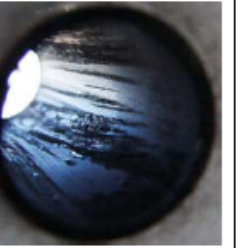
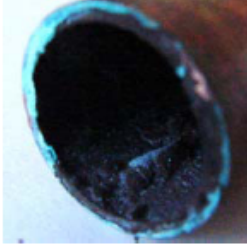

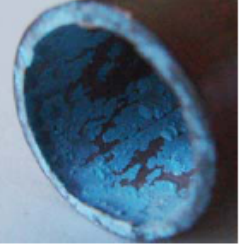

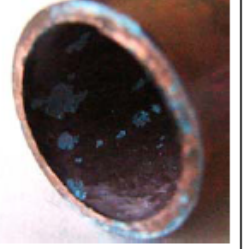

Day	Control	Polyphosphate	Orthophosphate	Zinc	Zinc Orthophosphate	NOM
0						
4						
11						

Figure A- 3: Last (1/2") Coupon from Each Container during Phase I Testing

Day	Control	Polyphosphate	Orthophosphate	Zinc	Zinc Orthophosphate	NOM
25						
45						
AR*						

**Figure A-3 Continued: Last (1/2") Coupon from Each Container during Phase I Testing
AR* - After Removed and Dried**




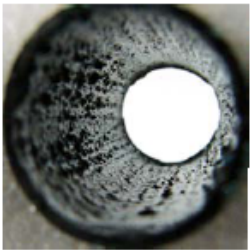
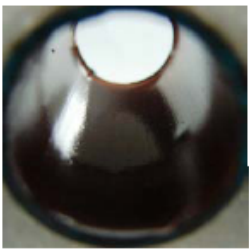

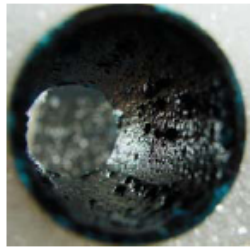
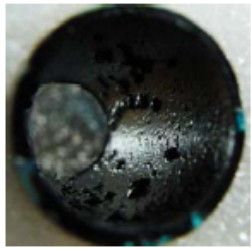
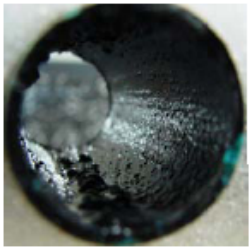

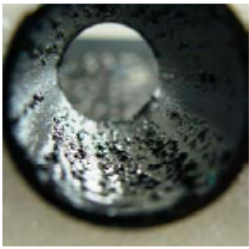
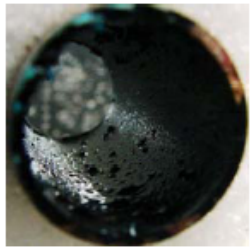
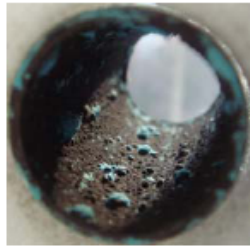


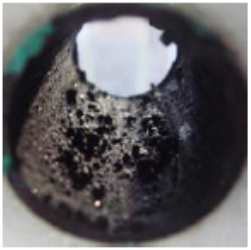
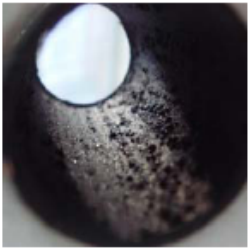
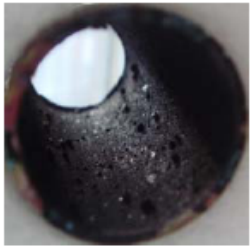
Day	Zinc Orthophosphate (Control)	Control (Polyphosphate)	Control (Orthophosphate)	Control (Zinc)	Control (Zinc Orthophosphate)	Control (NOM)
64						
103						
AR*						

Figure A- 4: First ($\frac{3}{4}$ ") Coupon from Each Container during Phase II Testing

