INVESTIGATION OF COPPER PITTING PROPENSITY USING BENCH AND FIELD SCALE TESTING

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ABSTRACT

A range of techniques designed to monitor copper pitting propensity were applied at two water utilities with known pitting disposition. In addition to traditional approaches including E_{Corr} rise, chlorine decay kinetics, and surface analyses, a novel method was attempted to develop ‘pitting currents’ between copper samples exposed to differential flow. This method allowed pitting current, potential, and resistance between ‘pits’ and sections of copper pipe to be measured. As part of this evaluation, effects of different corrosion inhibitors and secondary disinfectants were investigated in an attempt to identify water quality modifications that might alleviate copper pitting at each utility.

At a Florida utility where customers were experiencing a severe pitting problem, experiments investigated the effectiveness of corrosion inhibitors including orthophosphate, an orthophosphate-polyphosphate blend, and zinc polyphosphate. Results suggested that zinc polyphosphate provided the greatest likelihood of mitigating copper pitting corrosion, whereas orthophosphate and the orthophosphate-polyphosphate blend actually *increased* electrochemical indications of pitting. According to theory, orthophosphates can increase pitting intensity if applied in insufficient quantities, whereas cathodic inhibitors, such as zinc, can only reduce corrosion rates. Surface analyses determined that zinc polyphosphate produced the least amount of scale, whereas the control produced the greatest amount. Further, surface analyses also suggested that zinc and phosphorus may behave synergistically during precipitation reactions which decrease copper release. Subsequent testing at Virginia Tech laboratories confirmed that some of the benefits from the zinc polyphosphate product were directly attributed to zinc. Consistent with previous research, pitting propensity of the water in the absence of inhibitor decreased at pH 7.5 relative to pH 8.5 (Marshall, 2004). In addition, higher concentrations of chloramines increased the pitting propensity of the water, although the ratio of chlorine to ammonia had little effect.

Similar experiments were also conducted at a utility in Iowa. Copper pitting has always existed in this area at some low level; however an outbreak of copper pinhole leaks recently occurred that is temporally correlated with high chlorine and chloramine concentrations. Experiments investigated combinations of disinfectant type (free chlorine or chloramines) and corrosion inhibitor (orthophosphate or zinc polyphosphate) in an attempt to decrease pitting propensity. Results indicated that the addition of zinc polyphosphate decreased pitting propensity in free chlorine systems as well as systems dosed with chloramines. In contrast, the addition of orthophosphate seemed to be ineffective in either system. Final surface analyses confirmed that inhibitors performed most effectively in the free chlorine system, whereas no clear benefits were realized in chloramine systems.

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TABLE OF CONTENTS

CHAPTER 1: COPPER PITTING, INHIBITORS, AND MONITORING OF PITTING PROPENSITY

CHAPTER 2: CASE STUDY OF COPPER PITTING CORROSION – FLORIDA UTILITY

CHAPTER 3: CASE STUDY OF COPPER PITTING CORROSION – IOWA UTILITY

LIST OF TABLES

LIST OF FIGURES

Chapter 1: Copper Pitting, Inhibitors, and Monitoring of Pitting Propensity

Gregory Sheffer and Marc Edwards

INTRODUCTION

Corrosion refers to the degradation of metal by electrochemical reactions with the surrounding environment. At the anode, the metal is corroded, or oxidized, and releases electrons. For copper metal, this occurs according to the following reaction:

$Cu_{(s)} \rightarrow Cu^+ + e^-$ (anodic reaction of copper oxidation)

At the cathode, the electrons produced at the anode are consumed in a reduction reaction. In potable water, the most common reduction reactions are oxygen reduction and chlorine reduction as follows:

$\frac{1}{2} O_2 + 2H_2O + 2e^- \rightarrow H_2O + 2OH^-$ (cathodic reaction of oxygen reduction)

$HOCl + 2e^- \rightarrow Cl^- + OH^-$ (cathodic reaction of chlorine reduction)

Every electron that is produced by corrosion must be consumed by a reduction reaction with either oxygen or chlorine. Therefore, the overall reactions for copper corrosion via oxygen or chlorine reduction are, respectively:

$$2Cu_{(s)} + \tfrac{1}{2} O_2 + 2H_2O \rightarrow 2Cu^+ + H_2O + 2OH^-$$

$$2Cu_{(s)} + HOCl \rightarrow 2Cu^+ + Cl^- + OH^-$$

For copper pipes used in potable water, corrosive attack typically proceeds relatively evenly over the interior pipe surface. This mode of corrosion is referred to as ‘uniform’ corrosion and rarely causes pipe failure even after 70 years of service. In certain circumstances, the anodic corrosion reaction can be focused at specific points on the surface referred to as “pits”; the name of which is attributed to degradation of the metal and growing hole at this location. The diameter of these holes varies, but is usually between 0.1 and 1 mm. This mode of localized corrosion is specifically termed ‘pitting’ corrosion. In copper, once a pit has fully penetrated a pipe wall, the failure is known as a copper pinhole leak.

The frequency of copper pinhole leaks has reached epidemic levels in some instances in the U.S. Illustrative examples of documented problems include:

- A single dwelling that has experienced more than 40 pinhole leaks.
- A failure occurring in a house after 40 years of successful copper use. Sequentially, a second and third replumb was warranted after developing pinhole leaks in new copper pipe in only six and five months, respectively.
- Pinhole leaks that have occurred in new pipe in as little as seven days after installation.
- A homeowner who reported leaks to her insurance company was raised to a higher risk insurance category and was not able to renew her policy. As a result, her day care business could not operate and she lost her home.

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FUNDAMENTAL SCIENCE OF COPPER PITTING

Many purported causes of copper pitting have been offered. However, most of these causes, including the existence of carbon films, surface imperfections, excessive flux, poor installation practice, and poor electrical grounding have been tested in experiments conducted by the Edwards' research group at University of Colorado and at Virginia Tech and never caused formation of real pits in copper pipe under scientifically reproducible conditions. In fact, the only study that has ever led to the formation of fully penetrating pits in the laboratory demonstrated that water chemistry can be the sole cause of pitting. Specifically, Marshall (2004) illustrated that a combination of high pH, aluminum, and high free chlorine can cause fully penetrating holes in copper pipe in only 11 months. It is currently believed, but not yet proven with scientific certainty, that other factors can also cause pitting to occur. The most common suspected conditions for pitting are summarized in Table 1-1.

Essential features of a growing pit corroding through a copper pipe wall are illustrated schematically in Figure 1-1. The pit is the location of the anodic corrosion reaction which consumes the pipe wall. During the anodic reaction, copper metal is oxidized, cuprous ions are released, and electrons are produced. The electrons are transferred through the conductive copper pipe wall to a cathodic portion of pipe surface where they are consumed by oxygen and/or chorine. Although no visible attack is occurring at cathodic pipe surfaces surrounding a pit, cathodic reactions are critical to pit growth. In accordance with the overall copper corrosion reaction, anodic and cathodic reactions must proceed in lockstep.

During the pitting process, cuprous and cupric copper corrosion products are released at the pit. These products can remain soluble in the form of Cu^+ or Cu^{2+} ions and accumulate in the pit, or they can react with other constituents in the water such a Cl^- or

OH^- to form solids such as CuCl (cuprous chloride) or CuOH (cuprite). These solids can form a mound over the pit referred to as a tubercle. During tubercle formation, the removal of OH^- makes the pH of the pit more acidic, which can further increase the rate of attack.

For every atom of solid copper metal that corrodes, one negatively charged anion (e.g., Cl^-, ½ SO_4^{2-}, or OH^-) must be transported into the pit to replace electrons consumed by the cathodic reaction and maintain electroneutrality. Thus, tubercles on active pits must maintain a degree of porosity in their structure to allow anion transport into the pit as well as cuprous and cupric copper ion transport out of the pit. Likewise, in order to maintain electroneutrality, a pathway must exist for cations such as calcium to be transported to the cathode. This pathway is generally water in contact with the pipe. In summary, the essential features of copper pitting include 1) the anodic reaction site (the pit), 2) the cathodic reaction site (the adjacent copper surface), 3) a pathway for anions to be transported into the pit (the tubercle), 4) a pathway for cations to be transported to the cathode (water), and 5) a pathway for electron flow from the anode to the cathode (conductive pipe wall).

Although anodic and cathodic corrosion reactions must occur at the same rate, it often happens that the overall rate is set by one of these reactions almost exclusively. Thus, corrosion reactions can either be cathodically controlled if its rate is limited by the rate of reduction reactions at the cathode, or it can be anodically controlled if its 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.

The pitting process as described by Figure 1-1 can be conceptualized as a divided cell in which copper samples are exposed to different environments representative of pitting conditions at anodic and cathodic locations (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 different chemical environments, a battery develops between anodic copper samples and the copper cathode. Theoretically, an ammeter connected between anodic samples (collectively or individually) and the copper cathode would measure a current indicative of electron flow from the anode(s) to the cathode.

Other factors are important in pit initiation and propagation including water flow, pH, natural organic matter, hardness, silicates and the level of oxidants and anions. A comprehensive review of copper pitting corrosion was conducted in 1993 and recent advances in understanding were summarized in 2005 and are not repeated herein (Edwards, 1993, and Nguyen, 2005).

INHIBITION OF CORROSION

Corrosion inhibitors are chemical additives that can be added to drinking water to reduce the rate of corrosion processes. In addition to copper pitting corrosion, there are many other types of corrosion that are of concern in the water industry including concrete corrosion, iron corrosion, uniform copper corrosion, as well as copper and lead leaching into water. All of these corrosion reactions are complex and have different governing chemistries and electrochemistries. As a result, a corrosion inhibitor that may have a dramatic benefit for one type of corrosion may also have no effect on, or even worsen other types of corrosion. In addition, there is no requirement that a product marketed as a "corrosion inhibitor" must actually inhibit any specific type(s) of corrosion, much less all types of corrosion. However, due to the high costs of corrosion, utilities often add inhibitors to their water with the hope or expectation that corrosion problems will be reduced, even if proof of benefits is lacking.

Corrosion inhibitors can be classified by the targeted corrosion reaction they are presumed to hinder. This classification system is based on the concept that inhibitors can primarily reduce the rate of the anodic reaction, the cathodic reaction, or both. Thus, inhibitors are often categorized as anodic inhibitors, cathodic inhibitors, or mixed inhibitors. Such distinctions are more important in non-uniform corrosion applications such as pitting, for which the separation of the anode and the cathode is an essential element of attack. Generally, such distinctions are not made regarding inhibitors for leaching of copper or lead to water, which arises from detachment or dissolution of scale formed via uniform corrosion.

Anodic inhibitors interfere with the anodic corrosion reaction by typically forming sparingly soluble compounds on anodic metal surfaces, thus preventing key components of the anodic corrosion reaction from occurring. Common anodic inhibitors include hydroxides, phosphates, and silicates (Evans, 1936). If present in insufficient quantities, anodic inhibitors have the potential to initiate and/or accelerate localized corrosion attacks if all active anodic sites are not inactivated. For this reason anodic inhibitors are often referred to as 'dangerous' inhibitors (Evans, 1936).

Cathodic inhibitors function by suppressing the cathodic corrosion reaction. This is achieved by reducing the available surface area for the cathodic reaction to proceed. Typically, cathodic inhibitors seal cathodic sites by precipitating an insoluble species onto cathodic metal surfaces. This, in turn, either poisons the catalytically active cathodic location or screens the area from oxidizing agents such as oxygen. Cathodic inhibitors are often referred to as 'safe' inhibitors because they do not have the potential to initiate or accelerate localized corrosion. Common cathodic inhibitors include zinc and magnesium salts (Evans, 1936).

It is sufficient for understanding ‘dangerous’ and ‘safe’ inhibition to consider the following four extreme cases of corrosion inhibition in accordance with theory proposed by Evans (1936):

I. Anodic Control; Anodic Inhibitor
II. Anodic Control; Cathodic Inhibitor
III. Cathodic Control; Anodic Inhibitor
IV. Cathodic Control; Cathodic Inhibitor

The predicted effects of adding an increasing amount of inhibitor in the above cases are quantified with respect to the expected quantity of metal corroded (total corrosion), the expected area attacked, and the expected intensity of corrosion. The intensity of corrosion is defined as attack per unit area of affected parts. Specific to copper pitting, corrosion intensity corresponds to the rate at which a pit penetrates through a pipe wall.

Case I. Anodic Control; Anodic Inhibitor

In this case, the addition of an anodic inhibitor will increase the probability of forming an insoluble precipitate on the metal surface and lead to stifling of the attack considering that the attack is anodically controlled. Thus, it can be expected that the area attacked will decrease proportionally with the amount of inhibitor added, and since the anodic reaction controls the corrosion rate, the expected quantity of metal corroded will proportionally decrease as well. Thus, assuming that the addition of inhibitor is sufficiently small such that the probability of corrosion somewhere on the metal surface is nearly a certainty, the expected intensity of corrosion should remain unaffected. However, as the number of affected corrosion sites becomes increasingly unlikely, the expected intensity will begin to decrease as well.

In summary for Case I, adverse effects due to corrosion are decreased as the concentration of inhibitor is increased according to total corrosion, area attacked, and corrosion intensity. Although anodic inhibitor addition to an anodically controlled corrosion process may not always be very effective, it is a safe treatment in the regards that matters can not become worse than if no inhibitor was added. Figure 1-3 illustrates a qualitative plot of how each measure of corrosion is affected as inhibitor dose is increased in Case I conditions.

Case II. Anodic Control; Cathodic Inhibitor

In this situation, the addition of a cathodic inhibitor will not immediately decrease the total corrosion, but eventually a stage will be reached at which the cathodic reaction becomes so much impeded that it will be comparable to the anodic reaction rate and total corrosion will begin to decrease. The area suffering from corrosion is not likely to be decreased, and, if anything, will increase. This is due to interference from the cathodic inhibitor which prevents sites from supporting cathodic reactions, yet, in some instances, can allow these sites to turn anodic. As the total corrosion is decreased and the expected area attacked remains constant (or is increased in unusual circumstances), the intensity of corrosion is consequently decreased as the concentration of inhibitor increases. Thus, similar to Case I, the addition of a cathodic inhibitor to an anodically controlled corrosion process should be a safe proposition and there is no threat of increasing corrosion rates. Figure 1-4 illustrates a qualitative plot of how each measure of corrosion is affected as inhibitor dose is increased in Case II conditions.

Case III. Cathodic Control; Anodic Inhibitor

Interestingly, consequences are unique in the case of an anodic inhibitor being added to a cathodically controlled corrosion process. Similar to Case I, the addition of an anodic inhibitor will clearly reduce the available *anodic area* subject to attack. However, since corrosion is controlled by the cathodic reaction, total corrosion will actually begin to increase considering that a larger *cathodic area* is now available for the remaining active anodic sites. Thus, as small additions of inhibitor have decreased the expected corroded area yet increased total corrosion, the intensity of corrosion is augmented. In other words, although the area of active anodic sites has been decreased, the active anodic sites will corrode at an increased intensity proportional to the increase of anodic area which has been inactivated. Throughout the process, cathodic corrosion reaction rates will remain relatively unaffected. This condition is a dangerous proposition if the amount of added inhibitor is underestimated and, as stated, can initiate and/or accelerate localized attacks such as pitting.

Only when a sufficient concentration of inhibitor is added will benefits become realized as the reduction of active anodic areas is such that the anodic reaction rate is one comparable to the cathodic reaction rate. At this stage, the expected total corrosion will be reduced and, subsequently, the corrosion intensity will soon decrease as well.

In summary, if an anodic inhibitor is added to a cathodically controlled corrosion reaction in quantities insufficient to completely stop attack altogether, active corrosion area will decrease more quickly than the total destruction of metal, and thus increase the intensity of corrosion. Again, this is a dangerous proposal which is prone to intensify corrosion relative to the situation if no inhibitor was added at all. Figure 1-5 illustrates a qualitative plot of how each measure of corrosion is affected as inhibitor dose is increased in Case III conditions.

Case IV. Cathodic Control; Cathodic Inhibitor

In a corrosion process controlled by the cathodic reaction, the addition of a cathodic inhibitor will steadily lower the total corrosion attack. Although the area available for anodic corrosion will, if anything, slightly increase as seen in Case II, the intensity of attack will decrease steadily as intensity is defined as corrosion per unit area of affected surfaces. 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 illustrates a qualitative plot of how each measure of corrosion is affected as inhibitor dose is increased in Case IV conditions.

INHIBITION OF COPPER PITTING

As previously stated, the propagation and rate of pit growth in copper pipes is believed to be limited by the rate of the cathodic reaction (Nguyen, 2005). In these instances, the corrosion rate is largely fixed by the rate of the reduction reaction of chlorine and/or oxygen at cathodic surfaces and thus, the corrosion reaction is cathodically controlled. Therefore, Case III and Case IV of the previous section are applicable when considering copper pitting inhibition.

Anodic Inhibition of Copper Pitting and the Application of Orthophosphates and Polyphosphates

Case III considered the dangerous proposition of adding an anodic inhibitor to a corrosion process controlled by the cathodic reaction. Specific to copper pitting, this method of inhibition may function by forming a scale or 'cap' over the tubercle which would seal off the anodic site from the aquatic environment and reduce or prevent the transport of anions into the pit. In addition, the removal of Cu^+ and/or Cu^{2+} ions out of the pit would also be reduced or prevented, thus impeding the anodic reaction according to LeChatlier's Principle. Again, both of these components are imperative to pit growth. Figure 1-7 uses a divided cell concept to illustrate how an anodic inhibitor can effectively prevent pitting corrosion by inactivating anodic sites.

As stated, if the addition of an anodic inhibitor is underestimated, only a small fraction of active pits will be inhibited, yet the rate of the cathodic reaction will proceed unaffected. This occurs because the overall pitting reaction is limited by the cathodic reaction and not the anodic reaction, thus changes in the anodic reaction rate will not affect the overall reaction rate. Consequently, the rate of pit growth at remaining active pits will increase to account for repressed anodic reactions from inactivated pits at a rate proportional to the increase of pitting area which has been inactivated. In other words, fewer active pits will exist, but these pits will corrode at a much faster rate. For example, if the number of active pits was reduced by 50%, the rate of corrosion at remaining active pits will double. Figure 1-8 uses a divided cell concept to illustrate how an anodic inhibitor can perform dangerously and increase corrosion rates at active anodic sites if present in an insufficient amount. In practice, this event can ultimately lead to a greater number of pinhole leak failures occurring at a faster rate as illustrated in the generic anodic inhibitor dose response curve of Figure 1-9. Furthermore, this occurrence establishes the fact that an optimally 'bad' dose of anodic inhibitor can exist.

For a given anodic inhibitor, it would obviously be desirable for a water utility to know the dose response curve so that dangerous doses could be avoided. However, given the difficulty and length of time to measure a response as well as the expense of corrosion studies, establishing the dose response curve of an inhibitor for a given utility is not only costly, but impractical. Moreover, for numerous reasons including the complicated solubility of reaction products formed between copper species and anodic inhibitor products such as phosphates, it is likely that dose response curves are specific to a given water as a function of pH and other water quality parameters.

The application of orthophosphates and polyphosphates as anodic inhibitors is of particular interest in this work. Although no research has investigated the effects of orthophosphates or polyphosphates on copper pitting inhibition, McNeill (2000) observed consistent benefits from orthophosphates with respect to copper and lead leaching, and inconsistent, circumstantial or adverse trends from using polyphosphates. In addition, orthophosphates are commonly believed to be the more effective inhibitor between the two and perform by forming an insoluble scale on the metal surface. In regards to copper pitting, the ability for negatively charged phosphate anions to migrate into the pit, where copper cations exist at high concentrations, provides a likely scenario for copper-phosphate precipitates to form at active pit sites. This precipitation reaction explains why an insoluble scale would serve to inhibit the anodic reaction and form only at anodic locations. As polyphosphates are often applied as complexation agents used to complex soluble metal, they have the potential to have adverse effects on copper and lead leaching. Although polyphosphates can react directly to form insoluble scale, it is believed that the reversion of polyphosphates into orthophosphates may play an important role in the effectiveness of a polyphosphate inhibitor (McNeill, 2000). Thus, it is possible for the reversion of polyphosphates into orthophosphates to play an inhibitive role with respect to copper pitting as well.

The performance of phosphate-based inhibitors is very complex and has been shown to be a function of inhibitor type and dose, kinetic considerations, and importantly, water chemistry parameters including pH, temperature, ionic constituents, alkalinity, and natural organic matter concentrations (McNeill, 2000). Research to date has rarely been able to draw conclusions demonstrating cause and effect relationships, much less, identify how phosphate inhibitors specifically function. However, all research supports the general idea they perform by altering scale solubility and/or metal complexation. Figure 1-10 shows the general schematic of a phosphate-based anodic inhibitor and how it could function to inhibit copper pitting.

Cathodic Inhibition of Copper Pitting and the Application of Zinc

The alternative approach to suppress a cathodically controlled corrosion process was presented in Case IV, which considered the addition of a cathodic inhibitor. This method of inhibition is inherently safe, as opposed to the possible dangerous consequences of using an anodic inhibitor. In copper pitting applications, a cathodic inhibitor would perform by forming a scale or barrier on copper surfaces serving as cathodes, thereby screening active cathodic areas from chlorine and/or oxygen. As active cathodic sites produce hydroxide ions (Figure 1-1), high local pHs offer readily available hydroxide ions. The presence of these hydroxide ions, in turn, promotes the precipitation of solids such as calcium carbonate and zinc hydroxide. This is a key principle in effective cathodic inhibition. These precipitates will have a tendency to form at active cathodic sites where high local pHs exist, thereby reducing cathodic reaction rates, pitting currents, and ultimately, the overall pitting reaction and pit growth. Figure 1-11 uses a divided cell concept to illustrate how a cathodic inhibitor can effectively prevent pitting corrosion by inactivating the cathodic site.

Although some research has shown zinc has negligible affects on aspects of copper and lead corrosion such as leaching (McNeill, 2000), these problems do not arise due to non-uniform corrosion as mentioned previously. Thus, the fact that zinc inhibitors have negligible benefits on copper or lead leaching does not imply, circumstantially or conceptually, that it would not benefit copper pitting. Moreover, some research has demonstrated benefits from zinc inhibitors on non-uniform corrosion as would be expected based on theory. For instance, Evans (1939) performed fundamental divided cell experiments confirming zinc can act as a cathodic inhibitor. Specifically, zinc sulfate was shown to have inhibitive effects on an iron cathode connected to a zinc anode. A zinc hydroxide scale was confirmed to persist on the iron cathode even after the zinc-containing solution was removed and replaced by a solution which did not contain zinc. Evans noted that cathodic inhibitors never achieve complete cessation of an attack as do anodic inhibitors added in excess, but benefits of zinc were unambiguous in this type of non-uniform corrosion. Fundamentally, zinc hydroxide precipitation would proceed according to the following reaction:

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2$$

Zin et al. (2004) also identified inhibitive benefits due to zinc. In this case, zinc performed synergistically with calcium and phosphate to effectively cathodically inhibit the corrosion of zinc-coated mild steel coupons. This was achieved through experiments investigating the inhibitive properties of organic coatings containing different amounts and combinations of zinc, calcium, and phosphate inhibiting pigments. Surface analyses and electrochemical methods both determined that zinc, calcium, and phosphate were all necessary for effective inhibition. Zin's work also confirmed the theory that positive charged zinc ions migrate towards cathodic surfaces to form insoluble film depositions in a mechanism triggered by high local pHs. Further, Zin proposed that after zinc species are initially deposited, they can slowly transform into significantly less soluble species. This would imply long term benefits from using zinc as an inhibitor. Similar conclusions regarding increased protective and adhesive properties of calcium phosphate films onto stainless steel cathodes were also found due to synergistic effects from zinc in another study as well (Olesen et al., 1998).

In another study investigating the effects of zinc, Mayer and Featherstone (2000) found that the solubility products for hydroxyapatites containing zinc were markedly lower than for those without zinc and that precipitates had less structural defects when in the presence of zinc. Additional research has been done considering the variety of zinc hydroxide species which can exist, possible mechanisms of deposition, and factors affecting deposition (Jonassen, 1958). Figure 1-12 shows the general schematic of a zinc-based cathodic inhibitor and how it could function to inhibit copper pitting.

In summary, although no research has investigated zinc as an inhibitor for copper pitting, literature and theory suggest that some benefits might be expected in certain circumstances.

EXPERIMENTAL METHODOLOGY

Previous work led to the development of a new method to track pitting corrosion that can provide a direct measure of pitting, real time data, and is inexpensive (Nguyen, 2005). This technique was based on the fundamental concept that separation of anodic and cathodic areas, which is necessary for pit initiation, can occur via differential flow in at least some waters (Marshall, 2004). In practice, such differential flow regimes can occur from greater turbulence at points of the copper surface due to bends or burrs, or from lesser turbulence on copper surfaces under particulate deposits. The role of differential flow was exploited in developing this method which initiates pits on the ends of pieces of copper wire. This, in turn, provided a new way to track pitting by restricting the pit location to the end of the copper wires. This method allowed an electrical connection between the 'pit' and a section of copper pipe supporting flow, yet would also permit a multimeter or elaborate electrochemical instrument to be placed between the 'pit' and the pipe in order to measure the pitting current and resistance. In laymen's terms, this method separates the pit from the pipe. The electron flow passing from the 'pits' to the pipe is termed the '*pitting current*' in this work and is directly proportional to the instantaneous rate of corrosion. The associated voltage and resistance are termed the '*pitting voltage*' and '*pitting resistance*', respectively.

The pits, also referred to as 'pitting wires', were made by inserting solid 18 g electrical grade bare copper wire into a teflon sleeve (ID = 1/16", OD = 1/8"). One end of the pitting wire was flush with the sleeve and sanded to a smooth, circular copper surface using a small handheld sanding tool with a 60 grit sanding band. The resulting surface area (~1 mm^2) is representative of the size of a typical pit and was positioned in direct contact with experimental water. The other end of the pitting wire protruded approximately one inch from the sleeve. This length of copper wire provided the electrical connection to a copper pipe via alligator clips, insulated copper wire and battery clamps. Both ends of the pitting wires were sealed with silicone sealant to prevent water from intruding into the sleeve and contacting any area of the copper wire other than the cross-sectional surface area of the tip. The pitting wires were strategically placed so as to be subjected to flow of a different magnitude than the flow supported in the pipes.