APPENDIX B

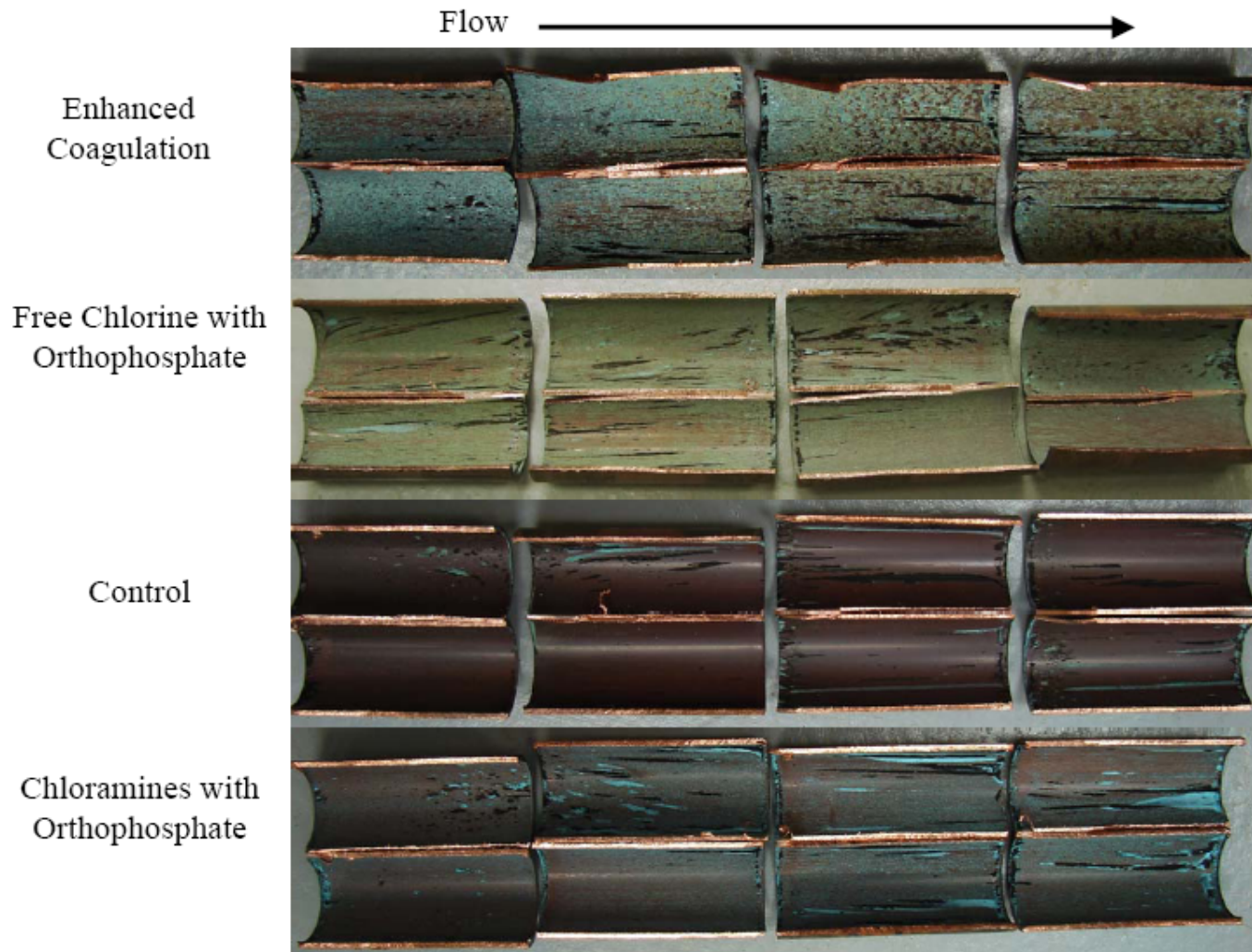


Figure B- 1: Surface of Copper Coupons from Patuxent Rigs

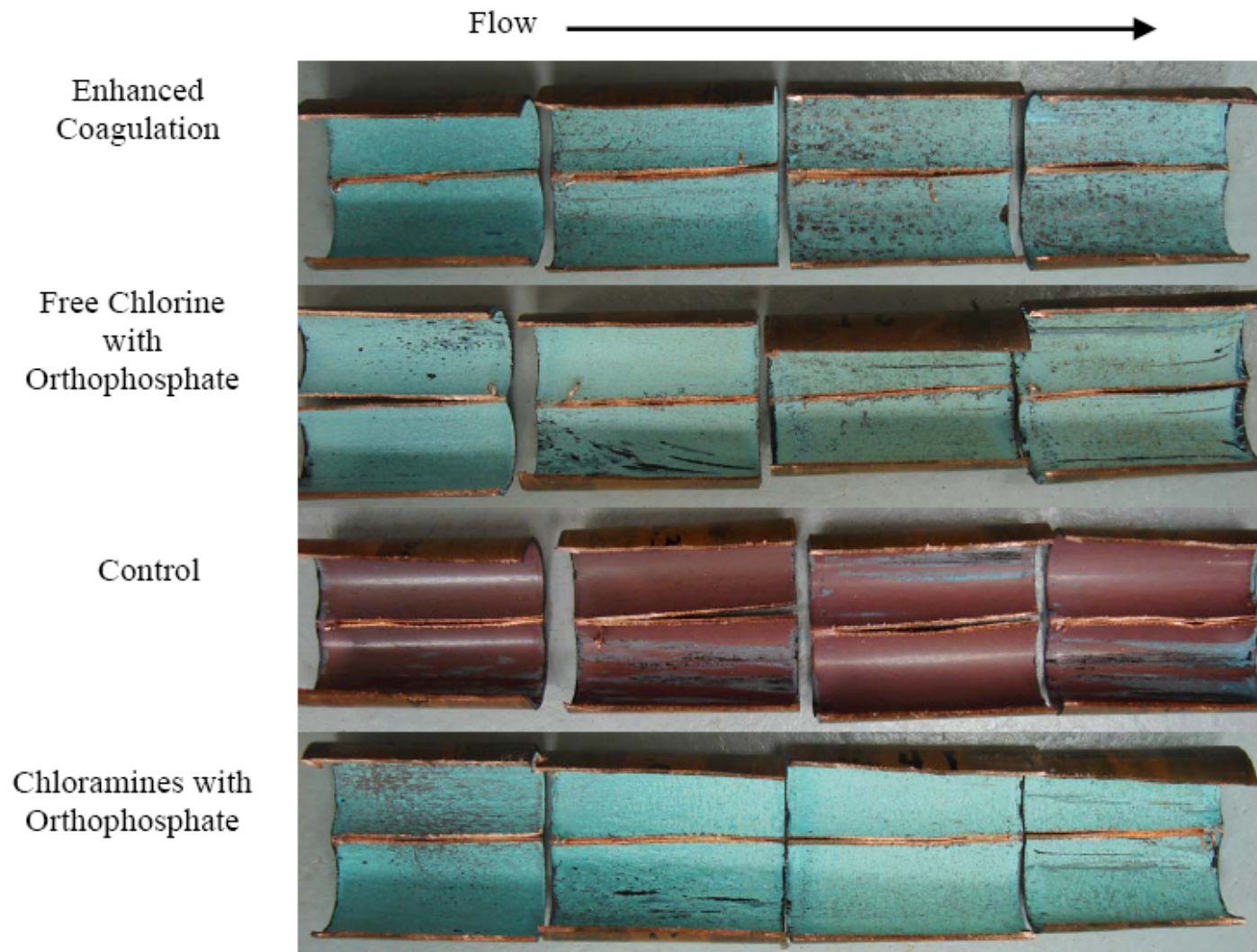


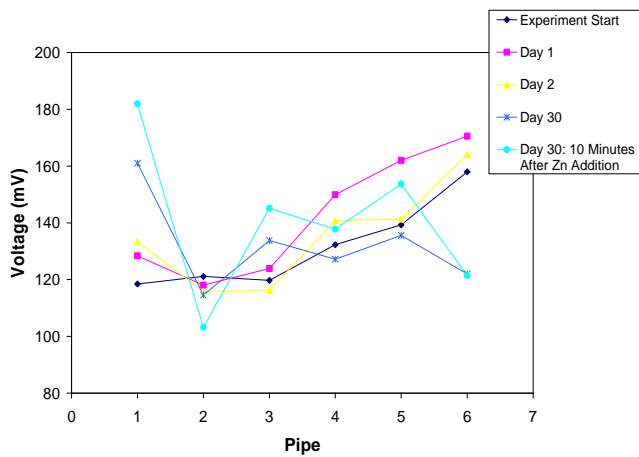
Figure B- 2: Surface of Copper Coupons from Potomac Rigs