Pitting voltage (potential), current, and resistance were measured using electrochemical instruments or a digital multimeter. Higher current and potential are deemed indicative of greater levels of corrosion. Based upon electrochemical configurations used herein, positive potentials and current would be indicative of anodic pitting on the copper wire tips. Thus, negative values indicate that the pitting wire is cathodic (non-pitting) relative to the pipe. A current density, or pitting rate, of 1 $\mu A/cm^2$ creates a pit in a Type M copper pipe in 61 years according to the following equation:

$$r = 0.129\left({}^{iA}\!/_{nD}\right)$$

Where, r = corrosion rate (milli-inches/year)
i = current density ($\mu A/cm^2$)
n = number of electrons transferred for each atomic weight reacted
a = atomic weight
D = density of alloy (g/cm^3)

Pitting resistance can also provide an indication of pitting propensity. Since the resistance of water is relatively low, higher resistances between pitting wires and the pipe indicate that a protective film is forming on the copper surfaces that may reduce rates of corrosion. In general, higher resistances are believed to indicate a more protective pipe scale.

This inexpensive method can be used to determine relative pitting propensities of a water under experimental conditions. Experimental conditions used in this work considered the addition of different corrosion inhibitors, different disinfectant methods, and/or altered water quality parameters. However, this experimental method can only work decisively in situations where it is possible to force the formation of a pit on the tip of a wire. Figure 1-13 illustrates the general schematic of the pitting wire experimental setup.

In addition to the aforementioned method, the following methods were also incorporated into the experimental methodology herein:

- Electrochemical Rise (E_{Corr})
- Surface Analysis
- Chlorine Decay Kinetics

Electrochemical rise, more commonly referred to simply as E_{Corr}, is the most widely applied and often most successful means of determining pitting propensity. An E_{Corr} measurement quantifies the electrical potential existing between a metal sample and a reference electrode such as a Ag-AgCl or Calomel electrode. In copper pitting, copper pipes represent the metal sample. Pourbaix determined that when a new copper was exposed into a water, E_{Corr} would typically rise to within 100 mV vs. Ag-AgCl after a period of days and then stabilize (Pourbaix, 1969). However, in waters that supported copper pitting, E_{Corr} would continue to rise over a period of months to a critical value at which point pit initiation and propagation would have occurred. This overall trend is collectively referred to as electrochemical rise. Mechanistically, E_{Corr} rise occurs from electron deficiency; thus it can be caused from the reduction of the anodic reaction, acceleration of the cathodic reaction, or both. The fact that E_{Corr} rise is often correlated with pitting propensities offers support in favor of Nguyen's hypothesis that copper pitting reactions are under cathodic control; given that factors which accelerate the cathodic reaction or hinder the development of anodic surfaces tend to encourage pitting.

Surface analysis of copper pipe and copper coupons can be used to quantify scale formation and weight loss due to corrosion. In addition, these samples can be examined for visual indications of pitting. In the experiments herein, a scanning electron microscope (SEM) equipped with electron dispersive spectrometry (EDS) was used to identify elements present on the interior surface of each coupon down to a depth of 1 µm.

Greater rates of chlorine decay are indicative of higher rates of reduction reactions at cathodic surfaces, which are a key factor driving copper pitting. Total chlorine concentrations were recorded in the experiments herein to determine chlorine decay kinetics and quantify relative pitting propensities among experimental conditions.

OTHER METHODS OF TRACKING AND PREDICTING PITTING

Only a few studies have been carried through to the point where large pits or fully penetrating pinholes formed on copper samples in the test water (Cornwell et al., 1973, Smith and Francis, 1990, Marshall, 2004, and Fuji et al., 1984). Table 1-2 summarizes the most common methods used to measure pitting propensities. A comprehensive review of these methods was conducted recently (Nguyen, 2005). It is important to note that any test that uses artificial currents, artificial potentials, or chemicals to initiate pits might not reproduce pits as they occur in practice and can therefore provide faulty advice. Techniques that can potentially track pitting without artificial currents, potentials or chemicals (E_{Corr} rise and electrochemical noise) have provided insight, although they are indirect methods and conventional interpretations might not be accurate.

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Table 1-1. Summary of suspected copper pitting mechanisms.

Probable 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
Cl2-Al-high pH	100%	Aluminum deposits cause non-uniform attack	pH > 7.8 Cl2 > 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 Cl2-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

Table 1-2. Historical summary of pitting test methods.

Pitting Test	Approach	Reference	Initiation/ Propagation	Comments
Macrocell with physically separate copper anode and copper cathode	Measure current and potential difference between anode and cathode to track pit initiation and propagation.	Bengough and May, 1924; May 1953, Lucey , Sosa et al., 1999; Poubaix, 1971	Initiation and Propagation	A chemical difference that initiated pitting was imposed artificially by adding CuCl or by removing oxygen from the anode. The potential differences and currents that resulted in different waters were reasonably correlated to pitting tendencies.
Macrocell with pit wire anode and copper cathode	Artificially impose constant potential difference between anode and cathode, measure pitting current	Mattsson et al., 1968; Campbell, 1954	Propagation only.	Reasonable correlation of pitting currents with the water chemistries known to allow pits to propagate in hot water. Addresses both anodic and cathodic reactions.
Potential rise	Measure E_{corr} for copper immersed in water	Pourbaix et al. 1971; Cornwell et al., 1973; Fuji et al, 1984; Rushing et al., 2002; Marshall et al., 2004	Initiation	In waters that support pitting, potential slowly rises to a critical value, at which point pitting begins. In waters that do not support pitting, this rise in potential does not occur. Good ability to distinguish between waters that cause pitting and those that do not in a given study.
Electrochemical noise	Two or three identical copper samples immersed in same pitting water, measure current between each.	Smith and Francis (1990); Sandenbergh et al., 1996; Kane et al, 2003; Rushing et al., 2004; Duranceau et al., 2004	Initiation	Results in Smith and Francis work and Duranceau et al. were considered promising. However, work by Sandenbergh et al. 1996 demonstrated that that the test actually detected uniform corrosion and not pitting tendencies. Rushing, Sandenbergh and Korshin both point out that much variation in E_{corr} occurs during changes in flow due to different disinfection concentration.
Electrochemical Pitting Test Cell with Applied Potential	8 copper wires used as anodes at distances from 1 to 25 cm from the wire cathode. A 4 uA current is imposed.	Goodman et al., 1984;	Propagation	In waters that support pitting, the majority of the current is concentrated at the copper wire closest to the cathode. In waters that do not support pitting, the current gradually moves towards anodes located further from the cathode.
Accelerated aging	Platinum cathode and copper anode, imposed potential.	Shalaby et al., 1990; Edwards et al, 1993 and 1994; Singh et al, 1992	Propagation	In waters that support pitting, the anodic current rises with time of polarization. In waters that do not support pitting, current decreases with time.
Electrochemical Pitting Test Cell with Applied Current	12 copper wire tips used as potential anodes and a long exposed copper wire cathode. A 15 uA current is imposed.	Goodman et al., 1984; modification developed by Ansuini, 1991	Propagation	In waters that support pitting, the majority (often 100%) of the anodic current is carried by the single wire that is partly screened from the bulk water. In waters that do not support pitting, the current carried by this water is less than 20% of the total.
Proposed test: Separate anode and cathode	Wire anodes connected to large pipe cathode	This work	Initiation and Propagation	Pits formed naturally by differential flow, pit growth measured directly using ammeter.

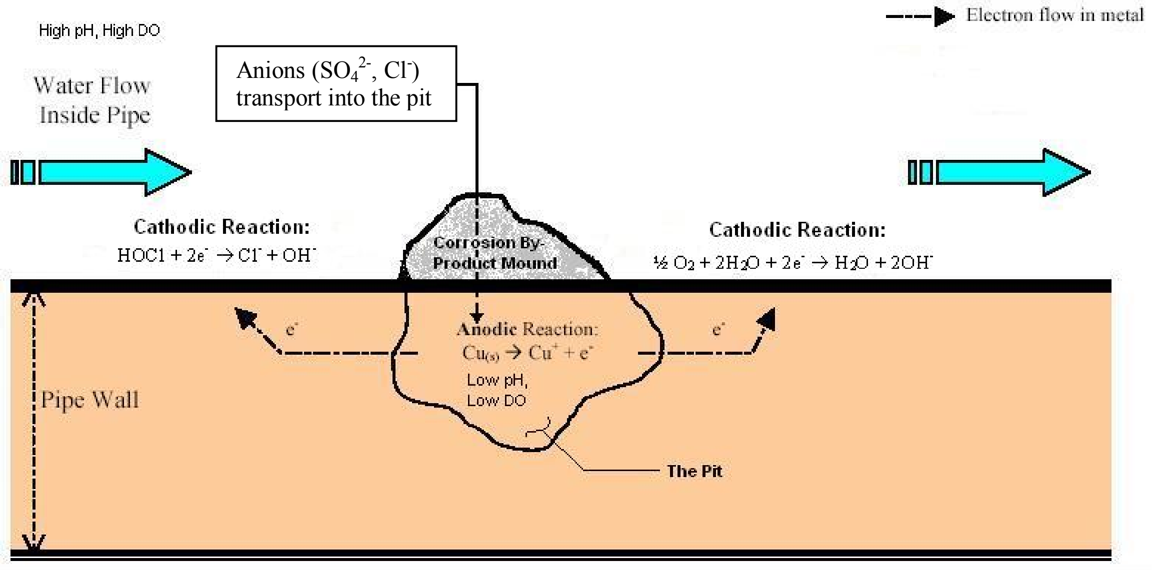

Figure 1-1. Key reactions, locations, and elements of copper pitting.

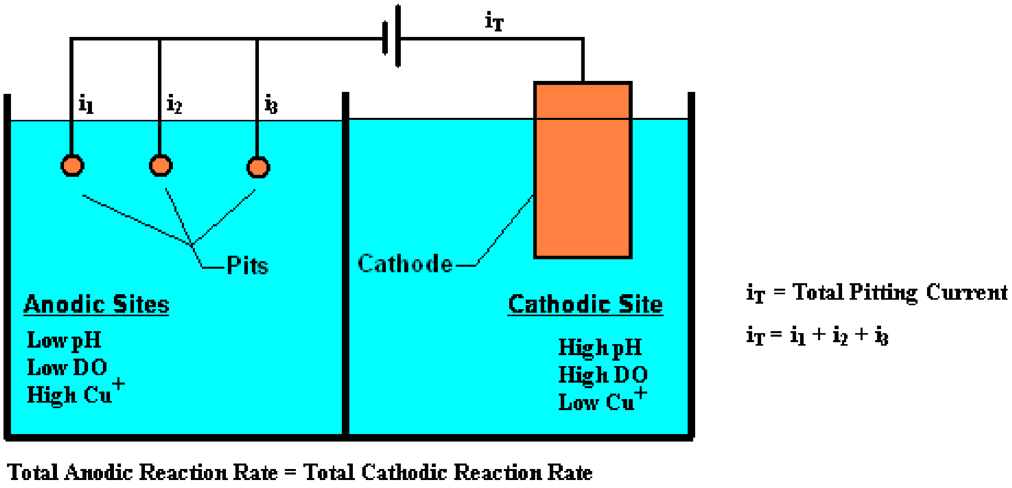

Figure 1-2. Divided Cell - Conceptual illustration of copper pitting process.

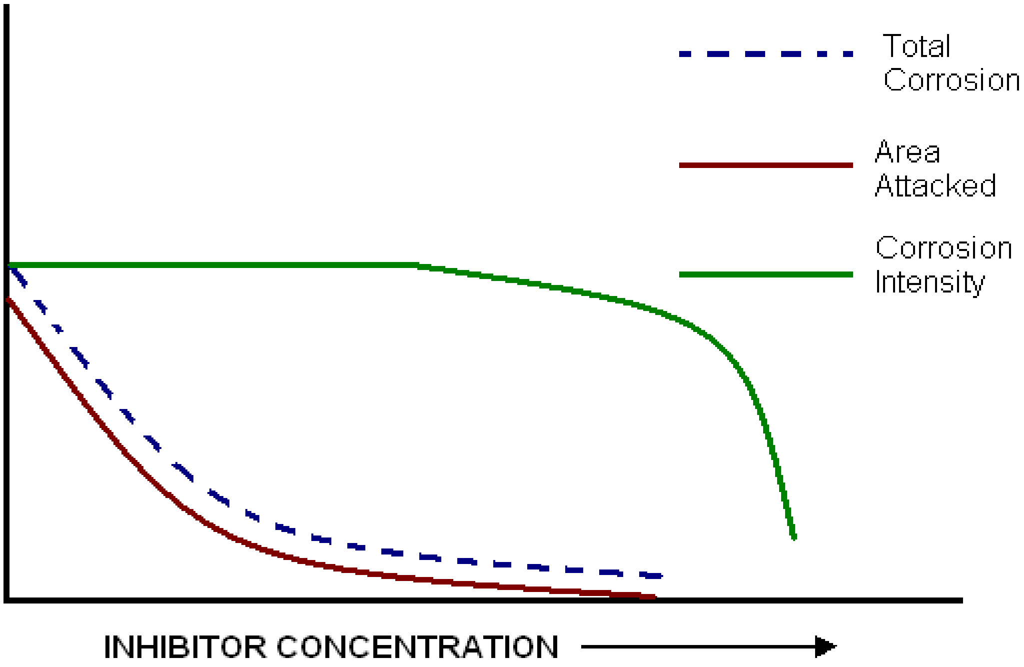

Figure 1-3. Case I - Anodic Control; Anodic Inhibitor – Plot of corrosion measurements per inhibitor concentration.

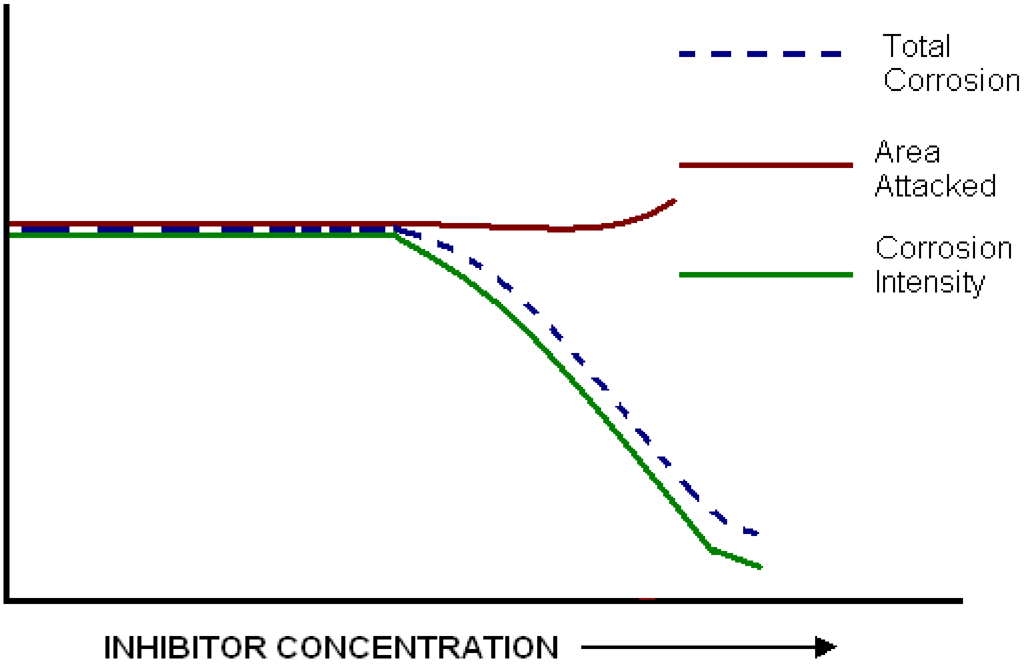

Figure 1-4. Case II - Anodic Control; Cathodic Inhibitor – Plot of corrosion measurements per inhibitor concentration.

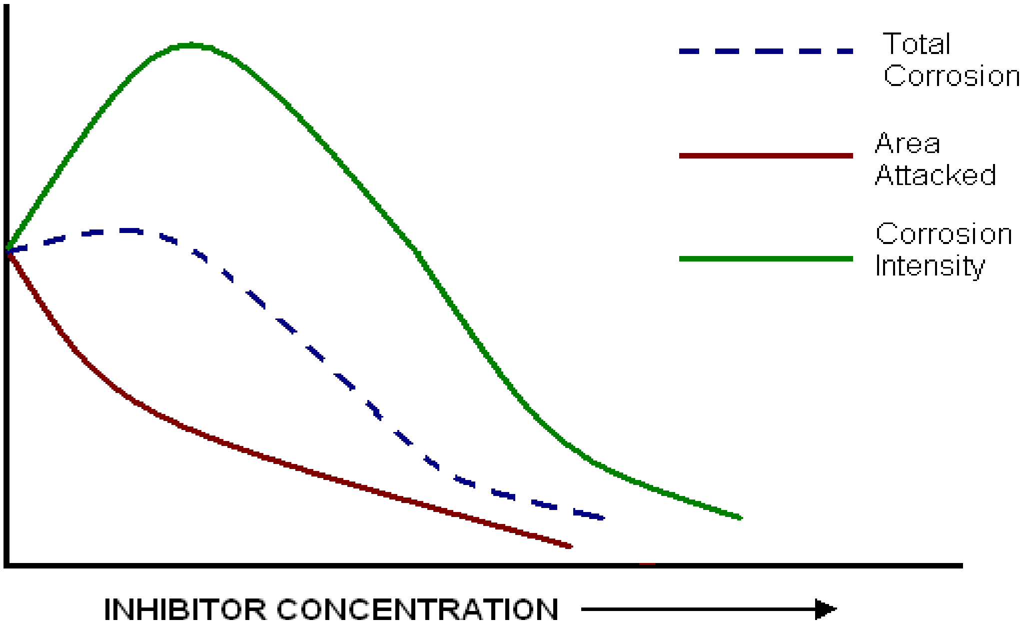

Figure 1-5. Case III - Cathodic Control; Anodic Inhibitor – Plot of corrosion measurements per inhibitor concentration.

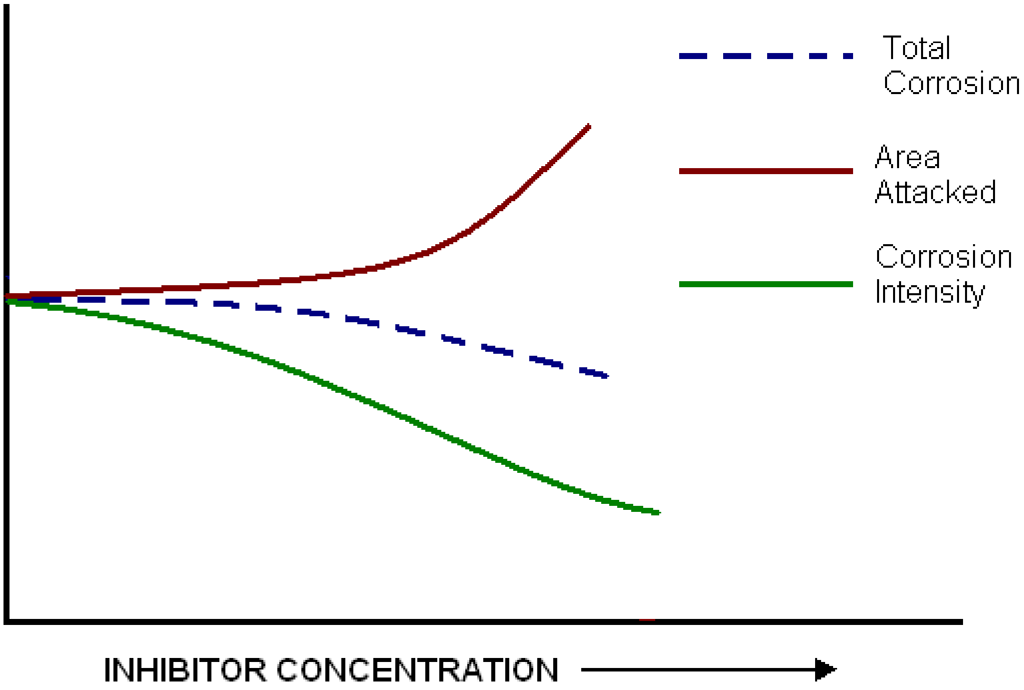

Figure 1-6. Case IV - Cathodic Control; Cathodic Inhibitor – Plot of corrosion measurements per inhibitor concentration.

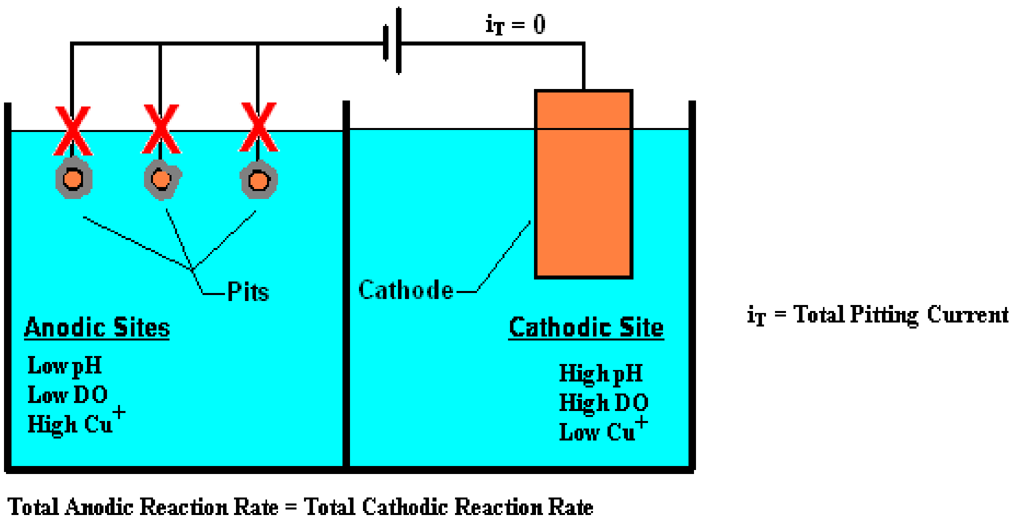

Figure 1-7. Divided Cell - Conceptual illustration of effective anodic inhibition.

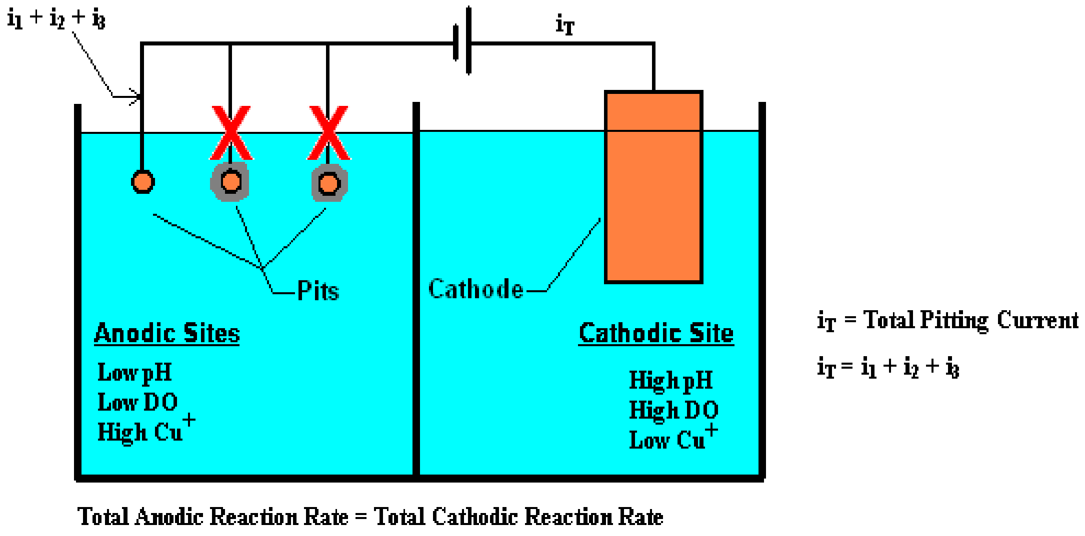

Figure 1-8. Divided Cell - Conceptual illustration of ineffective anodic inhibition.

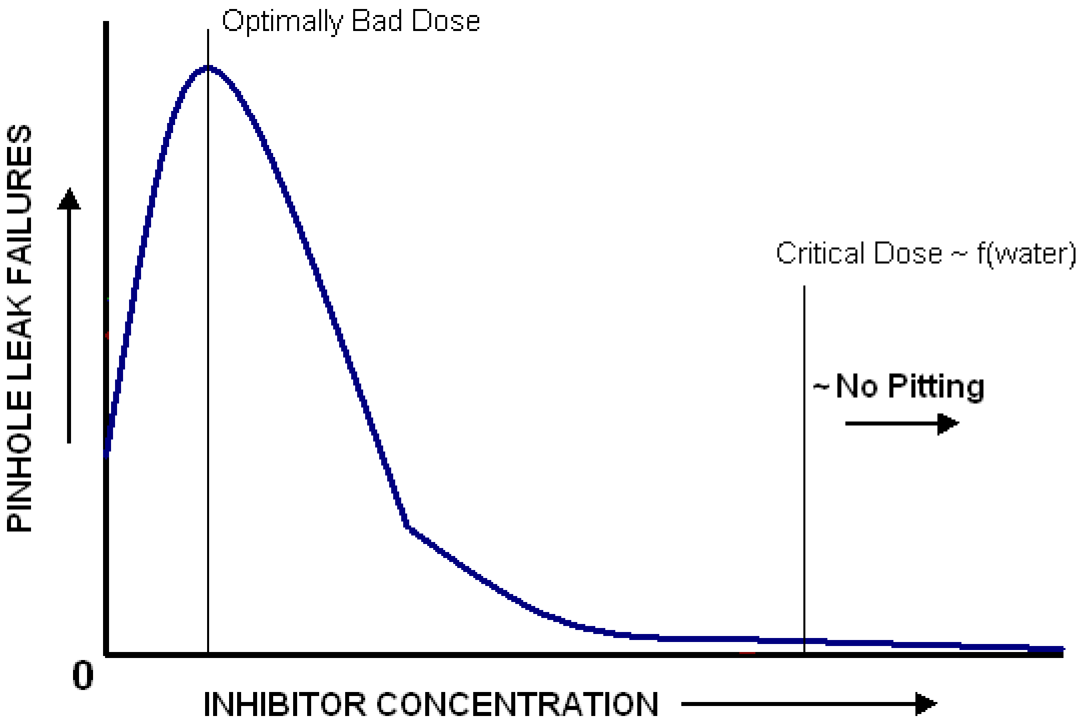

Figure 1-9. Typical anodic inhibitor response curve.