Table B- 1: Weight Loss Analysis for Patuxent Coupons

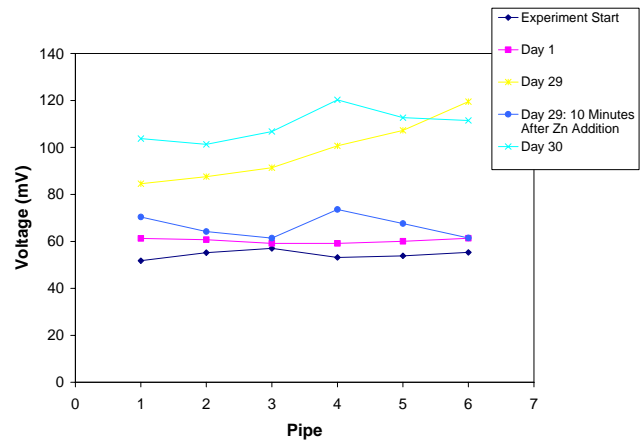
Rig	Coupon ID	Weight Loss mg	Initial Weight Loss per Unit Surface Area Prior to Scale Removal mg/in ²	Total Coupon Weight Loss After Cutting and Scale Removal mg/in ²
Enhanced Coagulation	A	-43.0	-8.58	6.32
	B	-40.2	-8.02	6.36
	C	-36.7	-7.67	6.36
	D	-29.4	-5.97	6.31
Free Chlorine with Orthophosphate	A	-28.9	-5.96	6.43
	B	-25.0	-5.07	6.32
	C	-23.4	-4.81	6.39
	D	-16.0	-3.20	6.35
Control	A	-13.9	-2.77	6.31
	B	-11.7	-2.37	6.39
	C	-6.9	-1.35	6.32
	D	2.0	0.40	6.27
Chloramines with Orthophosphate	A	-22.3	-4.66	6.41
	B	-21.2	-4.29	6.36
	C	-18.8	-3.86	6.36
	D	-15.3	-3.05	6.37

Table B- 2: Weight Loss Analysis for Potomac Coupons

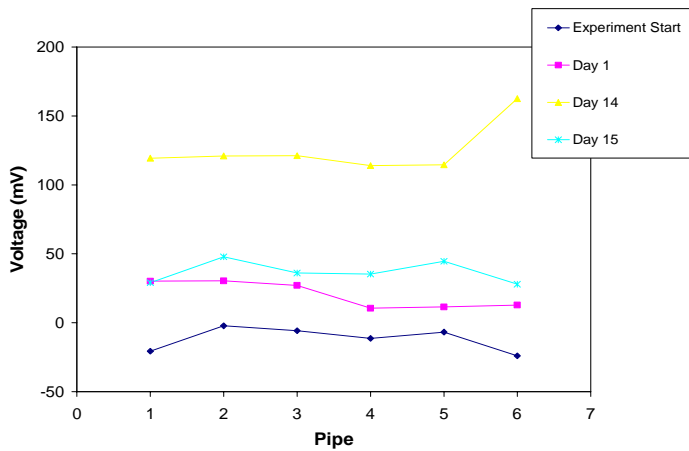
Rig	Coupon ID	Initial Weight Loss mg	Initial Weight Loss per Unit Surface Area Prior to Scale Removal mg/in ²	Total Coupon Weight Loss After Cutting and Scale Removal mg/in ²
Enhanced Coagulation	A	-28.6	-5.98	6.34
	B	-31.1	-6.22	6.29
	C	-31.7	-6.33	6.35
	D	-26.9	-5.36	6.31
Free Chlorine with Orthophosphate	A	-34.3	-6.96	6.39
	B	-32.1	-6.32	6.42
	C	-27.2	-5.59	6.23
	D	-20.3	-4.17	6.38
Control	A	-6.1	-1.25	6.34
	B	-4.5	-0.90	6.35
	C	0.2	0.03	6.35
	D	6.4	1.24	6.36
Chloramines with Orthophosphate	A	-39.0	-8.43	6.35
	B	-37.9	-7.24	6.34
	C	-23.7	-4.65	6.41
	D	-9.2	-1.90	6.31