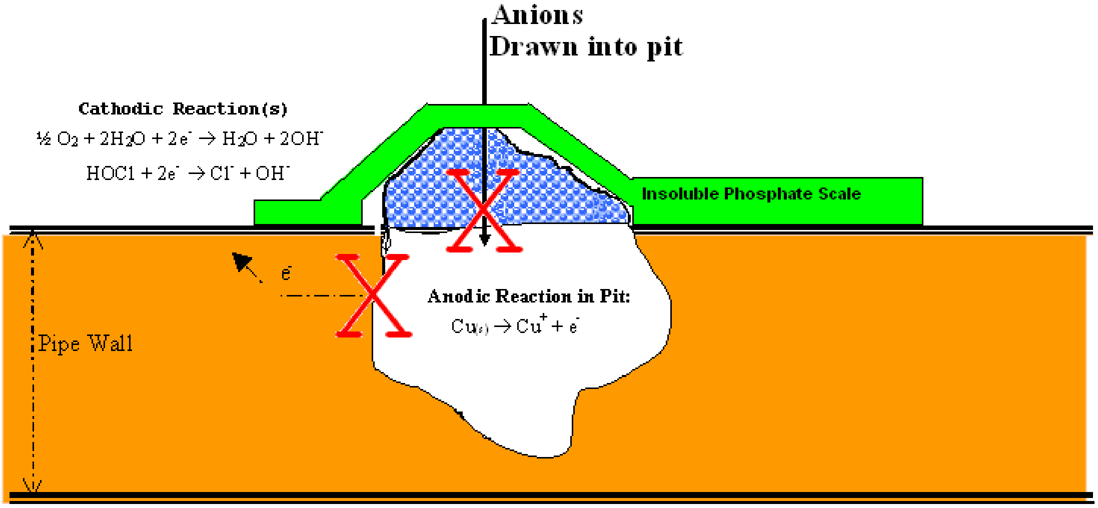

Figure 1-10. General schematic of copper pitting inhibition via phosphate-based anodic inhibitors.

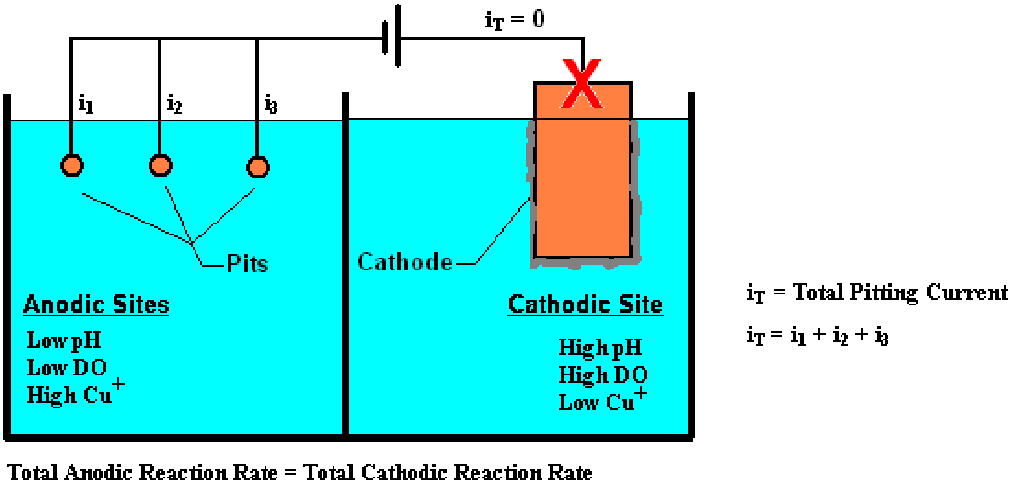

Figure 1-11. Divided Cell - Conceptual illustration of cathodic inhibition.

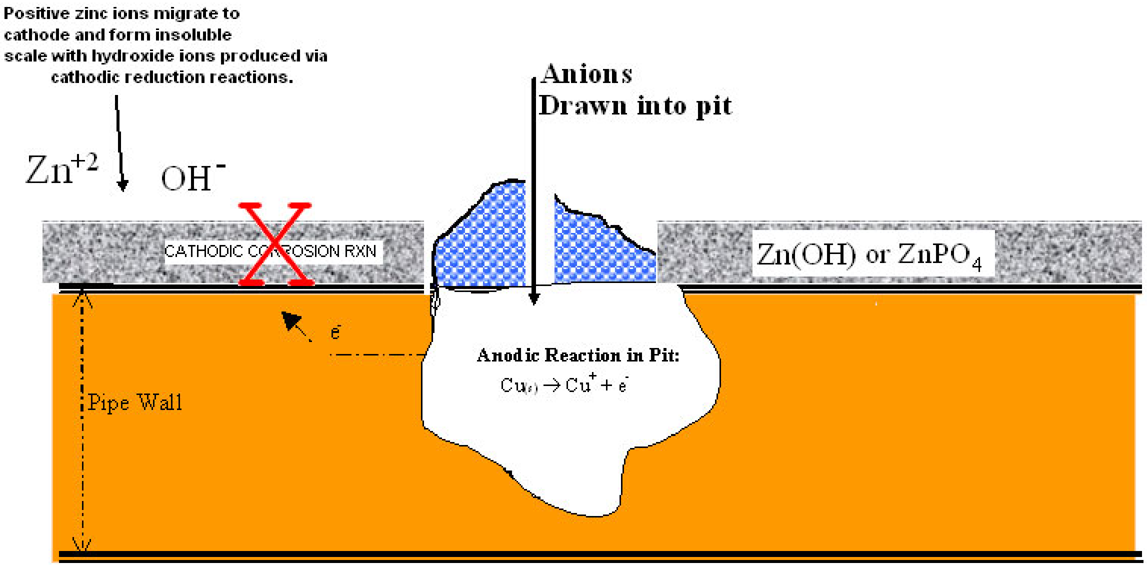

Figure 1-12. General schematic of copper pitting inhibition via zinc-based cathodic inhibitors.

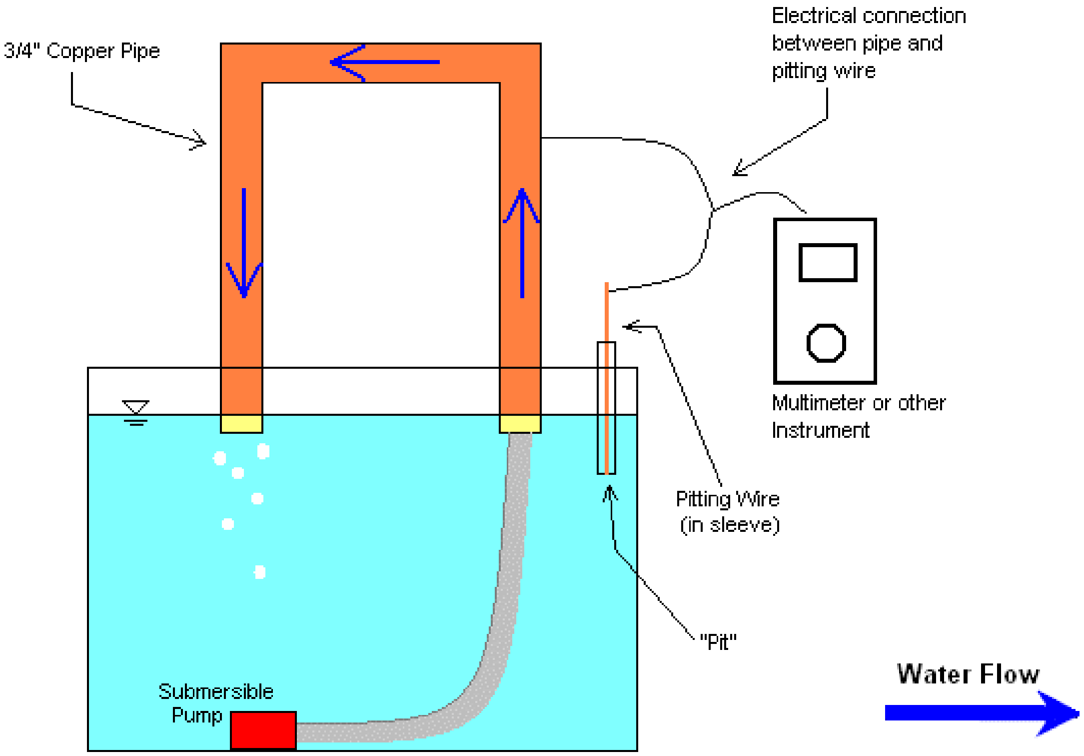

Figure 1-13. General schematic of experimental setup and pitting wire installation.

Chapter 2: Case Study of Copper Pitting Corrosion – Florida Utility

Gregory Sheffer, Marc Edwards, Nestor Murray, and Paolo Scardina

ABSTRACT

Effects of different phosphate-based corrosion inhibitors on copper pitting propensity were examined in potable water from a Florida utility whose customers are experiencing pitting problems. Electrochemical methods and surface analyses were used to evaluate inhibitors including orthophosphate, zinc polyphosphate, and a blend of orthophosphate and polyphosphate. Zinc polyphosphate significantly reduced electrochemical indications of pitting relative to the other inhibitors tested. E_{Corr} of the rig dosed with zinc polyphosphate was approximately 60 mV less than the other conditions. In addition, the zinc polyphosphate system produced less pipe scale corrosion than other conditions. Surface analyses suggested that zinc and phosphorus may behave synergistically when precipitating as an inhibitive scale. Electrochemical results provided indications that the use of either orthophosphate or the orthophosphate-polyphosphate blend would actually make pitting worse than if no inhibitor was used at all.

INTRODUCTION

Potable water in the portion of the distribution system that experienced severe pitting was produced by the subject utility using electrodialysis reversal (EDR) treatment of local groundwater. Prior to EDR, the groundwater is degassed, chlorinated, and passed through sand/GAC dual media filters. Following EDR treatment, chloramines (formed by addition of chlorine and ammonia) are added for secondary disinfection. The target pH of 8.5 is achieved by dosing sodium hydroxide. The average total chlorine and ammonia concentrations during 2005 were 4.7 mg/L as Cl_2 and 1.5 mg/L NH_3 as N, respectively. Other typical water quality parameters are listed in Table 2-1.

Before distribution, product water from the utility is blended in an approximate 1:1 ratio with treated surface water purchased from another entity. In 2005, total water production averaged 10.5 MGD. At a later phase of this study, the ratio of water produced by the utility to purchased water (UW:PW) was increased to 63:37 and average total water production increased to 12.3 MGD. The purchased water is also disinfected with chloramines and is transported through 25 miles of 42" pipeline leading to the subject utility.

Since 1999, nearly epidemic levels of copper pinhole leaks occurred in areas of the distribution system served by the subject utility. Door to door surveys by some homeowner associations revealed that about 50% of homes in some neighborhoods have experienced at least one leak. Even three year old homes in the area have experienced leaks. News of such serious problems prompted "pre-emptive" residential replumbs, and when added to the existing workload repairing systems with actual leaks, plumbers' backlogs were such that up to a three month wait was necessary before a new replumb job could be started. On the basis of beneficial effects observed elsewhere, orthophosphate was dosed at the subject utility in 2003 in an attempt to alleviate copper pinhole leaks. However, records from a plumbing supply store and other anecdotal evidence indicated that replumbs continued to double each year, suggesting that orthophosphate was not helping to reduce the extent or frequency of the problem (Edwards, 2005).

On the basis of a recommendation by Darren Lytle of the EPA and research by the University of Cincinnati, the utility stopped dosing orthophosphate in September 2005 and began dosing an orthophosphate-polyphosphate blend in the finished water. As of February 2006 (five months later), the consensus was that the inhibitor had not yet produced any noteworthy decrease or increase in the frequency of pitting relative to the use of orthophosphate based on reports of replumbs. In late 2005, the utility began to collect data from leak detection companies on the number of actual leaks responded to each month. From November 2005 to February 2006 leaks did not show a significant decline, but by March the number of reported leaks started to decline relative to levels observed in January. As of now, it is uncertain whether the new inhibitor was responsible for a real improvement or not. Specifically, so many homes had been re-plumbed (more than 50% in some areas) that the population of copper pipe has significant decreased. In addition, other utilities have reported seasonality in leak frequency which results in month to month declines. Among other confounding factors in comparing reduced leaks from January to March: 1) the percentage of the source water thought to have the highest pitting propensity was decreased in the finished water, 2) the total chlorine that contributes to drive pitting was decreased markedly, and 3) many Florida homeowners return north after the winter and close their homes.

This study was aimed at identifying the effectiveness of different corrosion inhibitors with respect to pitting propensity using surface analyses and electrochemical methods including E_{Corr} rise and the electrical potential measurement between adjacent sections of copper pipe. E_{Corr} has been widely related to the pitting propensity of a water, and it is generally observed that water quality changes that decrease E_{Corr} or that prevent a rise in E_{Corr} will reduce the severity of copper pitting (Marshall, 2004). In the area served by the subject utility, pits occurred with the greatest frequency on the horizontal sections of pipe bringing water into the home. Pits occurred with reduced frequency on sections of plumbing further from sections of pipe in first contact with the water. Thus, for a home, the first lines carrying water into the home is the site of the worst anodic activity (e.g., the greatest number of pits). Exactly why this occurs in practice is uncertain, but a similar trend was noted in Marshall's laboratory study of pitting using synthesized water. In Marshall's well controlled experiment, pits occurred in the part of the pipe closest to the reservoir. Thus, electrical potential measurements between sections of adjacent copper pipe can provide indications of relative pitting propensities.

In addition, an innovative approach in this work attempted to create live pits. In this method, attempts were made to develop pitting wires that allow pitting current, potential, and resistance of artificial pits to be measured with a simple multimeter as described in Chapter 1.

The corrosion inhibitors investigated were orthophosphate, zinc polyphosphate, and an orthophosphate and polyphosphate blend. Orthophosphate was used due to its popularity as a corrosion inhibitor, as well as for the fact it was being used in the product water of the subject utility at the time experimental work was initiated. At the time of this work, the consensus was that dosing orthophosphate had no benefits regarding pitting at this utility and may have even made things worse. Zinc polyphosphate, which is also commonly referred to as zinc metaphosphate or zinc hexametaphosphate, was tested because it was being used as an inhibitor by an adjacent utility whose water was serving another part of the same distribution system served by the subject utility. This part of the distribution system has not experienced severe pitting problems. However, many other differences between the waters of the two utilities exist that might explain the lower frequency of pitting in that part of the system including a lower pH and lower concentration of chlorine residual. Finally, an orthophosphate and polyphosphate blend present in a 1:1 ratio was also tested. This orthophosphate-polyphosphate blend was under consideration for use by the utility at the time these experiments were initiated and the inhibitor was eventually tested full-scale starting in September of 2005.

MATERIALS AND METHODS

The five month study used four 55 gallon reservoirs operating in a continuously circulated mode at the water utility. Each rig circulated water at 2 gpm using a submersible pump from within the 55 gallon reservoir upwards thru four 2” Type M copper coupons and three feet of ¾” Type M copper pipe to a 90° CPVC bend, horizontally across six inches of ¾” CPVC, and then back down three feet of ¾” Type L soft copper pipe (Figure 2-1). The outer surface of the soft copper pipe protruded only a few inches into the reservoir, and was protected by plastic tubing sealed with silicone sealant. Thus, only the inner surface of all copper pipe used was exposed to experimental water. Mixing pumps rated at 18 gpm were later installed to ensure uniform water quality.

The initial phase of work exposed all four rigs to water from the part of a distribution system close to homes with pitting problems. This water contained orthophosphate at a concentration of 2 mg/L PO_4 as P. After 18 days of exposure designed to allow pits to initiate, the pipes were then exposed to water from the subject utility without orthophosphate.

After baseline data was established, corrosion inhibitors were added to the rigs on Day 93 and were maintained at target concentrations. Inhibitors were dosed to three of the rigs to include either 1) orthophosphate, 2) zinc polyphosphate, or 3) the orthophosphate-polyphosphate blend. No inhibitor was added to the remaining fourth rig as a control.

On Day 115, the target pH was decreased from 8.5 to 7.5 to determine if pH played a role on pitting propensity as it has been shown that lower pHs decrease the pitting propensity of a water relative to higher pHs (Marshall, 2004). On Day 138, zinc was dosed into the rig containing the orthophosphate-polyphosphate blend to exclusively examine the effect of zinc considering that results from the rig containing zinc polyphosphate were very promising.

Over the course of the experiment, initiation of pits was monitored under a range of circumstances which altered chloramine concentrations, pH, and the UW:PW ratio. Aluminum was added to the rigs from Day 44 to Day 78, because high levels were known to have been in the water in areas experiencing pitting, and it was deemed possible that this helped to initiate the process. Higher total chlorine concentrations, higher pH, and aluminum have been shown to increase pitting propensity in a system with free chlorine (Marshall, 2004). A timeline summarizes water quality changes during the experiment as shown in Figure 2-2. Table 2-2 lists target experimental water quality parameters as well as additional information regarding constituents added to the rigs.

Water quality was typically maintained daily and parameters were recorded. Total chlorine concentrations were recorded to determine chlorine decay kinetics. Greater rates of chlorine decay are indicative of higher rates of reduction reactions at cathodic surfaces, which are a key factor driving copper pitting (Chapter 1). Unfortunately, chlorine decay rates calculated in this experiment did not produce any trends via t-tests at greater than 90% confidence. Trends were difficult to establish as limited data existed and water changes occurred frequently. In addition, samples were taken at the end of the experiment and analyzed for total metals concentrations using inductively coupled plasma mass spectroscopy (ICP-MS).

Real Time Electrochemical Measurements

Corrosion potential (E_{Corr}) and selected pitting current measurements were continuously collected for periods of the experiment using a Gamry ECM-8 multiplexer and potentiostat in a zero resistance ammeter mode. A positive current indicates that the pitting wire is anodic relative to the pipe, whereas a negative pitting current indicates that the pipe is anodic relative to the pit. Of these, a positive current is deemed worse with respect to pitting and the magnitude of current is proportional to the magnitude of the problem.

In general, higher E_{Corr} indicates increasingly aggressive water. Ag-AgCl reference electrodes, used to measure E_{Corr}, were maintained regularly to ensure accuracy. In addition, the potential between upstream and downstream sections of pipe was continuously measured using the Gamry instrument. According to the configuration used, a positive difference occurs when the first section of pipe (the pipe the water flows through first) is anodic to the second section. Thus, a negative potential difference indicates that the first section is cathodic to the second section. Of these, a positive difference is deemed worse with respect to pitting propensity.

Pitting Current, Potential, and Resistance

Pitting wires were made by inserting solid 18g electrical grade bare copper wire into a teflon sleeve (ID = 1/16”, OD = 1/8”). One end of the pitting wire was flush with the sleeve and sanded to a smooth, circular copper surface using a small handheld sanding tool with a 60 grit sanding band. This surface area (1 mm^2) represents the pit which was in direct contact with the water. The other end of the pit wire protruded approximately one inch from the sleeve. This length of copper wire was electrically connected to the pipes supporting flow via alligator clips, insulated copper wire and battery clamps (Figure 2-3). Both ends of the pitting wires were sealed with silicone sealant to prevent water from intruding into the sleeve.

The tips of the pitting wires were positioned in the water to investigate high and low flow conditions, as well as to consider effects of 90° bends immediately before a potential pitting location. Pits exposed to high flow conditions (high flow pits) were placed directly into the copper pipe effluent, pits exposed to low flow conditions (low flow pits) were placed 10” from the copper pipe effluent where the water was quiescent, and pits exposed after 90° bends (90 degree in-flow pits) were placed into the horizontal CPVC section connecting upstream and downstream copper pipes (Figure 2-3). Five new pitting wires were installed on each rig on Day 110 because most of the existing pits had died on all rigs. Although pitting wires failed at all locations, pits installed on Day 110 were only positioned in low flow conditions due to ease of installment.

Ultimately, nearly all of the pits died and results of the pitting wire tests cannot be deemed to have replicated “live” pits as had been anticipated. This indicates that pits could not reproducibly be formed on the pitting wires in question, and that some factor other than low or high water flow is involved in getting pits started in this particular water, at least with a high degree of reproducibility. However, relative pitting current comparisons among experimental conditions is still deemed a measure of pitting propensity in these tests, since it is believed that factors which tend to oppose separation of anodic and cathodic areas on pipe is a key factor that helps to stop copper pitting.

Pitting potential (voltage) and current were measured between the pitting wires and the pipe using a Fluke 189 True RMS Digital Multimeter. Higher current and potential are deemed indicative of greater levels of corrosion. The resistance between pitting wires and the pipe was also measured using the same instrument. Since the resistance of the water is relatively low, high resistances indicate that a protective film is forming on the copper surfaces that may reduce rates of corrosion. In general, higher resistances are believed to indicate a more protective pipe scale.

Surface Analysis of Copper Coupons

Each rig incorporated four ¾” Type M copper coupons. Each coupon was 2” in length. Coupons were weighed both before and after the experiment to quantify any scale formation and/or weight loss due to corrosion. Perhaps more significantly, these coupons were also examined for visual indications of pitting. A scanning electron microscope

(SEM) equipped with electron dispersive spectrometry (EDS) was used to identify elements present on the interior surface of each coupon down to a depth of 1 µm.

Short Term Jar Tests

After long term field test experiments, two jar tests were conducted to investigate the role of the ratio of chlorine to ammonia on pitting propensity, as well as the exclusive role of total chlorine concentrations at a constant chlorine to ammonia ratio. Tests were conducted in 1 L glass jars containing 2 cm square copper foil coupons (Figure 2-4). Final product water from the subject utility, dosed with the orthophosphate-polyphosphate inhibitor, was mailed to the lab at Virginia Tech and used in both tests. The average concentration of the inhibitor was 0.6 mg/L PO_4 as P. E_{Corr} was measured using a Ag-AgCl reference electrode and Fluke 189 multimeter.

Investigating the Role of the Chlorine to Ammonia Ratio

Product water was adjusted with sodium hypochlorite so that total chlorine concentrations were 12 mg/L as Cl_2 in all containers. Target ammonia concentrations were achieved with an ammonium hydroxide solution so that resulting chlorine to ammonia ratios were 2:1, 4:1, 5:1, or 6:1. All solutions were stirred at 350 rpm with a one inch stirbar for four days at which time all containers were emptied, filled with fresh water, and adjusted to target chlorine and ammonia concentrations. Following this water change, solutions were monitored for the next five days. E_{Corr} and chlorine concentrations were measured daily over the duration of the experiment. A target pH of 8.5 was obtained for all solutions.

Investigating the Role of Chlorine

Product water was adjusted with sodium hypochlorite so that the total chlorine concentration was 2, 4, 15, or 50 mg/L as Cl_2. Beforehand, ammonia concentrations were adjusted to target levels with an ammonium hydroxide solution so that the resulting chlorine to ammonia ratios were all 3.8:1. All solutions were stirred at 350 rpm with a one inch stirbar for four days at which time all containers were emptied, filled with fresh water, and adjusted to target chlorine and ammonia concentrations. Following this water change, solutions were monitored for the next four days. E_{Corr} and chlorine concentrations were measured daily over the duration of the experiment. A target pH of 8.5 was obtained for all solutions.

Short Term Rig Test of Zinc Effects

An additional short term, small scale, rig test was conducted using product water from the utility to exclusively investigate the role of zinc on copper pitting inhibition. This experiment also investigated inhibitive properties of the particular zinc polyphosphate product used in the chief rig experiments at the subject utility. The experiment ran in parallel to the short term jar tests and used the same bulk water which contained the orthophosphate-polyphosphate inhibitor. The experimental rig configuration mimicked the full scale rigs at the water utility. Rigs were constructed using an 8” length of ¾” Type M copper pipe to support flow, four pitting wires (two low flow, two high flow), and a 3.5 gallon reservoir (Figure 2-5). Water circulated at a rate of 2 gpm using a submersible pump.

Total chlorine was maintained at 10 mg/L as Cl_2 with daily water quality adjustments. The ammonia concentration was 2.5 NH_3 as N and pH was 8.5. Zinc was added as zinc chloride, and in part of the experiment the chloride concentration in the rig without added zinc was increased to match the chloride concentration in the rig with added zinc by dosing sodium chloride. Zinc concentrations ranged from 0.4 – 4.0 mg/L as Zn and were measured using inductively coupled plasma mass spectroscopy (ICP-MS). E_{Corr} and pitting current measurements were collected continuously using a Gamry ECM-8 multiplexer and potentiostat in a zero resistance ammeter mode.

After 11.5 days, the rigs were emptied, filled with fresh water, and adjusted back to target chlorine, ammonia, and pH levels. Pitting wires were also installed on Day 11.5. On Day 24.5, the zinc polyphosphate product was added to the rig which had been previously dosed with zinc. These short term rig tests operated for a total of 31.5 days.

RESULTS AND DISCUSSION

After collecting baseline data from the four test rigs to show that they were essentially identical, inhibitor dosing was initiated and electrochemical behavior was monitored. Thereafter, short-term lab tests were undertaken to focus on the role of total chlorine concentration and the ratio of chlorine to ammonia (used in forming chloramines) with respect to pitting propensity. The role of zinc in copper pitting inhibition was also investigated in a separate short-term test.

Baseline Data

The rigs were operated several months while exposed to identical water qualities in order to initiate pitting and confirm no substantial differences in E_{Corr} existed among the rigs. E_{Corr} measurements were taken for a period of days before making changes in water quality. Figure 2-6 illustrates that all E_{Corr} values were within 15 mV of one another. Thus, no systematic bias was present in the samples before adding inhibitors.

Initial Results after Addition of Inhibitors

Electrochemical measurements were taken on the days immediately before and after the addition of inhibitors. Benefits were realized from all inhibitors nearly immediately according to continuous pitting current measurements of selected 90 degree in-flow pitting wires (Figures 2-7, 2-8, and 2-9). Pitting wires at this location were used for comparison as they produced the greatest pitting currents among all pitting wires. It is noteworthy to mention that high flow pitting wires and low flow pitting wires, respectively, sustained the next greatest pitting currents.

According to pitting currents, the greatest benefits were measured in the rig dosed with zinc polyphosphate. From this perspective, the zinc polyphosphate significantly decreased the current of both pits measured (Figure 2-7). Before the inhibitor was dosed, the pits in this rig supported the highest currents among all the rigs. However, after the addition of zinc polyphosphate, these pitting currents decreased to the two lowest currents measured among all rigs. In fact, in the system dosed with zinc polyphosphate, the current was initially anodic (e.g., positive current indicates the wire is pitting) and turned cathodic (protective). This indicates that the inhibitor completely eradicated pitting tendencies for these wires.

Pitting currents in the orthophosphate-polyphosphate system decreased as well; however, one of the two pits measured was still slightly pitting because a small positive current was supported (Figure 2-8). The other pitting wire supported a slight non-pitting current. Similar results were obtained for the orthophosphate rig; however, both pits originally supporting pitting currents turned slightly non-pitting upon adding orthophosphate (Figure 2-9). In comparison, the two pitting wires measured in the control rig demonstrated contradicting results. One of the pits originally supported a slight non-pitting current, but once inhibitors were added to the other rigs, the system supported a small pitting current (Figure 2-10). The other pit in the control rig initially supported a strong pitting current, but eventually decreased. However, the original pitting current was still sustained for approximately six days after the time of inhibitor addition. Overall, while the results must be deemed inconclusive due to problems initiating pits on the ends of the pitting wires, the trends indicate clear relative benefits from the zinc polyphosphate product and indicate the orthophosphate and orthophosphate-polyphosphate inhibitors did not completely inhibit the anodic reaction at the inhibitor doses tested.

The electrical potential between the two sections of pipe was also measured immediately before and after inhibitor addition. This potential was dramatically impacted by the addition of zinc polyphosphate. Specifically, the voltage decreased from +8 mV to -16 mV (Table 2-3), indicating that the first section of the pipe, initially anodic relative to the second section, had been turned cathodic after dosing the zinc polyphosphate product. The relative position of the anodic and cathodic copper pipe sections and the magnitude of the potential remained unchanged in all other conditions tested. This is again deemed promising in terms of the inhibitive effects of zinc polyphosphate on pitting propensity, as it suggests that anodes (e.g., pits) could be turned into cathodes and thereby eliminate undesirable localized corrosion.

Long Term Results

Inhibitor Conditions at pH 8.5

For most of the experiment, testing was conducted at pH 8.5. E_{Corr} and the potential between pipe sections were continuously measured from Day 110 to Day 115. Pitting voltage, current, and resistance of low-flow pitting wires were measured from Day 110 to

Day 115. Again, these pitting were installed on Day 110 as original pitting wires at all locations failed to sustain significant pitting currents.

E_{Corr} of the zinc polyphosphate rig was much lower than all other rigs at an average value of 18.5 mV versus a Ag-AgCl reference electrode (Figure 2-11). The E_{Corr} values were all comparable between the control rig, orthophosphate rig, and the orthophosphate-polyphosphate rig and in the range of 90-105 mV. Thus, E_{Corr} of the zinc polyphosphate rig was at least 70 mV lower than the other conditions. Differences in E_{Corr} of the remaining rigs were small, however trends were still established. At 95% confidence, paired t-tests determined that the control rig maintained the highest E_{Corr}, followed by the orthophosphate-polyphosphate rig and then the orthophosphate rig. From this perspective, the ranking of pitting propensity is control > ortho-poly > ortho >> zinc polyphosphate.

The erratic behavior in E_{Corr} of the rig dosed with zinc polyphosphate is noteworthy. The cause of this variation may be due to gradual decreases in soluble zinc from the rig between water changes and chemical adjustments. Additional research would be needed to resolve this issue, and measurements in these tests did determine that soluble zinc concentrations decreased markedly with time.

Qualitatively similar trends as seen in E_{Corr} data were established considering results from potential measurements between the sections of pipe (Figure 2-12). The zinc polyphosphate rig had the lowest potential which ranged from -10 to 20 mV and averaged 2.2 mV. Measuring first a positive and then a negative potential means that the anodic-cathodic relationship between the pipes switched, being first anodic and then cathodic. Again, practical experience and laboratory results indicated that, in some pitting waters, the section of pipe first contacting the flowing water tends to become anodic relative to the later sections (Marshall, 2004). Thus, from this perspective, the addition of zinc polyphosphate opposed this tendency and suggests the water became non-pitting.

The average potential measured between the sections of pipe for the other experimental conditions were within 15 mV of each other (Figure 2-12). Paired t-tests at 95% confidence concluded that the orthophosphate-polyphosphate rig supported the greatest positive potential followed by the orthophosphate rig and then the control rig. Again, greater positive potentials indicate stronger anodic (pitting) activity in the first sections of pipe contacting the water flowing through the rig. It is interesting to note that the control rig had the lowest potential (besides the zinc polyphosphate rig), but supported the highest E_{Corr}.

Data collected from pitting wires installed on Day 110 was consistent with E_{Corr} trends and potential measurements between sections of pipe. Pitting voltage and current were lowest for the zinc polyphosphate rig (Figures 2-13 and 2-14) and averaged 4.1 mV and 0.07 µA, respectively. Negative voltage and current values indicate pitting wires were non-pitting. Thus, new pitting wires installed in the zinc polyphosphate rig became non-pitting almost immediately after briefly supporting only a very slight pitting current.

No significant differences were measured between the control rig and the rigs dosed with either orthophosphate or orthophosphate-polyphosphate. However, these rigs did support positive pitting voltages and currents at an average of 42.3 mV and 1.87 μA, respectively (Figures 2-13 and 2-14). Thus, these wires were the site of very significant anodic (pitting) activity, further supporting the idea that no benefits were obtained from the orthophosphate or orthophosphate-polyphosphate inhibitors relative to the control. Finally, the resistance of the scale at the surface of the pitting wires was drastically greater for the zinc polyphosphate rig. The resistance for the rig containing zinc polyphosphate averaged 143.8 kΩ, whereas the resistances for all other rigs were indistinguishable at an average of 14.5 kΩ (Figure 2-15).

Inhibitor Conditions at pH 7.5

In order to evaluate possible benefits or detriments of lower pH values, the pH was decreased to 7.5 on Day 115. E_{Corr} and the potential between pipe sections were continuously measured from Day 115 to Day 138. Pitting voltage, current, and resistance of the pitting wires installed on Day 110 were also measured on these days.

As before, E_{Corr} of the zinc polyphosphate rig was the lowest at an average of 27.4 mV (Figure 2-16). E_{Corr} in the remaining rigs averaged within 70 to 85 mV. Most interestingly though, E_{Corr} in the control rig went from being the highest at pH 8.5, to becoming lower than the E_{Corr} in both the orthophosphate and the orthophosphate-polyphosphate rigs. Specifically, E_{Corr} of the control rig dropped by nearly 30 mV upon lowering the pH to 7.5 and decreased to an average value of 72.8 mV. Paired t-tests indicated this trend was significant at greater than 95% confidence. Further, the trend is consistent with the conclusive data of Rushing (2002) and Marshall (2004) indicating that greater pitting propensities occur at higher pHs.

E_{Corr} of the orthophosphate-polyphosphate rig was still greater than that of the orthophosphate rig despite the decrease in pH. Paired t-tests indicated this trend was significant at greater than 95% confidence. In comparison to conditions at pH 8.5, the average E_{Corr} of the orthophosphate and the orthophosphate-polyphosphate rigs both decreased by more than 10 mV after dropping to pH 7.5 (Figure 2-16). At pH 7.5, the average E_{Corr} in the orthophosphate and orthophosphate-polyphosphate rigs were 82.6 and 83.9 mV, respectively, compared to 72.8 mV in the control system. Thus, the data suggests that at lower pHs, the dosing of the phosphate inhibitors (orthophosphate and orthophosphate-polyphosphate) tends to worsen pitting propensity relative to the control water which contained no inhibitor.

The potential measured between the sections of pipe offered similar qualitative results (Figure 2-17). The potential measured on the control rig significantly decreased when comparing results at pH 7.5 versus pH 8.5, indicating that the first section of pipe became less anodic (less pitting) relative to the second section at pH 7.5. In fact, the potential decreased to values even lower than that of the zinc polyphosphate rig. The potential measured in the control rig and the zinc polyphosphate rig averaged 1.9 and 6.5 mV, respectively. These differences were significant at greater than 95% confidence. From

Day 123 onward, negative potentials indicate that the anodic-cathodic relationship even reversed in the control rig and the first section of pipe became cathodic relative to the second. This data suggests that decreasing pH to 7.5 might reduce pitting propensity in the water, but only if inhibitors are not present. However, if zinc polyphosphate is used at lower pHs, the effectiveness of inhibitor will not be compromised relative to the situation in which no inhibitor is added.

The potential between sections of pipe in the orthophosphate and orthophosphate-polyphosphate rigs were not affected by the decrease in pH and maintained their previous relationship (Figure 2-17). The potential measured in the rigs dosed orthophosphate or orthophosphate-polyphosphate averaged 20.3 and 25.6 mV, respectively. This difference was significant at greater than 95% confidence.

Pitting wire data reinforced the idea that, for the control water, pitting propensity was reduced at pH 7.5 relative to orthophosphate and orthophosphate-polyphosphate systems (Figures 2-18 and 2-19). Again, the pitting voltage and current were lowest for the zinc polyphosphate rig averaging -7.8 mV and -0.22 μA, respectively; however at pH 7.5, pitting currents in the control rig decreased in just a few days to levels comparable to results in the zinc polyphosphate rig. Specifically, the average pitting voltage and current in the control rig were 3.9 mV and -0.09 μA, respectively. The pitting voltage and current of the orthophosphate and orthophosphate-polyphosphate rigs at pH 7.5 were not significantly different, as was the case at pH 8.5. In these rigs, the average pitting voltage was roughly 25 mV and the average pitting current was 0.7 μA. These pitting currents are quite significant and were sustained for at least 5 days.

At pH 7.5, the average resistance of the pitting wires became much higher in the control rig and the zinc polyphosphate rig than the other conditions (Figure 2-20). The zinc polyphosphate created the greatest average resistance at 62.8 kΩ. Resistances in the control, orthophosphate, and orthophosphate-polyphosphate rig followed at averages of 34.3, 24.8, and 18.4 kΩ, respectively (Figure 2-20).

Overall at pH 7.5, the control rig (with no inhibitor) did not support pitting, whereas the orthophosphate rig and orthophosphate-polyphosphate rig seemed to still support indications of pitting. Zinc polyphosphate did not increase pitting tendencies at pH 7.5 and sustained its non-pitting propensity.

Inhibitor Conditions at pH 7.5 with Zinc Added to Orthophosphate-Polyphosphate Rig

On Day 138, zinc was added, as zinc chloride, at a concentration of 2 mg/L as Zn to the rig containing orthophosphate-polyphosphate inhibitor. This was done to investigate the possible role of zinc in copper pitting inhibition as based on the promising results of the zinc polyphosphate rig. Here, dosing at a more representative zinc concentration would also test results under more realistic conditions, given that the zinc polyphosphate had originally been dosed at unrealistically high concentrations. During this phase of work E_{Corr} and the potential between pipe sections were continuously measured from Day 138 to Day 145.

Previously at pH 7.5, the orthophosphate-polyphosphate rig sustained the highest E_{Corr}. However, upon adding zinc, E_{Corr} in this rig decreased to 16 mV lower than values in the control rig and the orthophosphate rig (Figure 2-21). Through Day 138 to Day 145, E_{Corr} values in the orthophosphate, control, and orthophosphate-polyphosphate rig (with zinc) averaged 102, 97, and 68 mV, respectively. Furthermore, E_{Corr} of the control rig and the orthophosphate rig actually increased by 25 and 19 mV, respectively, in comparison to their previous averages from Day 115 to 138. This indicates the overall pitting propensity of the test water had increased. Thus, if the orthophosphate-polyphosphate rig would have had a similar increase without the zinc, a 35 mV decrease in E_{Corr} can be attributed to addition of the zinc. Again, the zinc polyphosphate rig sustained the lowest average E_{Corr} at 19 mV.

The potential measurement between the pipes showed no qualitative change in the orthophosphate-polyphosphate rig upon the addition of zinc (Figure 2-22). However, even at a higher dose of zinc, the qualitative change of this measurement in the zinc polyphosphate rig may have taken up to ten days (Table 2-3), and it is possible that at lower zinc doses seven days of testing was not adequate to produce an effect. The potential measured between sections of pipe in the rig dosed with zinc polyphosphate consistently measured a negative potential during this phase of the experiment. This suggests that the first section of pipe became totally cathodic relative to the second section over the life of the experiment (Figure 2-22 and 2-23).

At the end of the experiment, water samples were taken for metals analysis using inductively coupled plasma mass spectroscopy (ICP-MS). The zinc polyphosphate rig contained the lowest concentration of copper at 0.077 mg/L Cu. This was lower than the concentration of copper in the orthophosphate-polyphosphate rig, control rig, and orthophosphate rig at 0.171, 0.188, and 0.279 mg/L Cu, respectively.

Surface Analysis of Copper Coupons

Four 2” copper pipe coupons were incorporated into each rig (Figure 2-1). Water recirculating through the rig contacted the coupons first and then passed through the remaining copper pipe before exiting back into the reservoir. Coupons were labeled A – D on each rig and were consistently positioned such that water flowed through Coupon D first, and then through the remaining coupons in decreasing letter sequence. At the end of the experiment the coupons were disassembled and the interior pipe scale was examined.

Visual examination discovered distinctive differences in comparing *sets* of coupons between different experimental conditions as well as differences among the four *individual* coupons of each given experimental condition. When comparing sets of coupons between experimental conditions, the coupons from the control rig (with no inhibitor) appeared to be the most heavily corroded based upon scale abundance and the formation of tubercles (Figure 2-24). Interestingly, coupons from the orthophosphate rig seemed to have the least amount of corrosion, although followed very closely by the zinc polyphosphate coupons (Figures 2-25 and 2-26). The orthophosphate-polyphosphate coupons had the most apparent corrosion among rigs exposed to an inhibitor, and it was difficult to distinguish between these coupons and those from the control system (Figure 2-27).

Differences among individual coupons of each experimental condition also provided interesting results. Specifically, the coupon first receiving flow (Coupon D) consistently produced the most pronounced corrosion scale (Figures 2-24, 2-25, 2-26, and 2-27). The amount or degree of corrosion gradually decreased across the remaining three coupons in the direction of flow such that the last coupon receiving flow (Coupon A) sustained the least amount of corrosion. This trend suggests that coupons receiving flow became more anodic relative to latter coupons. Similar observations were observed by Marshall (2004), where copper pitting occurred predominantly at the entrance of pipe sections. Furthermore, this is consistent with trends established from potential measurements between sections of pipe on the rigs, as a positive potential indicated first sections were anodic relative to latter sections (Figures 2-12, 2-17, 2-22, and 2-23).

Analysis of the coupons provided information regarding the mass of scale accumulated on each coupon as well. Results confirmed visual trends as coupons from the control system and the orthophosphate-polyphosphate system generally produced the greatest amount of scale indicative of greater amounts of corrosion in these systems (Figure 2-28). Also, coupons from the zinc polyphosphate system and the orthophosphate system consistently measured the least amount of scale production.

Portions of the interior coupon pipe scale were removed for surface analysis with the SEM-EDS. Attempts were made to select portions thought to be non-aggressive uniform corrosion as well as sections most closely resembling tubercles. The amount of aluminum was consistently higher in tubercle samples than in portions of uniform scale (Tables 2-4, 2-5, 2-6, and 2-7). This is consistent with a copper pitting mechanism driven in part by aluminum deposits (Marshall, 2004).

Further, zinc was found on the surface of coupons from the zinc polyphosphate rig as well as the orthophosphate-polyphosphate rig which was later dosed with zinc chloride (Tables 2-4 and 2-5). In the latter, the presence of zinc was somewhat unanticipated as the system was dosed with zinc for only the final 18 days of the experiment. At first inspection, the presence of zinc seemed to influence the composition of the surface. To confirm this trend, the raw energy data collected by the SEM-EDS in the form of energy counts per second was evaluated for individual surface site measurements. When considering the presence of zinc, the measured amount of copper (due to copper release at anodic sites) seemed to decrease with increasing amounts of zinc (Figure 2-29 and Table 2-4). In addition, increasing amounts of zinc appeared to enhance the precipitation of phosphorus as well (Figure 2-30 and Table 2-5). Zin et al. (2004) and Olesen et al. (1998) have also noted a synergistic effect between zinc and phosphate in other precipitation applications. In general, raw energy data also suggested that increasing amounts of phosphorus correlated to decreases in copper release (Figure 2-31). Interestingly, the SEM measured very little phosphate on any of the orthophosphate coupons which appeared to have the least amount of corrosion and would be expected to have significant phosphorus deposition (Table 2-6).

Summary of Results

Table 2-8 summarizes the results from all testing methods during each experimental phase and provides a relative ranking of corrosion activity for each system based on the data. This review clearly illustrates that the zinc polyphosphate system produced the least corrosion activity during all phases of the experiment and according to all testing methods. In addition, Table 2-8 shows that dosing orthophosphate or orthophosphate-polyphosphate does not have any benefits and may even produce detriments relative to corrosion activity measured in the control rig with no inhibitor.

Short Term Jar Tests

The full scale experiments raised several interesting questions worthy of further investigation under tightly controlled conditions. Specifically, examination of full-scale distribution system data and location of pinhole leaks suggested that high concentrations of chloramines might be associated with increased frequency of pinhole leaks. Field measurements also occasionally measured high levels of free chlorine in homes subject to pitting, which is inconsistent with the goal of maintaining chloramines. Consequently, it was deemed desirable to conduct a detailed examination of the role of the chlorine to ammonia ratio, as well as the effects of total chlorine dose in short term pitting tests.

Investigating the Role of the Chlorine to Ammonia Ratio

Similar E_{Corr} values were observed in waters containing chlorine to ammonia ratios of 2:1, 4:1, and 5:1 (Figure 2-32). However, E_{Corr} measured in the jar with a 6:1 chlorine to ammonia ratio became considerably lower with time at the beginning of the experiment and also immediately following the water change on Day 3.9. The decreased E_{Corr} in this rig was correlated to the rapid decay of total chlorine in this system (Figure 2-33). More rapid decay of chlorine at a 6:1 ratio is expected given that dichloramines and trichloramines which form at higher chlorine to ammonia ratios are unstable (Snoeyink and Jenkins, 1980). No trends can be ascribed to different ratios of chlorine to ammonia.

Investigating the Role of Chlorine

Greater E_{Corr} values occurred for copper exposed to higher concentrations of total chlorine (Figure 2-34). All chlorine to ammonia ratios were kept constant during this experiment. Thus, the results confirm there is a relationship between total chlorine concentrations and E_{Corr}. This indicates that higher total chlorine in the system is correlated with higher pitting propensity, consistent with most trends in practical data of pinhole leak frequency observed at the water utility.

Short Term Rig Test of Zinc Effects

The role of zinc in copper pitting inhibition was unexpected, controversial and deserving of additional study. While no research has studied zinc inhibition of copper pitting in potable water as mentioned in Chapter 1, some studies have suggested that zinc has little effect on other aspects of copper and lead corrosion including metals leaching (McNeill, 2000). However, other data has demonstrated that zinc can be an effective cathodic inhibitor of iron, steel, and zinc (Evans, 1939, Olesen et al., 1998, and Zin et al., 2004). Studies have also been completed establishing that solubility products of hydroxyapatites containing zinc are markedly lower than for those without zinc (Featherstone and Mayer, 2000).

However, the data from the pitting experiments at the Florida utility does not give 100% conclusive evidence that zinc functioned as an effective inhibitor for several reasons. First, the zinc polyphosphate had a higher percentage of polyphosphates relative to the orthophosphate-polyphosphate blend. The percentage of polyphosphates and molecular weight of the polyphosphates can vary considerably between products, and it is therefore possible that polyphosphates were the key inhibitor in the zinc polyphosphate product and not zinc. Of course, some limited data was collected that showed reduced pitting propensity when zinc chloride was added to the rig containing the orthophosphate-polyphosphate product, but additional data would still be desired. Consequently, a short term, small scale rig test under very rigorously controlled conditions was conducted to determine whether any discernable benefits could be attributed to the presence of zinc.

In the short term rig test, the addition of zinc immediately decreased the pitting propensity of the water containing the orthophosphate-polyphosphate blend. Specifically, E_{Corr} decreased by 20 mV within one week after zinc addition, whereas the control rig, which contained only the orthophosphate-polyphosphate product, *increased* by nearly 15 mV (Figure 2-35). Thus, a 35 mV differential developed during the addition of zinc. Further, pitting currents were supported to a greater extent in the rig that did not contain zinc (Figure 2-36). The average pitting current in the rig with zinc from Day 11.5 to Day 13 was 0.09 μA, whereas that of the rig with only orthophosphate-polyphosphate supported an average current of 0.33 μA.

On Day 24.5 zinc polyphosphate was dosed into the rig containing zinc. Results from the addition of the zinc polyphosphate product were also promising. E_{Corr} of the rig containing zinc polyphosphate became slightly less (about 10 mV) than that of the rig with only orthophosphate-polyphosphate (Figure 2-37).

The concentrations of zinc, copper, and phosphorus were measured throughout the experiment. The concentration of zinc constantly decreased in the water following zinc polyphosphate additions, consistent with its attachment to and coating of the copper surfaces (Figure 2-38). The concentration of soluble copper was also consistently greater in the rig that did not contain any zinc (Figure 2-39). Finally, phosphorus was lower in the rig which contained zinc (Figure 2-40); indicating zinc was enhancing phosphorus deposition onto the pipe.

CONCLUSIONS

- All methods suggested a significant benefit from adding zinc polyphosphate as a pitting inhibitor at both pH 7.5 and pH 8.5 in this water.
- No benefits were realized from adding orthophosphate or orthophosphate-polyphosphate. These inhibitors may even produce adverse effects at the lower pHs.
- Decreasing the pH from 8.5 to 7.5 reduced pitting propensity in the water of the control system which did not contain any inhibitor.
- Adding zinc to the system containing orthophosphate-polyphosphate caused a significant decrease in E_{Corr} and other aspects of pitting propensity which suggests that zinc may act as an effective cathodic inhibitor.
- Surface analyses determined that the zinc polyphosphate system produced scale on copper pipe to a lesser extent; whereas the control system produced the greatest amount of scale. Further analysis suggested that zinc and phosphorus may behave synergistically to decrease copper release.
- Changes in the chlorine to ammonia ratio have no effect on pitting propensity, however higher total chlorine (as chloramines) increased pitting propensity.
- Adding zinc in a controlled short-term test which contained an orthophosphate-polyphosphate inhibitor caused a decrease in E_{Corr} and pitting currents. The addition of the zinc polyphosphate also lowered the pitting propensity in these short-term bench scale tests.

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Table 2-1. Typical Water Quality - Florida Utility Product Water.

Constituent	Concentration	
Aluminum, Al	0.005	mg/L
Calcium, Ca	64.1	mg/L
Chromium, Cr	0.000	mg/L
Copper, Cu	0.001	mg/L
Iron, Fe	0.001	mg/L
Potassium, K	4.56	mg/L
Magnesium, Mg	18.6	mg/L
Nickel, Ni	0.000	mg/L
Phosphorus, P	0.346	mg/L
Lead, Pb	0.001	mg/L
Silicon, Si	6.81	mg/L
Tin, Sn	0.005	mg/L
Zinc, Zn	0.003	mg/L
Fluoride, F	0.520	mg/L
Nitrate, NO_3	0.590	mg/L
Sulfate, SO_4	124	mg/L
Chloride, Cl^-	45.3	mg/L
Dissolved Oxygen	8.60	mg/L
H_2S	3.00	µg/L
Alkalinity	39.0	mg/L as $CaCO_3$
TOC	2.96	mg/L as C

Table 2-2. Target Water Quality Parameters – Experimental Conditions

Parameter	Chemical(s)	Concentration	
pH	H_2SO_4 or NaOH	8.5, 7.5	pH units
NH_3	NH_4OH	1.5, 4.0	mg/L as N
Chlorine	NaOCl	6.5, 16	mg/L as Cl_2
Aluminum	Al solids	4	mg/L as Al
Orthophosphate	Calciquest ORTHO	1	mg/L as P
Ortho/Polyphosphate	Calciquest 5050	1	mg/L as P
Zinc Polyphosphate	Shannon Chemical Corporation SHAN-NO-CORR	6	mg/L as P
Zinc Polyphosphate	Shannon Chemical Corporation SHAN-NO-CORR	1.5	mg/L as Zn
Zinc	$ZnCl_2$	2	mg/L as Zn

Table 2-3. Potential between sections of pipe before and after addition of inhibitors on Day 93.