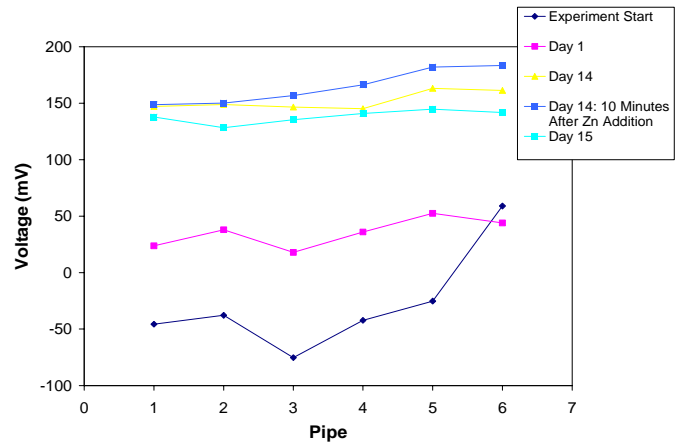
Enhanced Coagulation Rig at Patuxent



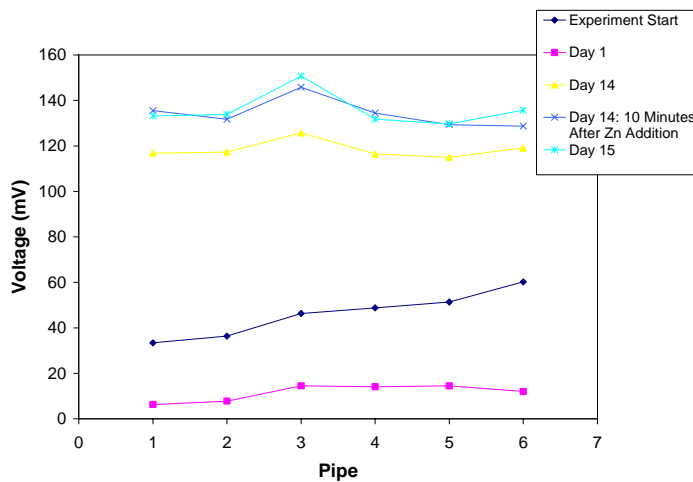
Free Chlorine with Orthophosphate Rig at Patuxent



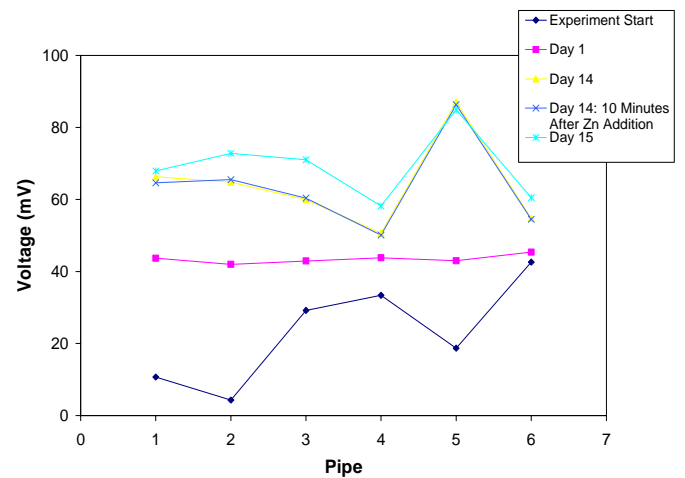
Control at Potomac



Enhanced Coagulation Rig at Potomac



Free Chlorine with Orthophosphate Rig at Potomac



Chloramines with Orthophosphate Rig at Potomac

Figure B- 3: E_{Corr} Data from the Flow Electrification Experiment on the Separate Pipe Loop

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EDUCATION

Virginia Polytechnic Institute and State University, Blacksburg, VA
Master of Science in Environmental Engineering **2007**
Thesis: "Non-Uniform Copper Corrosion in Potable Water: Theory and Practice"
Grade Point Average 4.0/4.0
EIT Certified

Purdue University, West Lafayette, IN
Bachelor of Science in Civil Engineering **2005**
Area of Concentration: Environmental
Grade Point Average 3.91/4.0
Graduated With Distinction

WORK EXPERIENCE

Virginia Polytechnic Institute and State University, Blacksburg, VA
Graduate Research Assistant **2005 - present**
Completed studies that examined the effects of copper pitting corrosion in drinking water systems. Experiments tested the application of inhibitors and the impacts on flow electrification in both bench scale and field studies. Studies also investigated electrochemical noise as a pitting detection method.

Purdue University, West Lafayette, IN
Undergraduate Research Assistant **2004 - 2005**
Research focused on microbial growth and kinetics of aerobic bacteria in the treatment of graywater in the BREATHe Systems for NASA Advanced Life Support Operations.

General Motors Corporation, Bedford, IN
Environmental Engineering Intern **2003**
Completed a plant-wide point of generation waste study, stack testing, chemical inventory, aided in waste reduction and initiated plastic recycling program.

HONORS AND AWARDS

- Sussman Fellowship **2006**
- 2nd Place in VA AWWA/VWEA 2006 Student Design Competition **2006**
- Charles E. Via, Jr. Fellowship **2005 - 2006**
- National Science Foundation CSEM Scholarship **2004**

PRESENTATIONS

AWWA Annual Conference and Exposition 2006. "Copper Pinhole Leaks." Corrosion Control and Water Quality in the Distribution System Workshop. *Rebecca Lattyak, Marc Edwards and Paolo Scardinda*