	Potential Between Pipes, ΔV_{Pipes} (mV)			
DAY	**Control**	**Ortho/Poly**	**Ortho**	**ZnPoly**
90	12	14	23	8
100	10	19	0.9	-4
104	16	25	15.5	-16

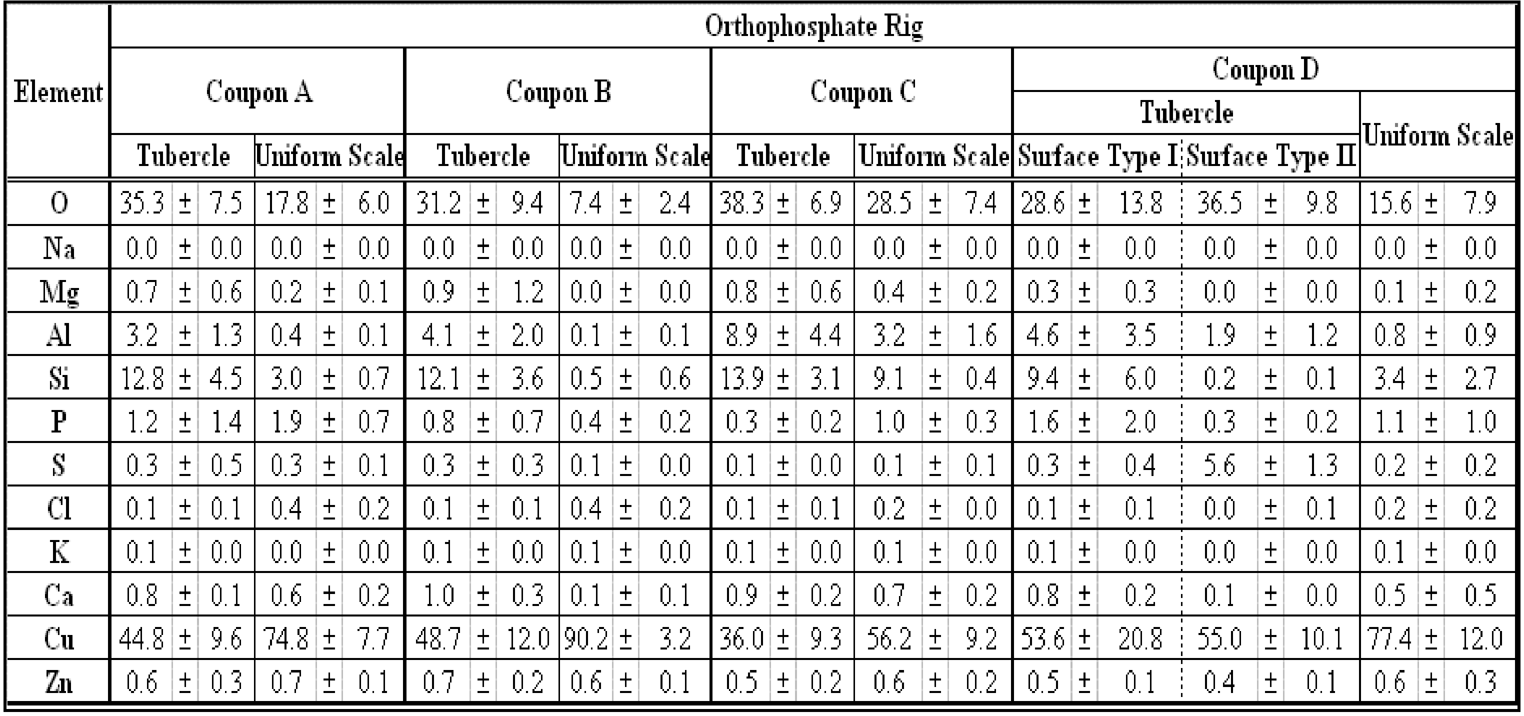
Table 2-4. Zinc Polyphosphate Rig - Elemental Percent Abundance (% by mass) of interior coupon surface.

Element	Zinc Polyphosphate Rig					
	Coupon A		Coupon B		Coupon C	Coupon D
	Tubercle	Uniform Scale	Tubercle	Uniform Scale	Tubercle	Tubercle
O	54.5 ± 5.5	50.0 ± 12.3	55.3 ± 6.8	46.1 ± 5.4	53.9 ± 8.8	39.6 ± 8.2
Na	1.5 ± 0.7	2.4 ± 1.1	2.1 ± 2.3	2.2 ± 1.2	1.1 ± 1.6	0.0 ± 0.1
Mg	0.6 ± 0.3	0.7 ± 0.4	1.8 ± 2.6	1.1 ± 0.7	0.8 ± 0.5	0.4 ± 0.6
Al	7.6 ± 3.0	1.4 ± 0.8	3.8 ± 4.5	1.3 ± 1.3	4.6 ± 3.7	3.8 ± 2.5
Si	7.6 ± 1.4	5.8 ± 4.2	8.0 ± 6.1	2.7 ± 0.8	9.6 ± 5.3	7.6 ± 5.3
P	7.3 ± 2.4	7.9 ± 1.5	8.7 ± 5.1	8.7 ± 1.6	7.5 ± 5.5	4.9 ± 2.5
S	0.2 ± 0.3	0.7 ± 0.6	0.1 ± 0.1	0.4 ± 0.3	0.1 ± 0.1	0.4 ± 0.7
Cl	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.1	0.3 ± 0.2
K	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
Ca	3.1 ± 1.2	2.5 ± 0.9	4.2 ± 2.8	2.2 ± 0.6	4.0 ± 3.5	2.6 ± 0.8
Cu	12.9 ± 5.9	25.1 ± 16.1	10.4 ± 6.8	31.8 ± 10.1	13.6 ± 8.4	36.3 ± 9.6
Zn	4.4 ± 1.5	3.3 ± 1.2	5.5 ± 3.2	3.3 ± 1.1	4.7 ± 3.8	3.9 ± 1.5

Table 2-5. Orthophosphate-Polyphosphate Rig - Elemental Percent Abundance (% by mass) of interior coupon surface.

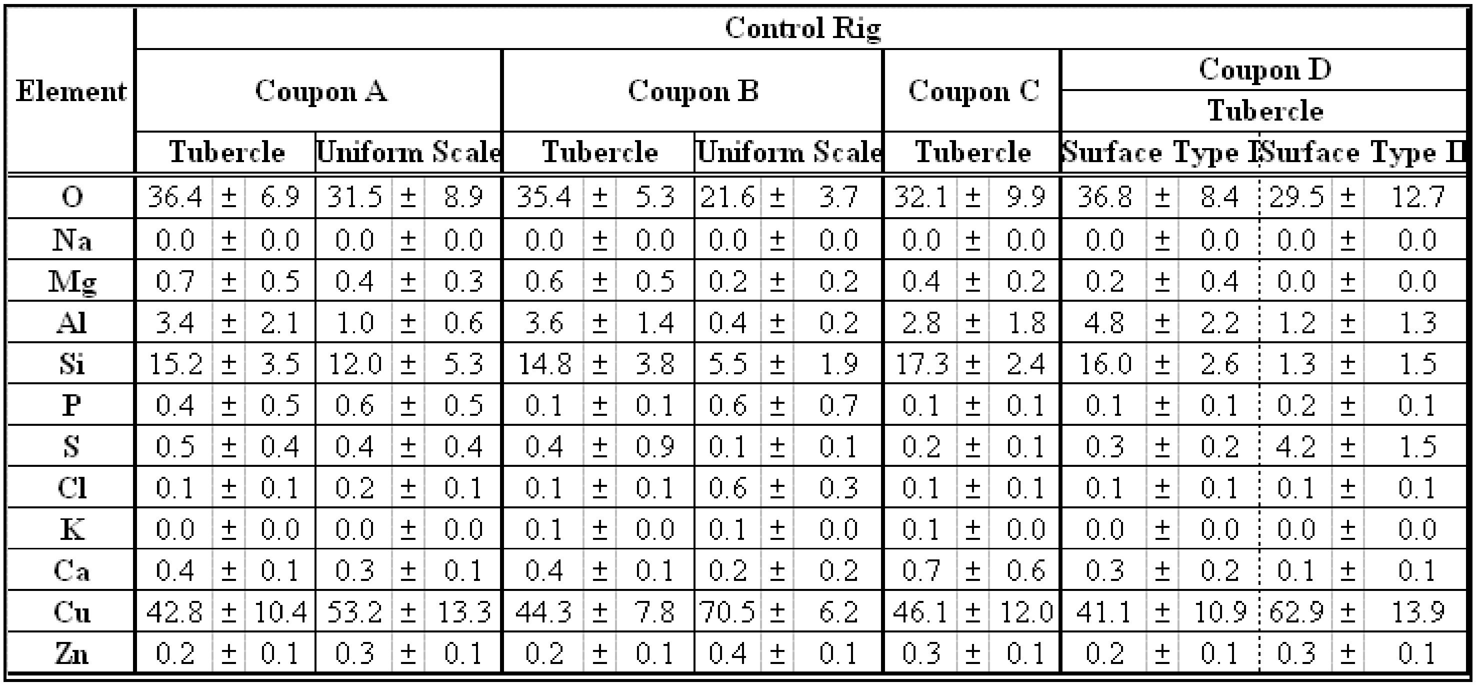
Element	Orthophosphate-Polyphosphate Rig					
	Coupon A	Coupon B	Coupon C		Coupon D	
	Tubercle	Tubercle	Tubercle	Uniform Scale	Tubercle	Uniform Scale
O	30.0 ± 11.4	33.0 ± 6.8	37.3 ± 7.8	21.5 ± 9.0	36.8 ± 6.1	19.5 ± 11.3
Na	1.2 ± 1.6	4.0 ± 4.4	0.4 ± 0.9	0.4 ± 1.1	0.1 ± 0.2	2.8 ± 3.2
Mg	0.2 ± 0.2	0.3 ± 0.2	0.5 ± 1.4	0.1 ± 0.1	0.2 ± 0.3	0.2 ± 0.1
Al	1.2 ± 1.7	2.0 ± 1.2	3.9 ± 3.5	0.5 ± 0.5	3.4 ± 1.5	0.7 ± 0.7
Si	23.6 ± 18.8	11.1 ± 6.1	11.4 ± 4.7	5.2 ± 5.0	11.0 ± 4.1	6.9 ± 6.2
P	1.3 ± 1.0	3.0 ± 3.0	1.5 ± 1.6	1.3 ± 1.2	1.5 ± 0.8	2.4 ± 2.1
S	0.8 ± 1.1	0.2 ± 0.4	0.1 ± 0.4	0.1 ± 0.0	0.1 ± 0.1	0.0 ± 0.0
Cl	1.9 ± 3.8	0.1 ± 0.1	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0	0.2 ± 0.2
K	0.1 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
Ca	0.4 ± 0.3	1.1 ± 0.5	0.6 ± 0.2	0.4 ± 0.3	0.5 ± 0.2	0.9 ± 0.5
Cu	34.8 ± 30.8	28.2 ± 15.5	39.8 ± 14.0	67.6 ± 17.5	43.3 ± 11.1	49.1 ± 26.2
Zn	4.6 ± 4.8	17.0 ± 14.8	4.2 ± 2.8	2.8 ± 2.6	2.9 ± 2.4	17.3 ± 16.9

Table 2-6. Orthophosphate Rig - Elemental Percent Abundance (% by mass) of interior coupon surface.



Element	Orthophosphate Rig								
	Coupon A		Coupon B		Coupon C		Coupon D		
							Tubercle		Uniform Scale
	Tubercle	Uniform Scale	Tubercle	Uniform Scale	Tubercle	Uniform Scale	Surface Type I	Surface Type II	
O	35.3 ± 7.5	17.8 ± 6.0	31.2 ± 9.4	7.4 ± 2.4	38.3 ± 6.9	28.5 ± 7.4	28.6 ± 13.8	36.5 ± 9.8	15.6 ± 7.9
Na	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Mg	0.7 ± 0.6	0.2 ± 0.1	0.9 ± 1.2	0.0 ± 0.0	0.8 ± 0.6	0.4 ± 0.2	0.3 ± 0.3	0.0 ± 0.0	0.1 ± 0.2
Al	3.2 ± 1.3	0.4 ± 0.1	4.1 ± 2.0	0.1 ± 0.1	8.9 ± 4.4	3.2 ± 1.6	4.6 ± 3.5	1.9 ± 1.2	0.8 ± 0.9
Si	12.8 ± 4.5	3.0 ± 0.7	12.1 ± 3.6	0.5 ± 0.6	13.9 ± 3.1	9.1 ± 0.4	9.4 ± 6.0	0.2 ± 0.1	3.4 ± 2.7
P	1.2 ± 1.4	1.9 ± 0.7	0.8 ± 0.7	0.4 ± 0.2	0.3 ± 0.2	1.0 ± 0.3	1.6 ± 2.0	0.3 ± 0.2	1.1 ± 1.0
S	0.3 ± 0.5	0.3 ± 0.1	0.3 ± 0.3	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.3 ± 0.4	5.6 ± 1.3	0.2 ± 0.2
Cl	0.1 ± 0.1	0.4 ± 0.2	0.1 ± 0.1	0.4 ± 0.2	0.1 ± 0.1	0.2 ± 0.0	0.1 ± 0.1	0.0 ± 0.1	0.2 ± 0.2
K	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
Ca	0.8 ± 0.1	0.6 ± 0.2	1.0 ± 0.3	0.1 ± 0.1	0.9 ± 0.2	0.7 ± 0.2	0.8 ± 0.2	0.1 ± 0.0	0.5 ± 0.5
Cu	44.8 ± 9.6	74.8 ± 7.7	48.7 ± 12.0	90.2 ± 3.2	36.0 ± 9.3	56.2 ± 9.2	53.6 ± 20.8	55.0 ± 10.1	77.4 ± 12.0
Zn	0.6 ± 0.3	0.7 ± 0.1	0.7 ± 0.2	0.6 ± 0.1	0.5 ± 0.2	0.6 ± 0.2	0.5 ± 0.1	0.4 ± 0.1	0.6 ± 0.3

Table 2-7. Control Rig - Elemental Percent Abundance (% by mass) of interior coupon surface.



Element	Control Rig						
	Coupon A		Coupon B		Coupon C	Coupon D	
						Tubercle	
	Tubercle	Uniform Scale	Tubercle	Uniform Scale	Tubercle	Surface Type I	Surface Type I
O	36.4 ± 6.9	31.5 ± 8.9	35.4 ± 5.3	21.6 ± 3.7	32.1 ± 9.9	36.8 ± 8.4	29.5 ± 12.7
Na	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Mg	0.7 ± 0.5	0.4 ± 0.3	0.6 ± 0.5	0.2 ± 0.2	0.4 ± 0.2	0.2 ± 0.4	0.0 ± 0.0
Al	3.4 ± 2.1	1.0 ± 0.6	3.6 ± 1.4	0.4 ± 0.2	2.8 ± 1.8	4.8 ± 2.2	1.2 ± 1.3
Si	15.2 ± 3.5	12.0 ± 5.3	14.8 ± 3.8	5.5 ± 1.9	17.3 ± 2.4	16.0 ± 2.6	1.3 ± 1.5
P	0.4 ± 0.5	0.6 ± 0.5	0.1 ± 0.1	0.6 ± 0.7	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1
S	0.5 ± 0.4	0.4 ± 0.4	0.4 ± 0.9	0.1 ± 0.1	0.2 ± 0.1	0.3 ± 0.2	4.2 ± 1.5
Cl	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.6 ± 0.3	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
K	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Ca	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.2 ± 0.2	0.7 ± 0.6	0.3 ± 0.2	0.1 ± 0.1
Cu	42.8 ± 10.4	53.2 ± 13.3	44.3 ± 7.8	70.5 ± 6.2	46.1 ± 12.0	41.1 ± 10.9	62.9 ± 13.9
Zn	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.1

Table 2-8. Summary of results and relative rankings of corrosion activity. Number 1 is the least corrosion activity and Number 4 is the most corrosion.

Condition	Measurement	Control		Ortho/Polyphosphate		Orthophosphate		Zinc Polyphosphate		Figure(s)
		Average	Rank	Average	Rank	Average	Rank	Average	Rank	
pH 8.5	E_{Corr} (mV)	100.8	4	97.1	3	93.6	2	18.5	1	2-11
	ΔV_{pipes} (mV)	12.1	2	26.3	4	21.3	3	2.2	1	2-12
	Pitting Current (µA)	1.74	2	1.98	4	1.88	3	0.07	1	2-14
	Pitting Voltage (mV)	42.1	3	43.9	4	40.8	2	4.1	1	2-13
	Pitting Resistance (kΩ)	15.6	2	13.1	4	14.8	3	143.8	1	2-15
pH 7.5	E_{Corr} (mV)	72.9	2	83.8	4	82.8	3	27.4	1	2-16
	ΔV_{pipes} (mV)	1.9	1	25.6	4	20.3	3	6.5	2	2-17
	Pitting Current (µA)	-0.09	2	0.76	3	0.65	4	-0.22	1	2-19
	Pitting Voltage (mV)	3.9	2	23.3	4	25.7	3	-7.8	1	2-18
	Pitting Resistance (kΩ)	34.2	2	18.35	4	24.8	3	62.8	1	2-20
pH 7.5 + Zn to O/P	E_{Corr} (mV)	97.4	3	67.8	2	101.8	4	19.3	1	2-21
	ΔV_{pipes} (mV)	1.0	2	22.1	4	20.8	3	-10.8	1	2-22
	Visual Inspection	n/a	3 or 4	n/a	3 or 4	n/a	1	n/a	2	2-24-2-27
	Scale Formation - Coupon D (mg)	185.3	4	162.4	3	90.6	1	111.1	2	2-28

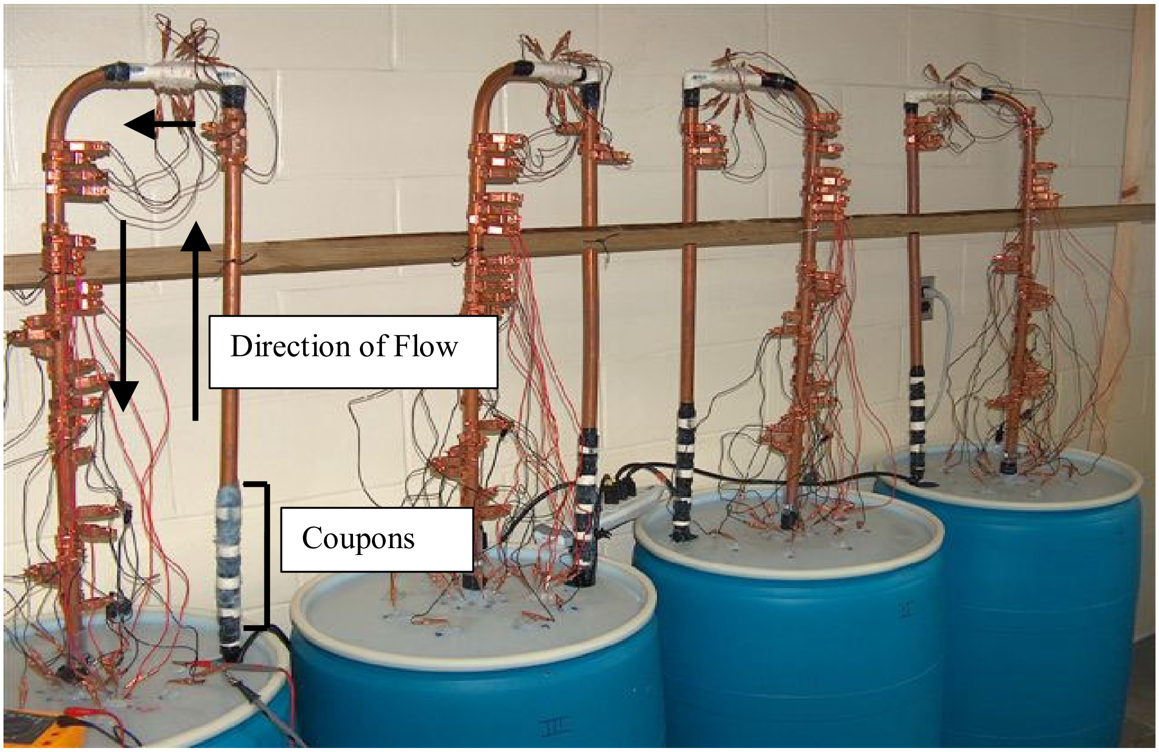


Figure 2-1. General pitting rig experimental setup.

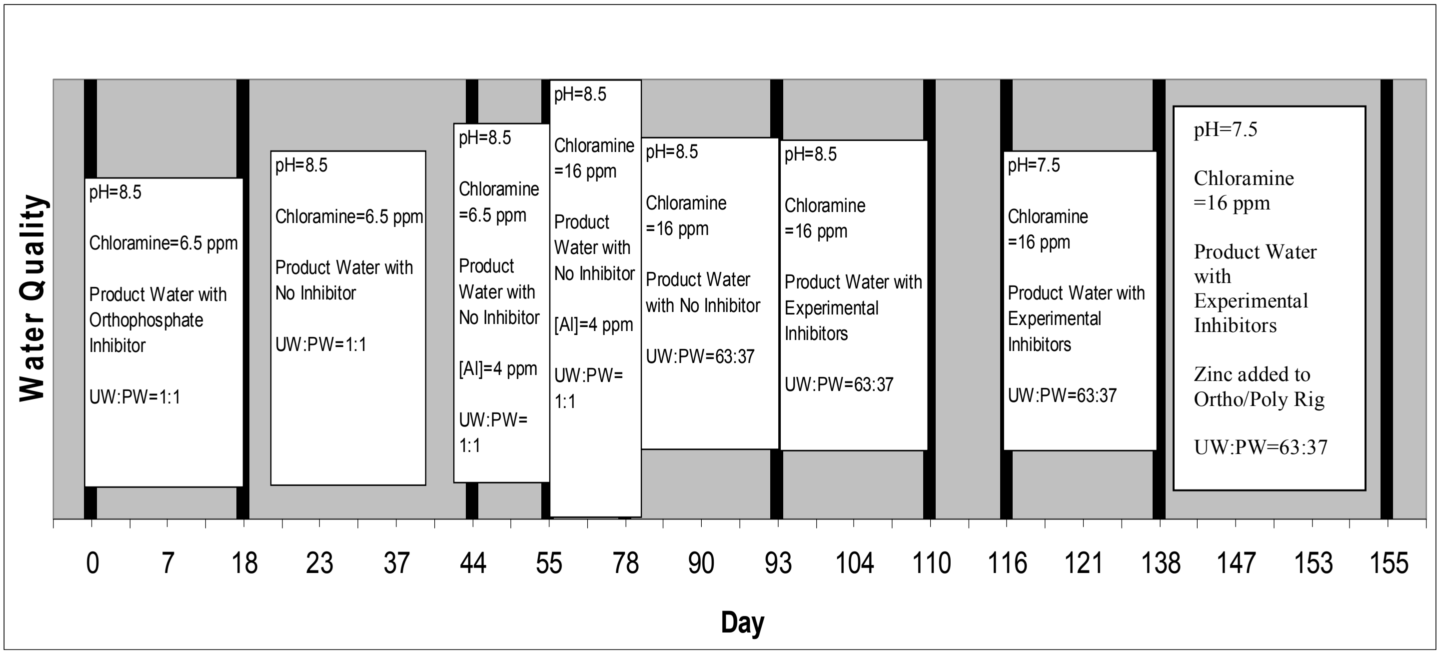


Figure 2-2. Experiment timeline and water quality.

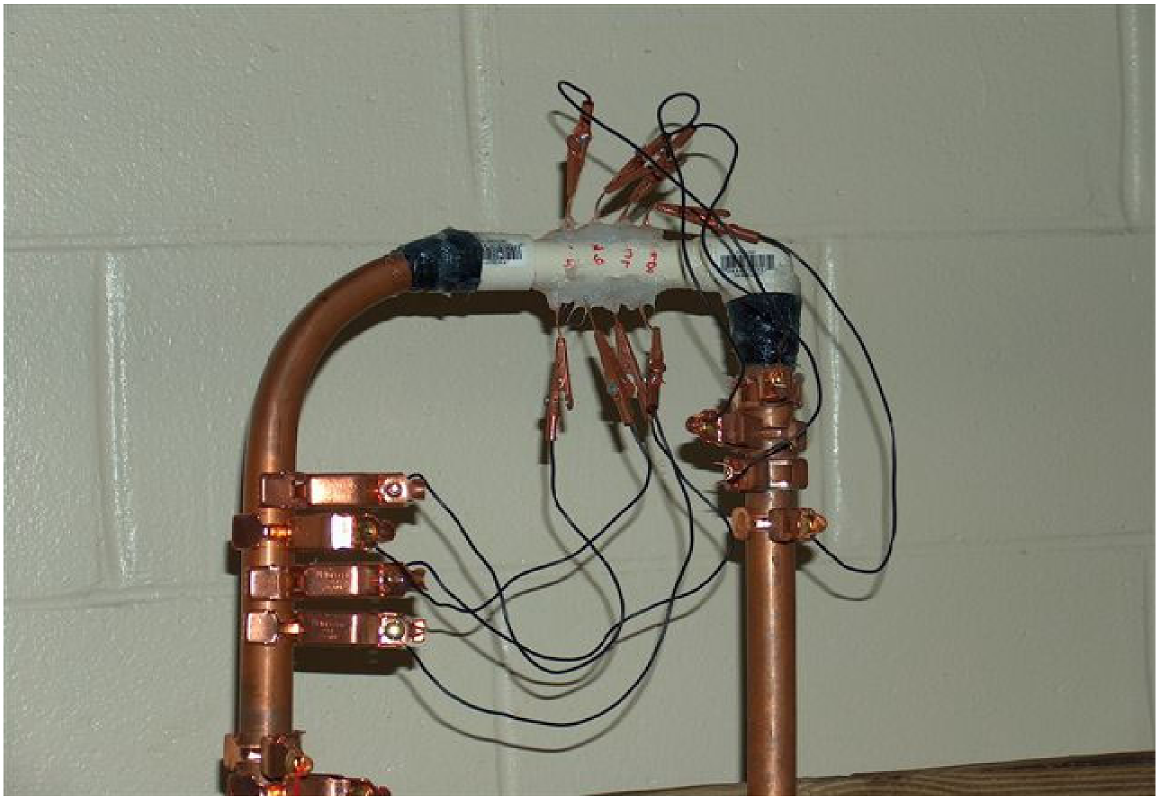


Figure 2-3. Electrical connection between 90 degree in-flow pit wires and pipe.

Figure 2-4. Jar tests with copper coupons installed.

Figure 2-5. General short term rig experimental setup.

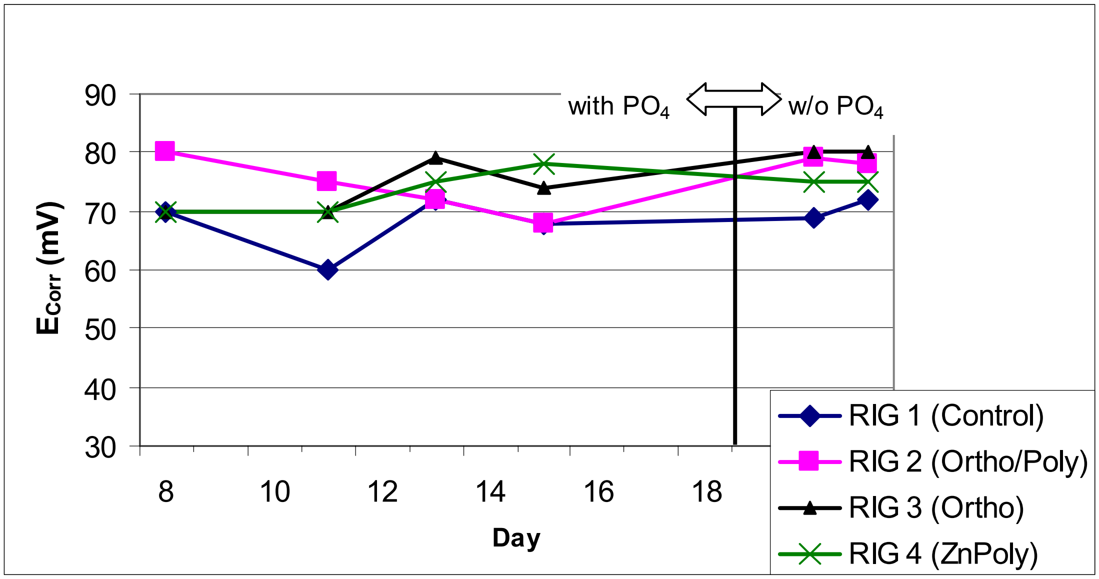


Figure 2-6. E_{Corr} of utility distribution water prior to addition of inhibitors.

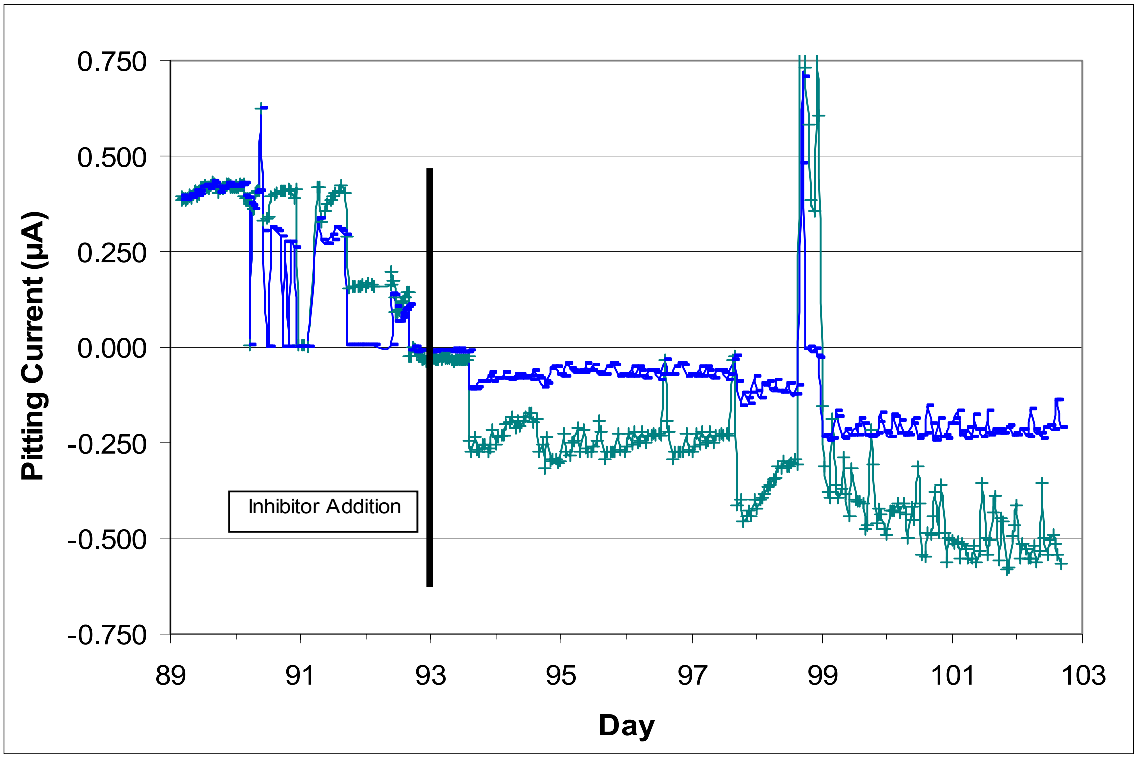


Figure 2-7. Pitting currents before and after addition of inhibitors – Zinc Polyphosphate Rig.

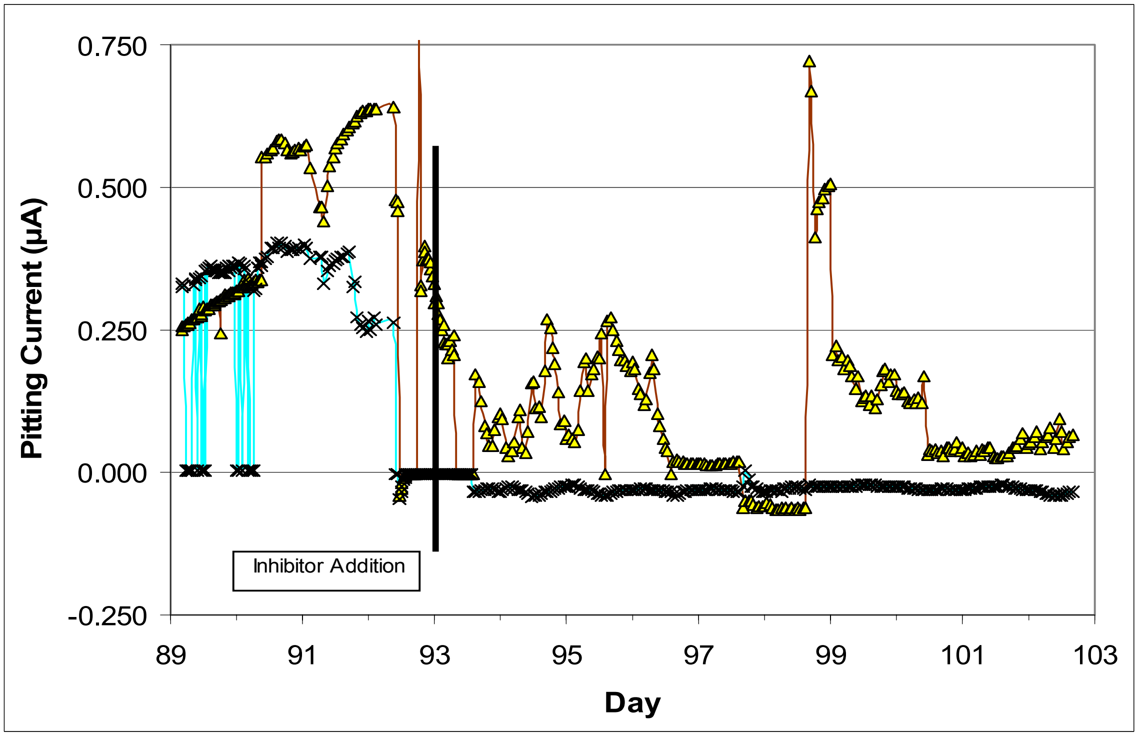


Figure 2-8. Pitting currents before and after addition of inhibitors - Orthophosphate-Polyphosphate Rig.

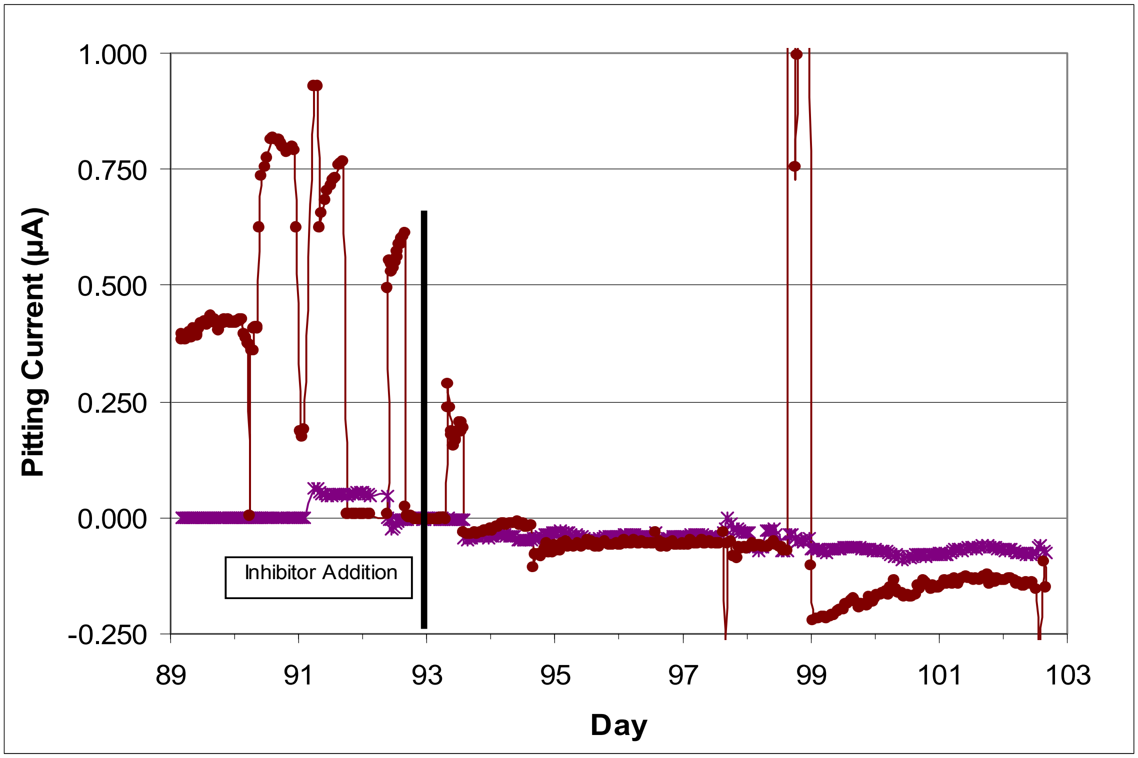


Figure 2-9. Pitting currents before and after addition of inhibitors - Orthophosphate Rig.

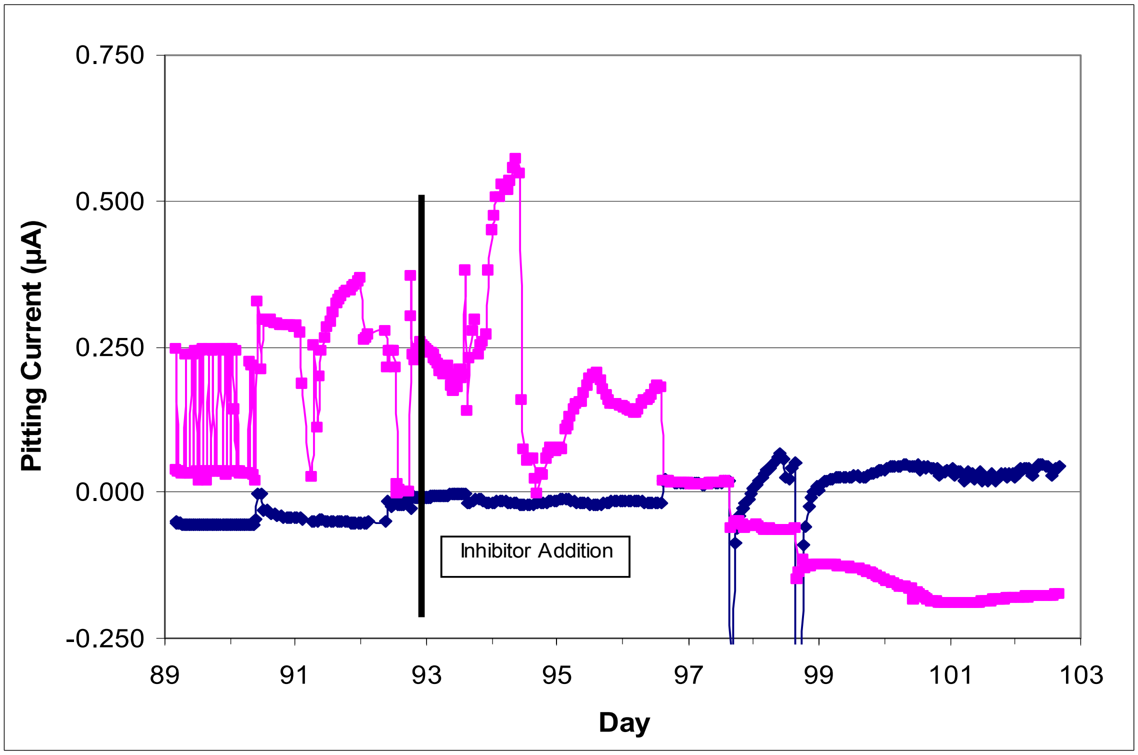


Figure 2-10. Pitting currents before and after the addition of inhibitors - Control Rig.

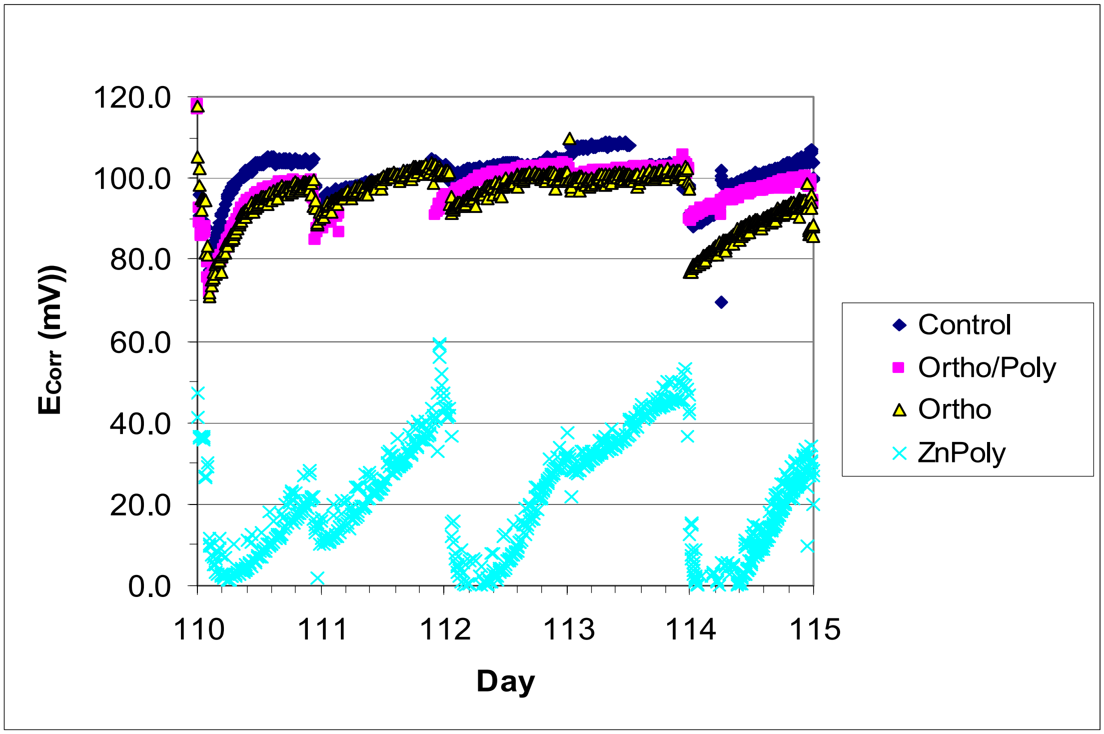


Figure 2-11. E_{Corr} measurements at pH 8.5.

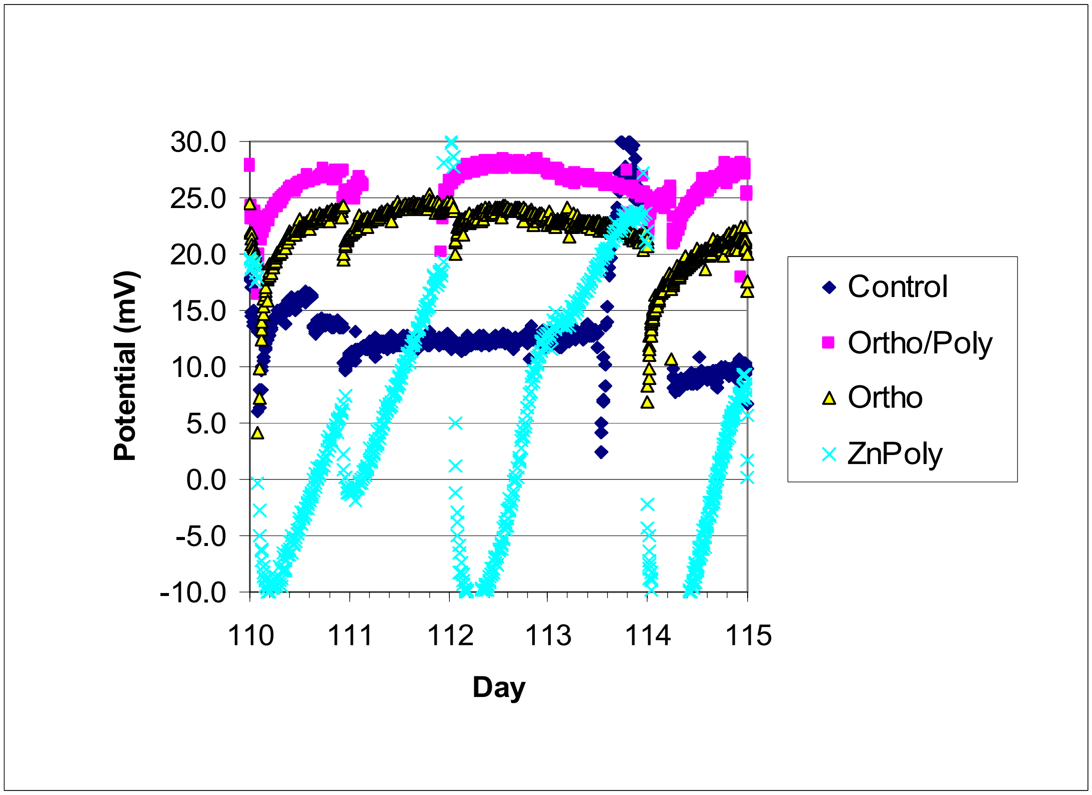


Figure 2-12. Potential between sections of pipe at pH 8.5.

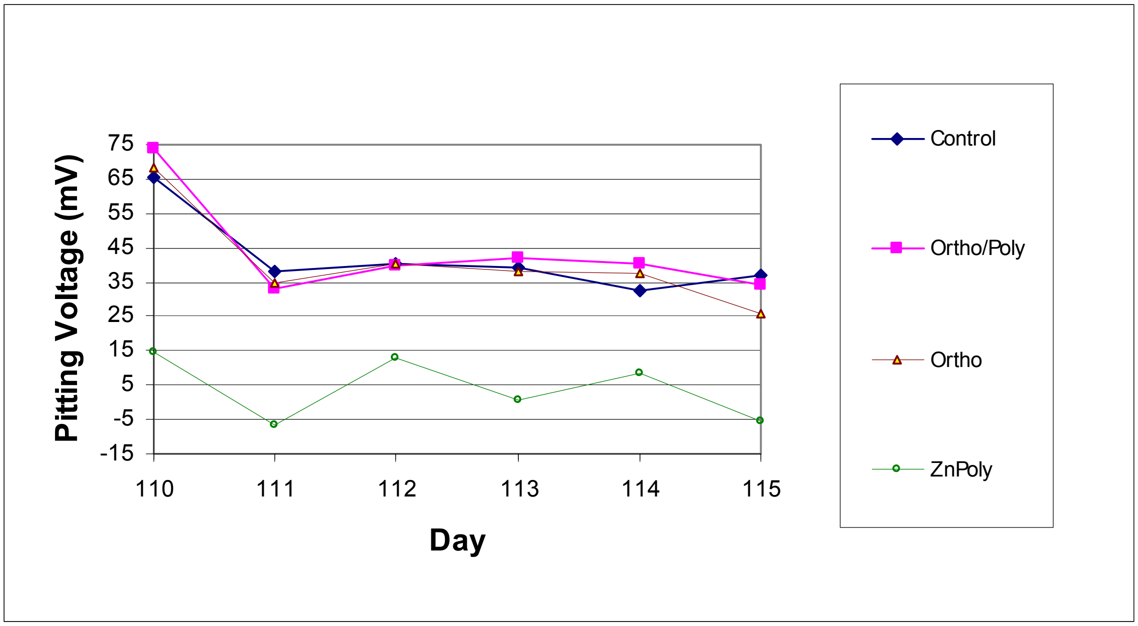


Figure 2-13. Average pitting voltages at pH 8.5. Data shown for low-flow pitting wires installed on Day 110.

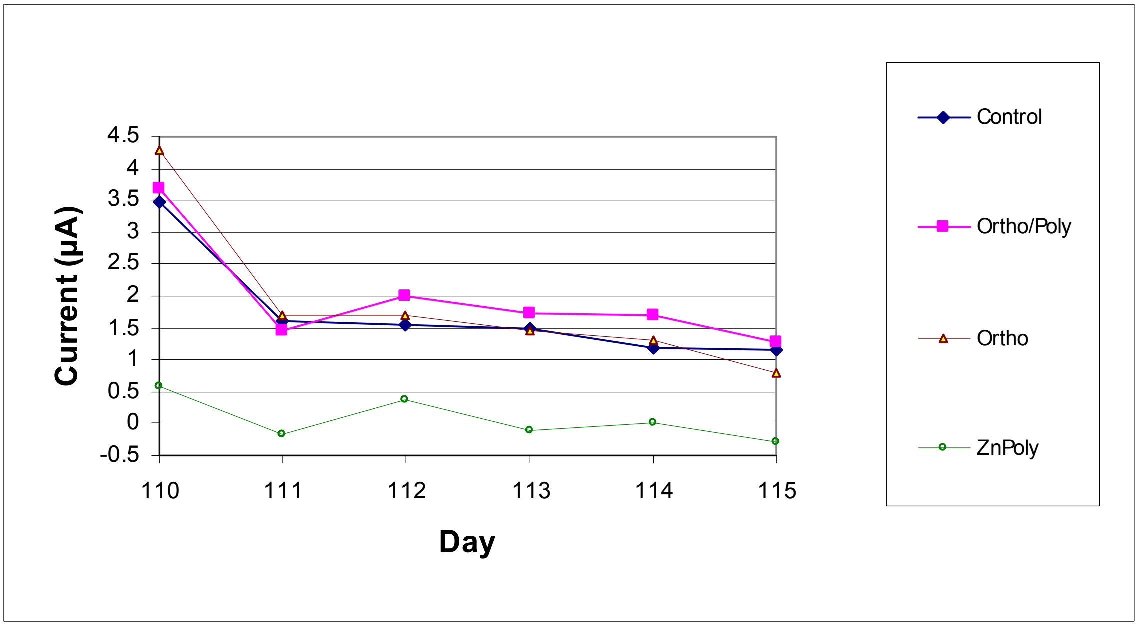


Figure 2-14. Average pitting currents at pH 8.5. Data shown for low-flow pitting wires installed on Day 110.

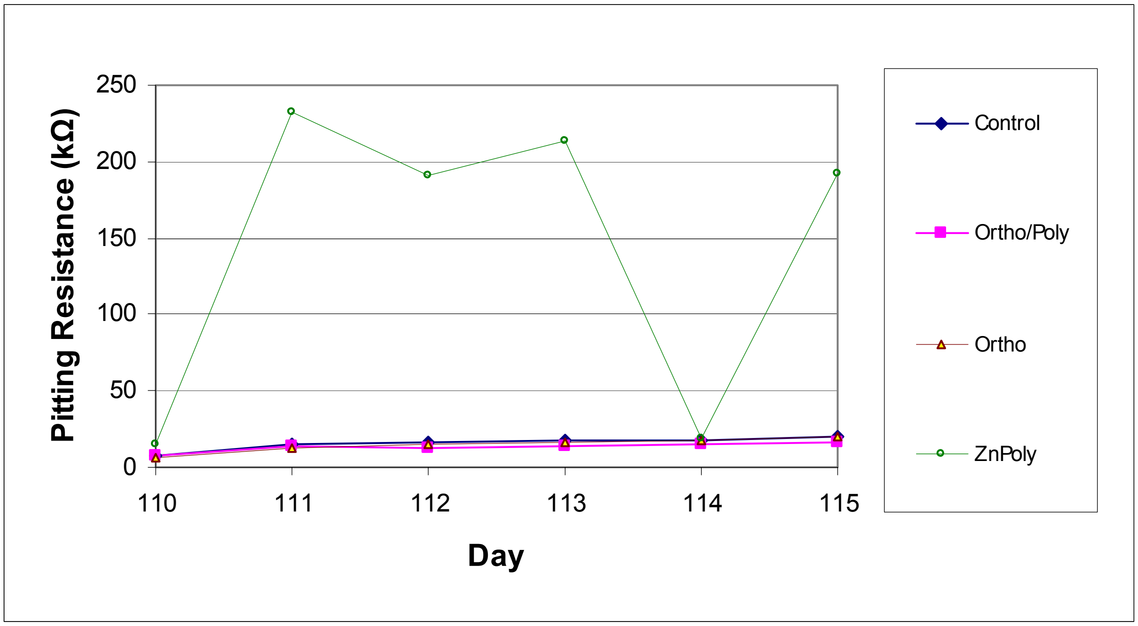


Figure 2-15. Average pitting resistances at pH 8.5. Data shown for low-flow pitting wires installed on Day 110.

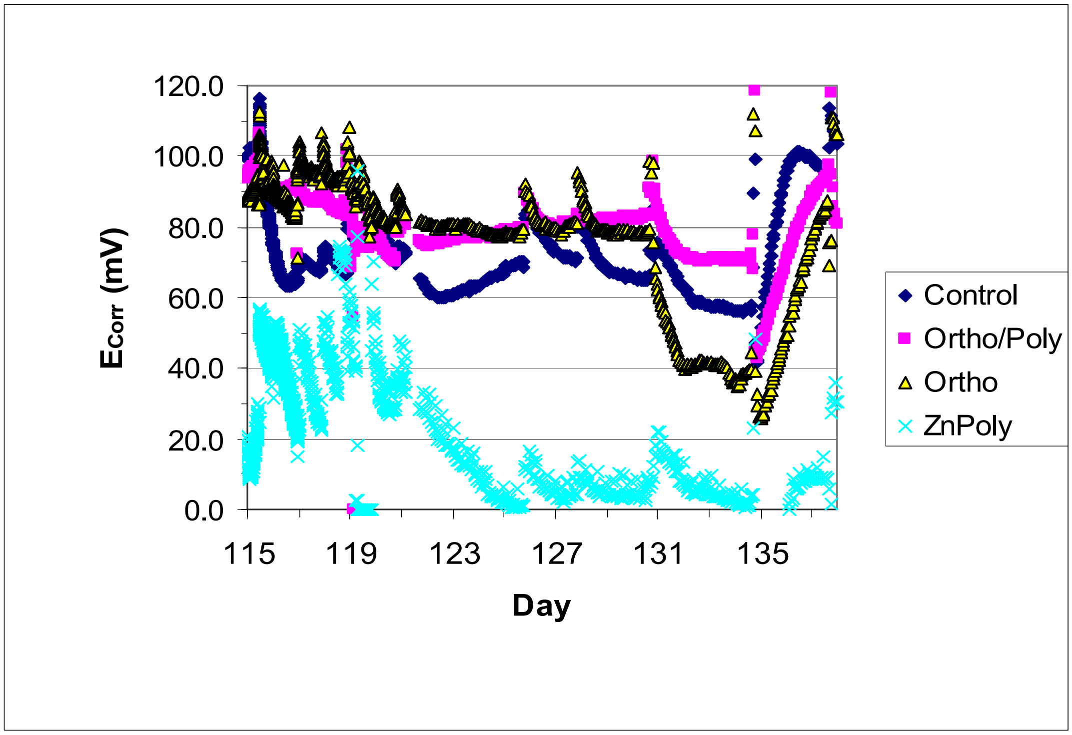


Figure 2-16. E_{Corr} measurements at pH 7.5.

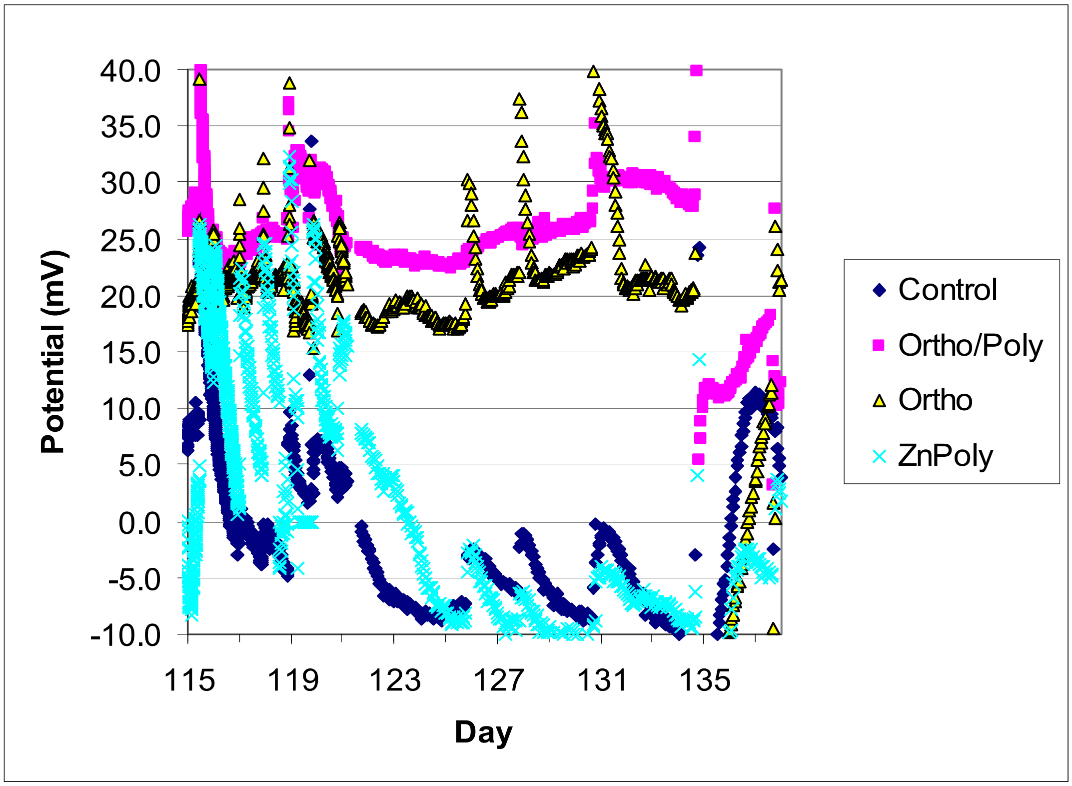


Figure 2-17. Potential between sections of pipe at pH 7.5.

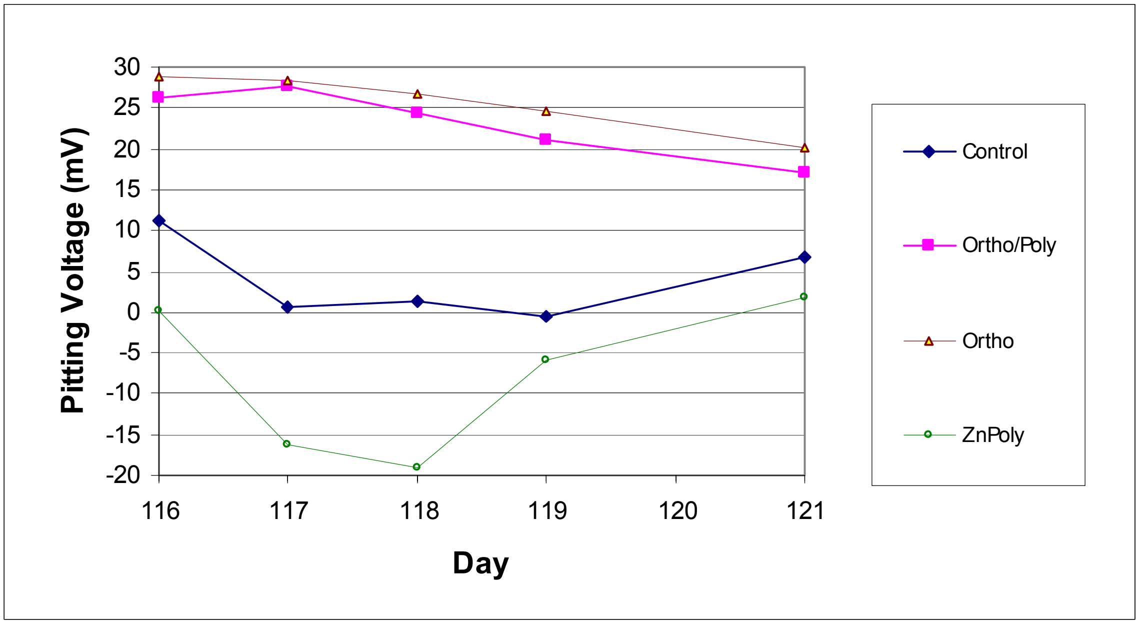


Figure 2-18. Average pitting voltages at pH 7.5. Data shown for low-flow pitting wires installed on Day 110.

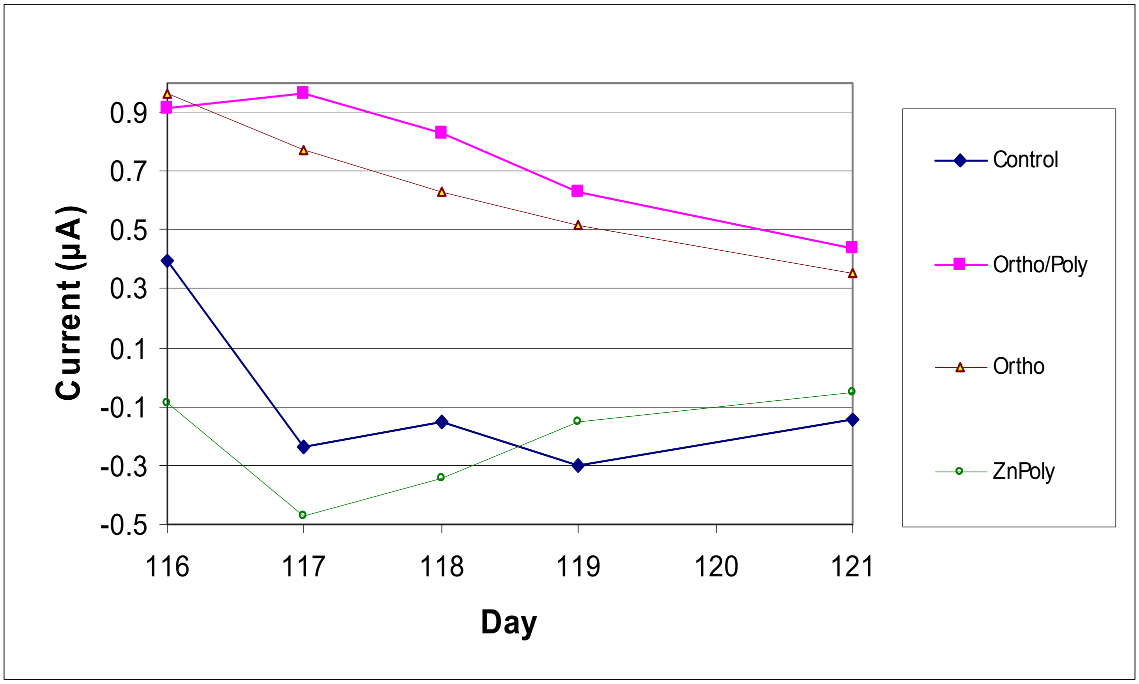


Figure 2-19. Average pitting currents at pH 7.5. Data shown for low-flow pitting wires installed on Day 110.

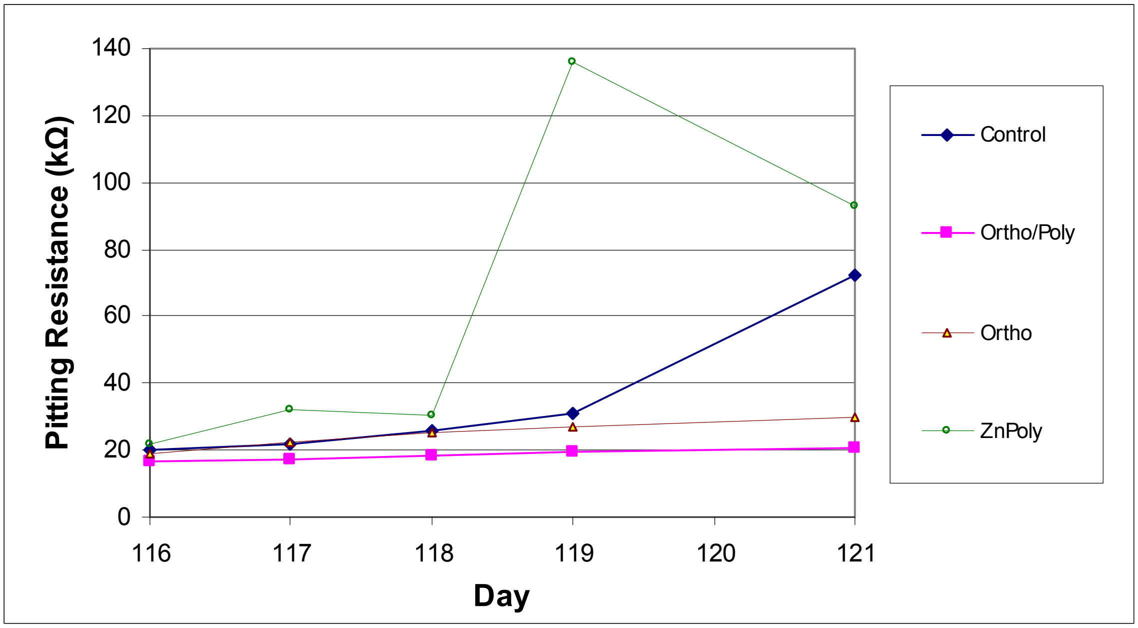


Figure 2-20. Average pitting resistances at pH 7.5. Data shown for low-flow pitting wires installed on Day 110.

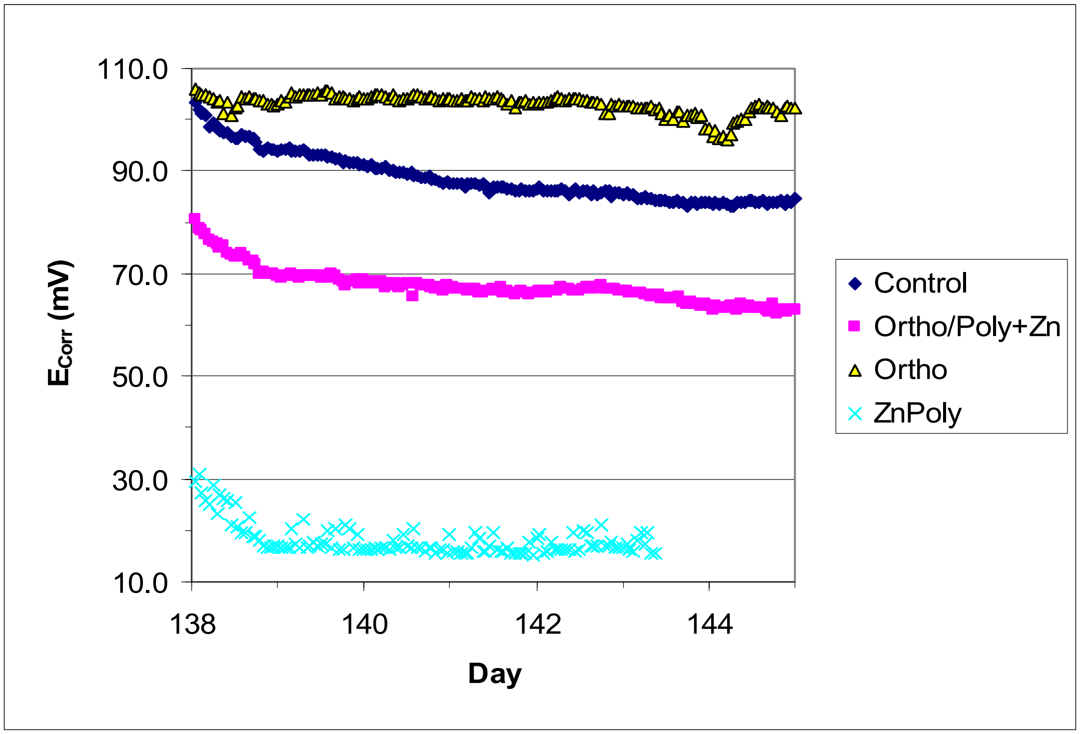


Figure 2-21. E$_{Corr}$ measurements at pH 7.5 with zinc added to Orthophosphate-Polyphosphate Rig.

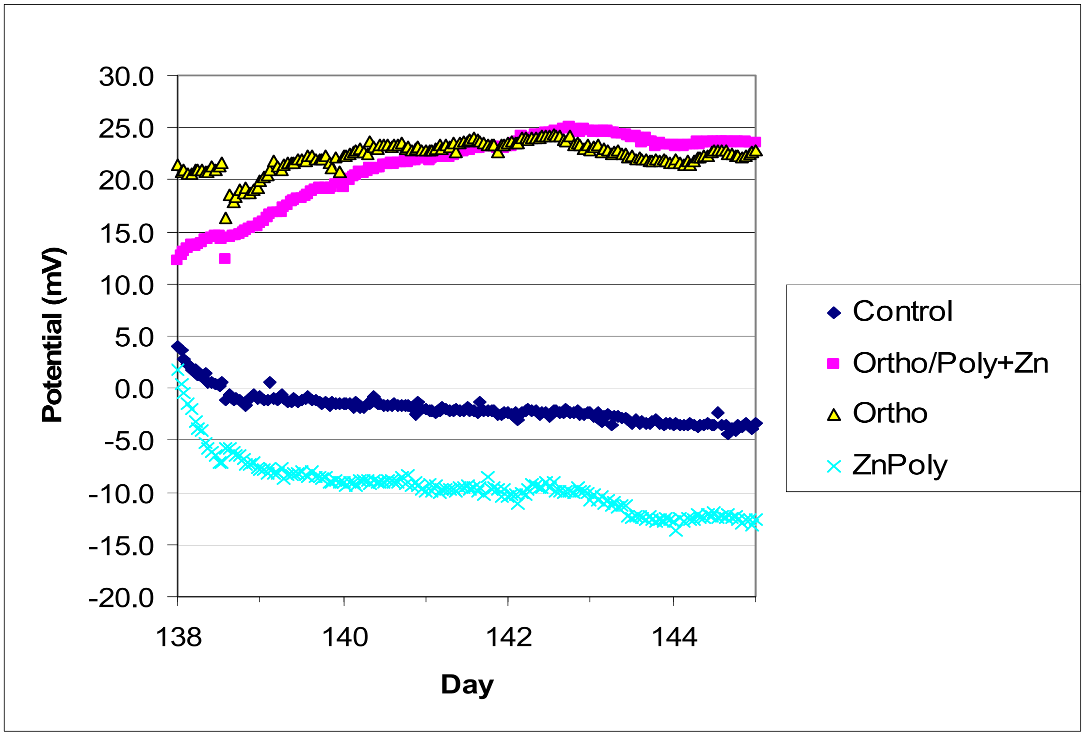


Figure 2-22. Potential between sections of pipe at pH 7.5 with zinc added to Orthophosphate-Polyphosphate Rig.

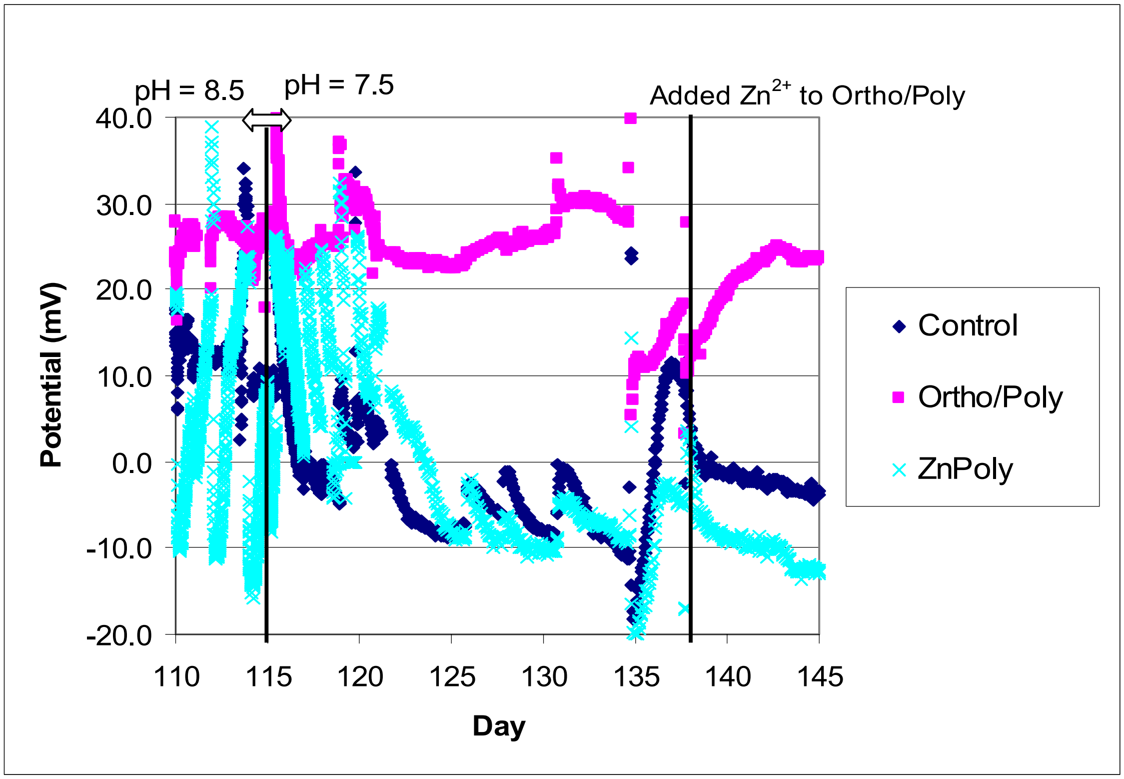


Figure 2-23. Potential between sections of pipe over the life of experiment.

Figure 2-24. Control Rig Coupons. Coupons A – D shown left to right.

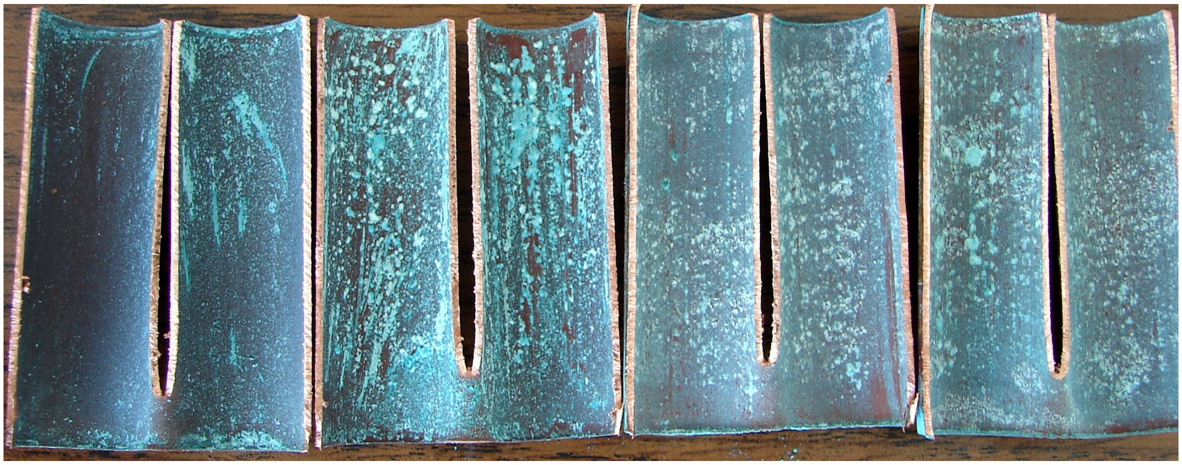


Figure 2-25. Orthophosphate Rig Coupons. Coupons A – D shown left to right.

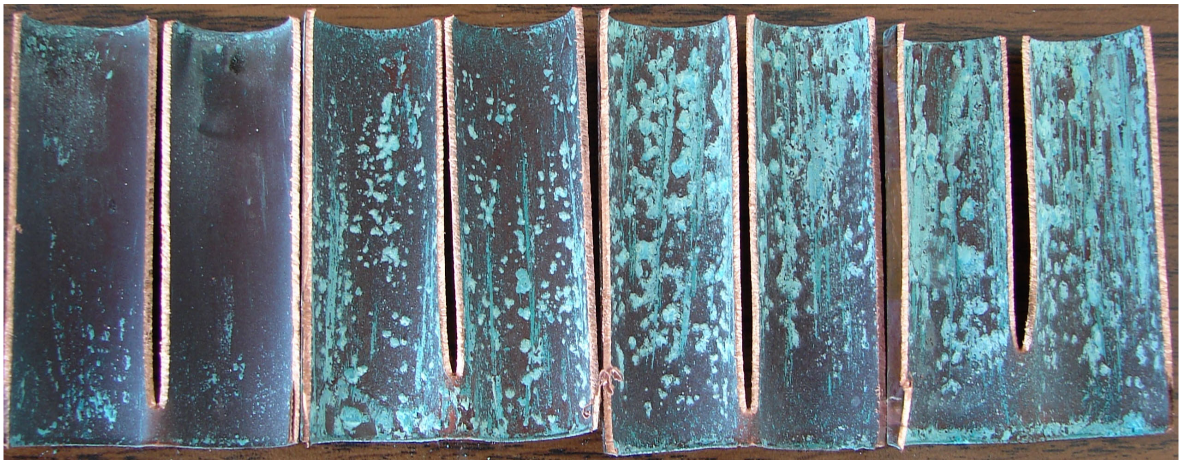


Figure 2-26. Zinc Polyphosphate Rig Coupons. Coupons A – D shown left to right.

Figure 2-27. Orthophosphate-Polyphosphate Rig Coupons. Coupons A – D shown left to right.

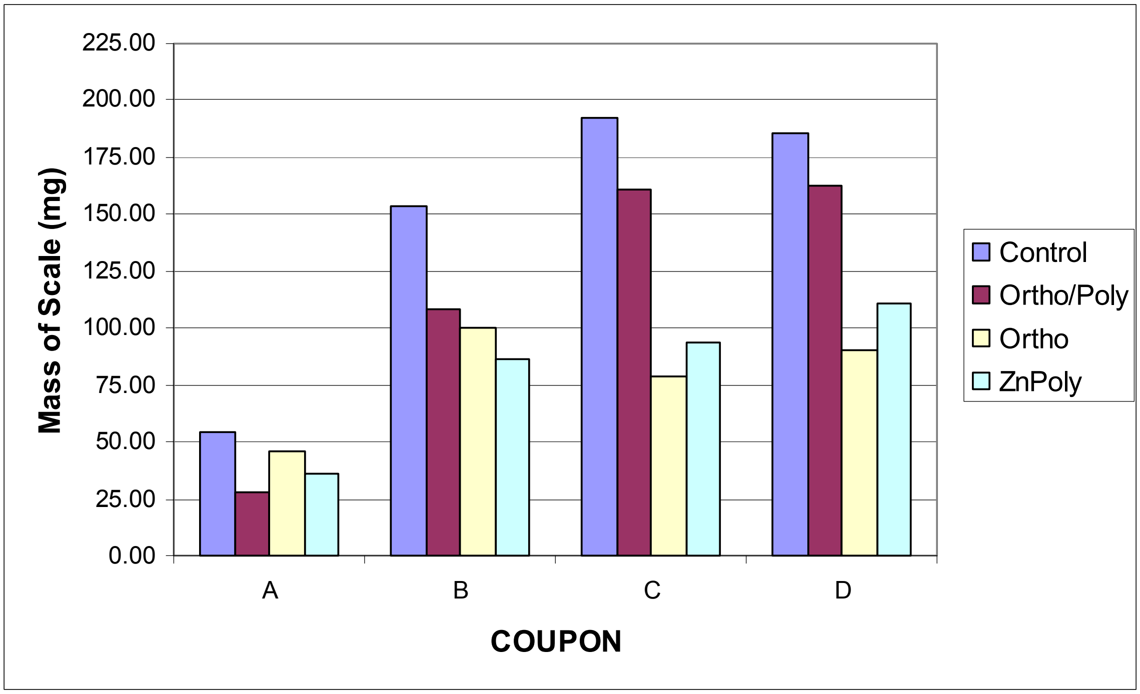


Figure 2-28. Mass of scale accumulation on coupons.

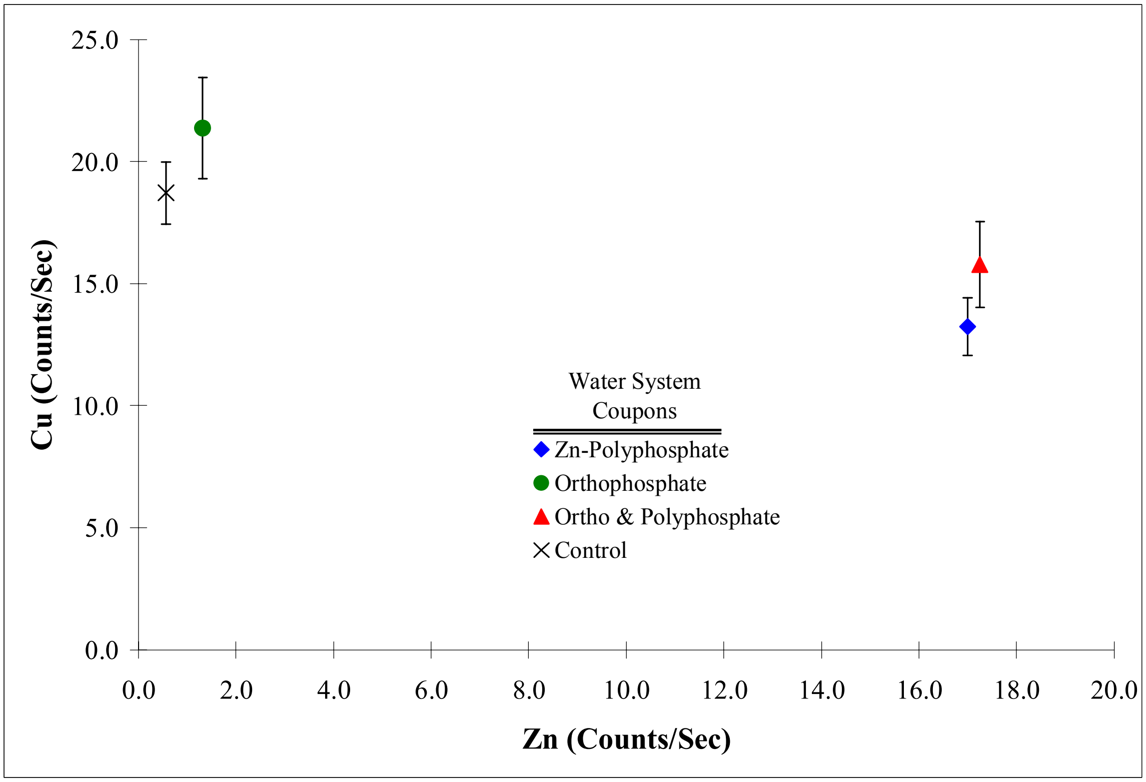


Figure 2-29. Raw Cu and Zn Data as collected by the SEM-EDS during surface analyses. Error bars represent 90% confidence intervals.

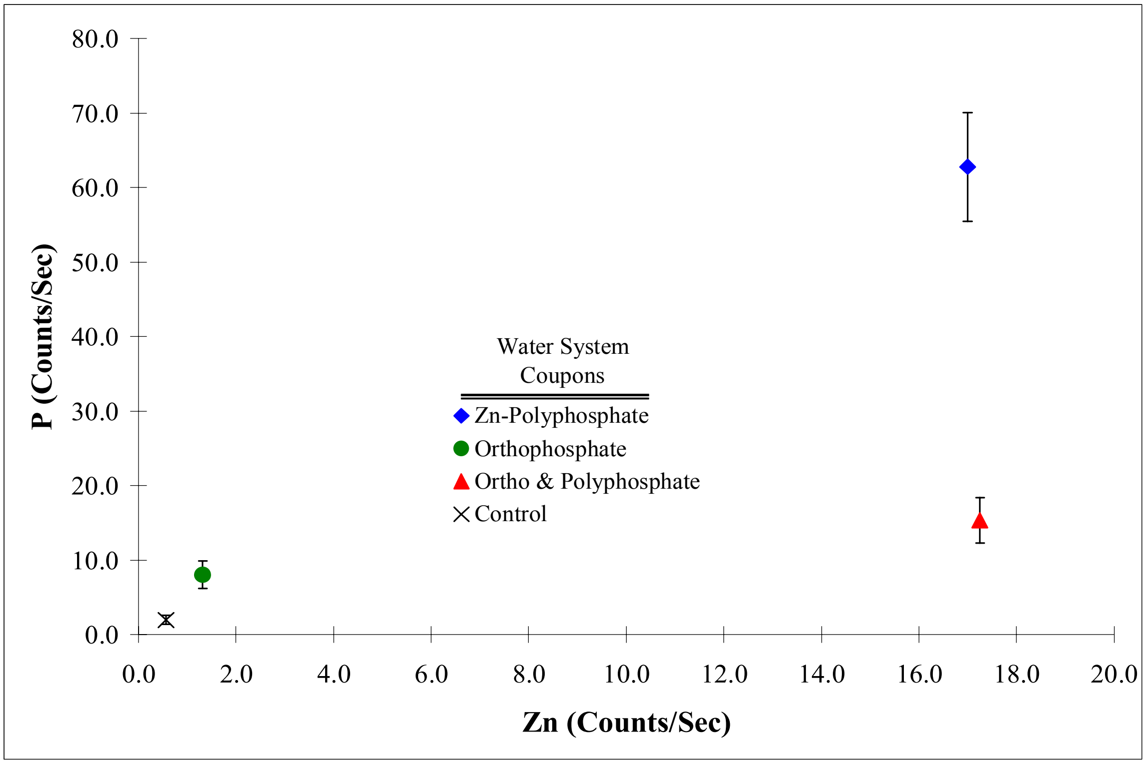


Figure 2-30. Raw P and Zn Data as collected by the SEM-EDS during surface analyses. Error bars represent 90% confidence intervals.

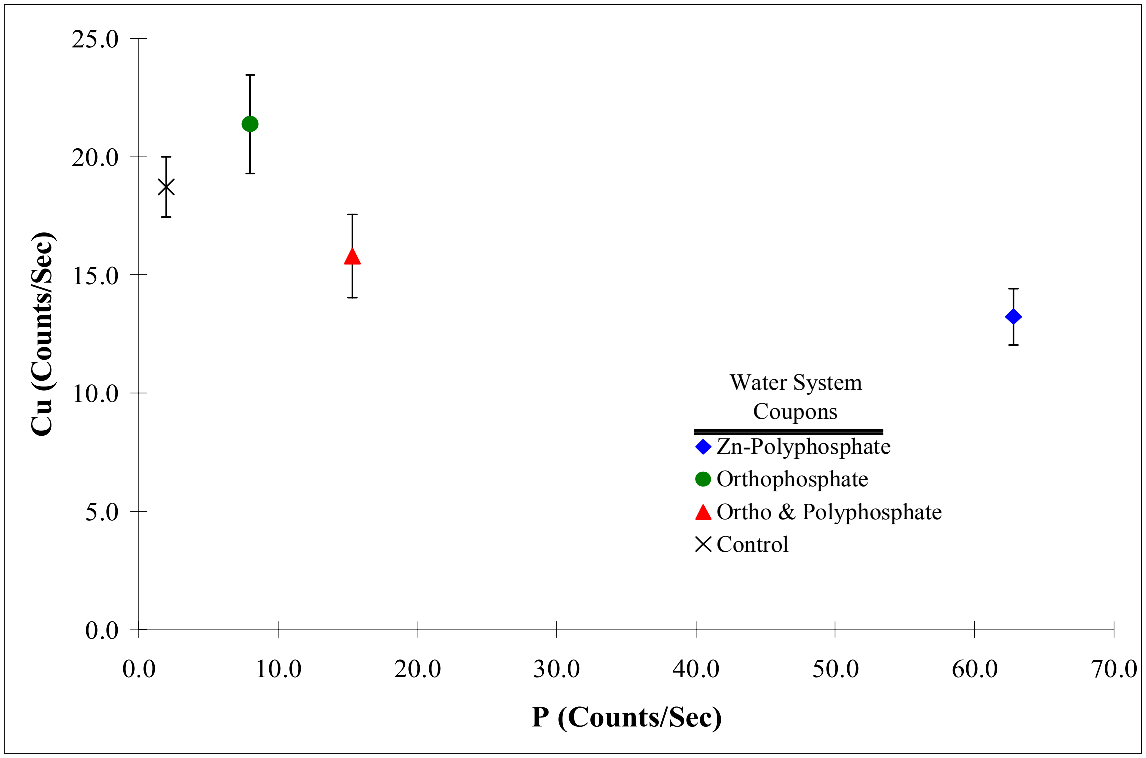


Figure 2-31. Raw Cu and P Data as collected by the SEM-EDS during surface analyses. Error bars represent 90% confidence intervals.

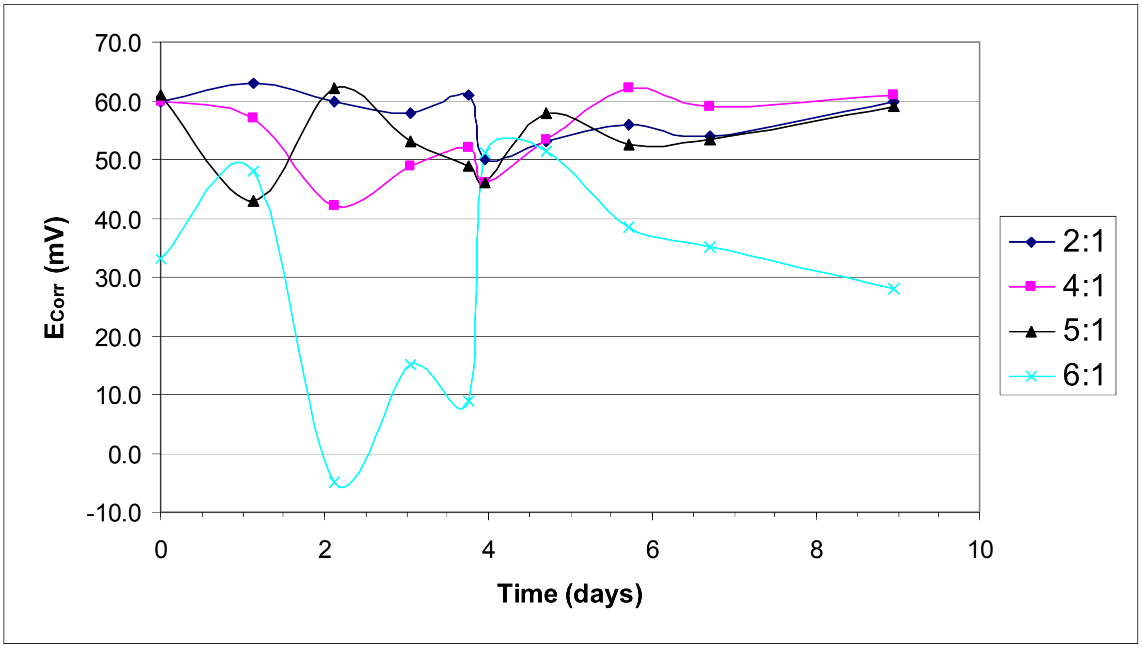


Figure 2-32. Jar Test - Effect of chlorine to ammonia ratio on E_{Corr}.

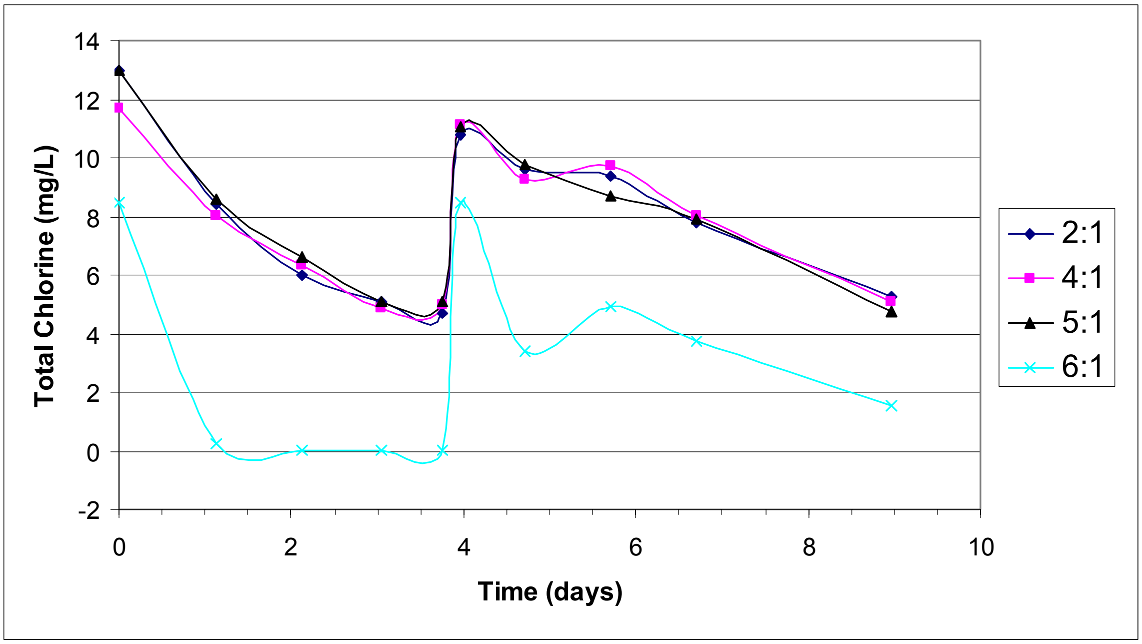


Figure 2-33. Jar Test - Effect of chlorine to ammonia ratio on chlorine decay.

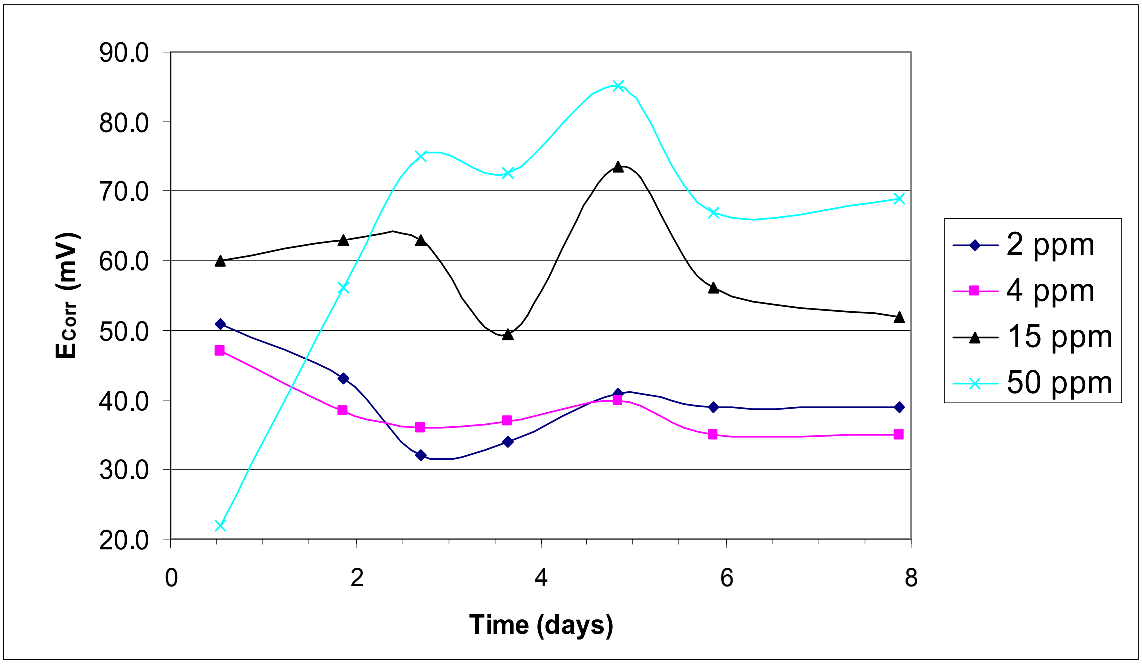


Figure 2-34. Jar Test - Effect of total chlorine on E_{Corr}.

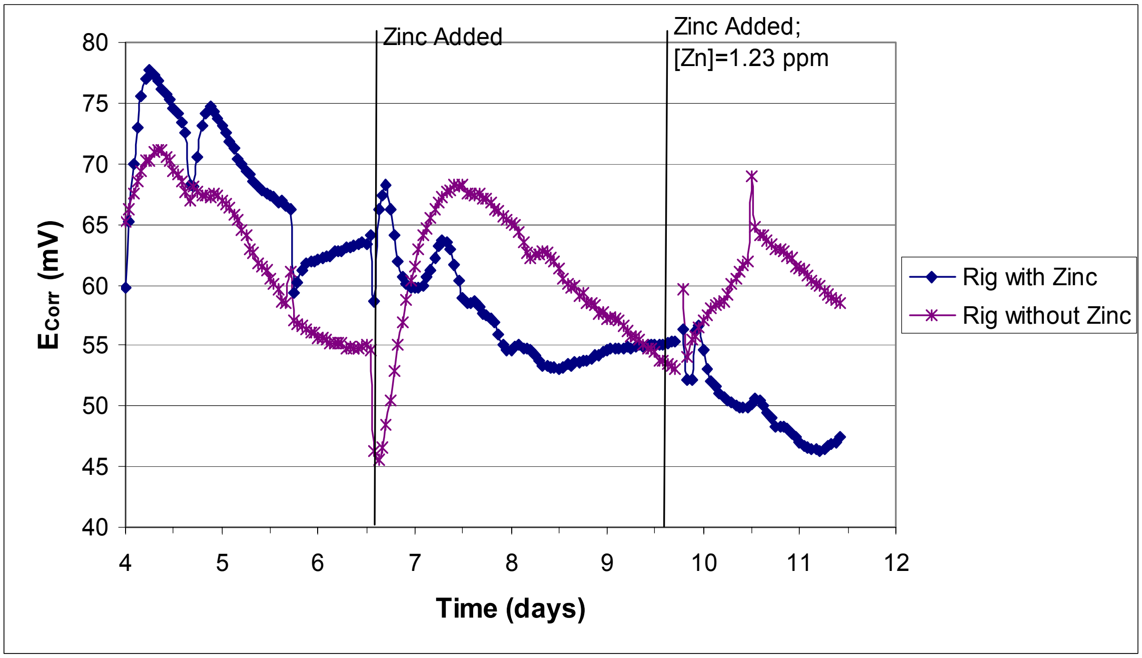


Figure 2-35. Rig Test - Effect of adding zinc to orthophosphate-polyphosphate on E_{Corr}.

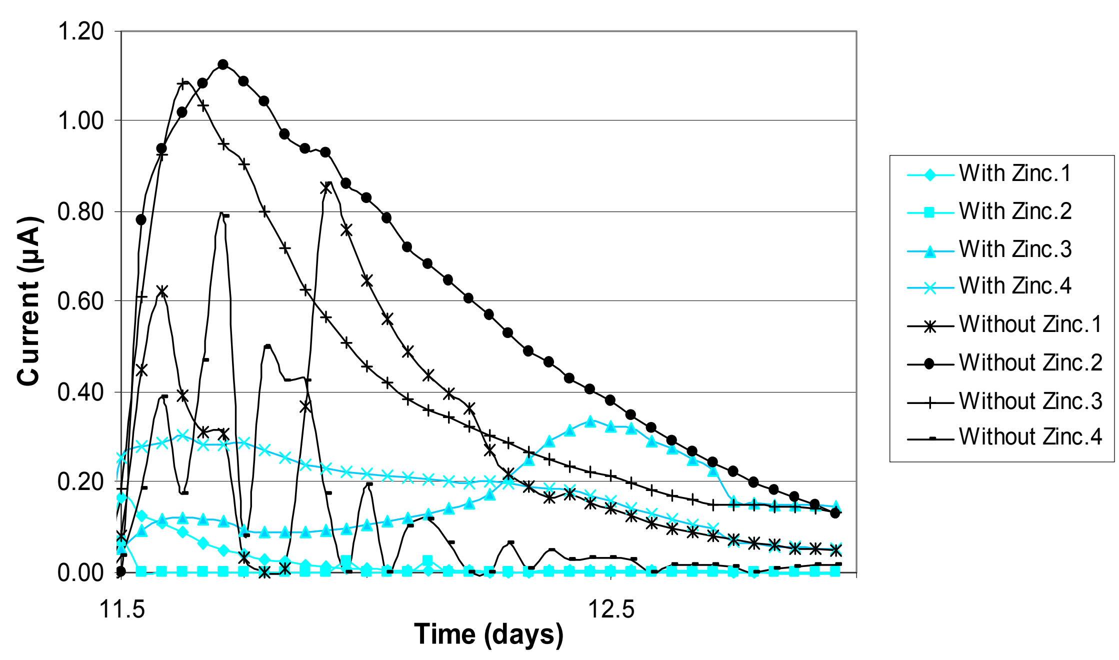


Figure 2-36. Rig Test - Effect of adding zinc to orthophosphate-polyphosphate on pitting currents.

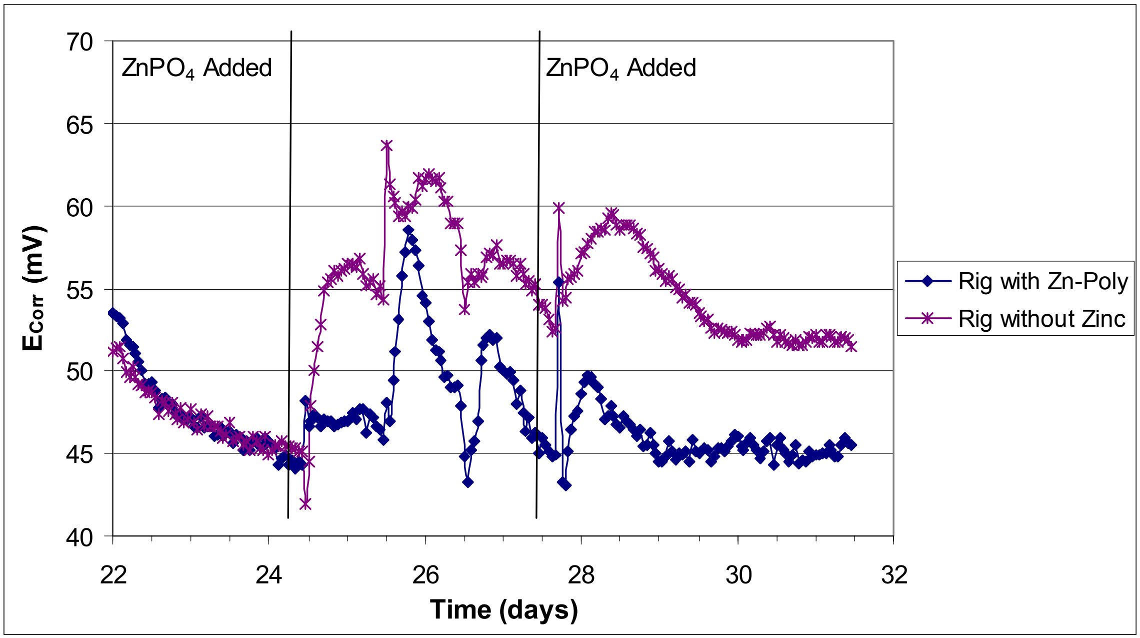


Figure 2-37. Rig Test - Effect of adding zinc polyphosphate to orthophosphate-polyphosphate on E_{Corr}.

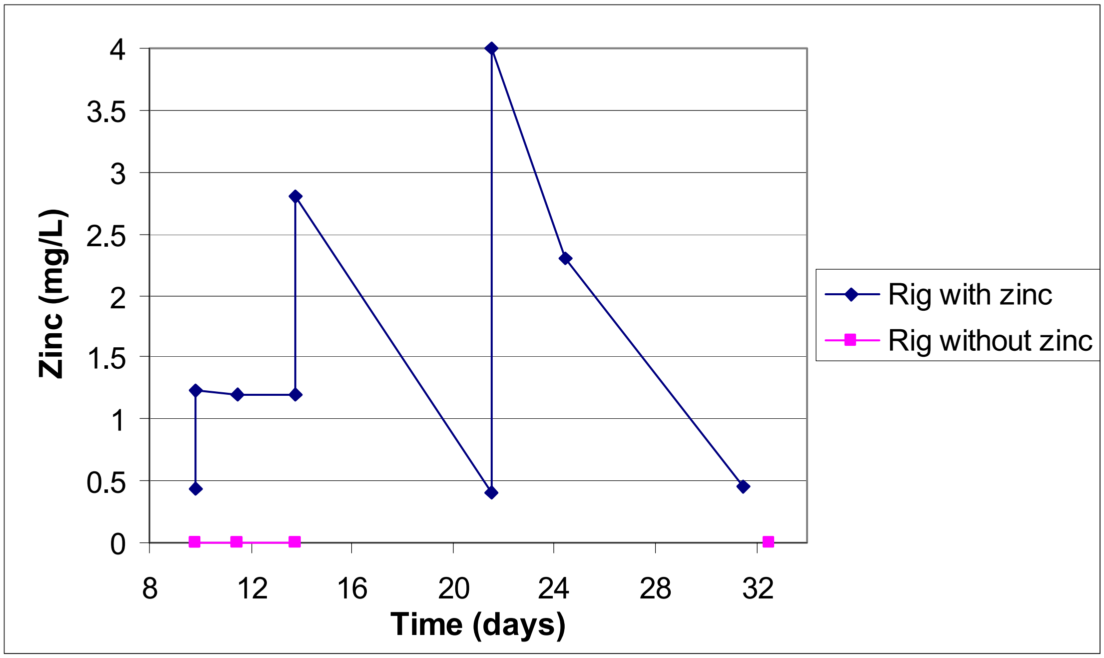


Figure 2-38. Zinc concentration measured in short term pitting rigs.

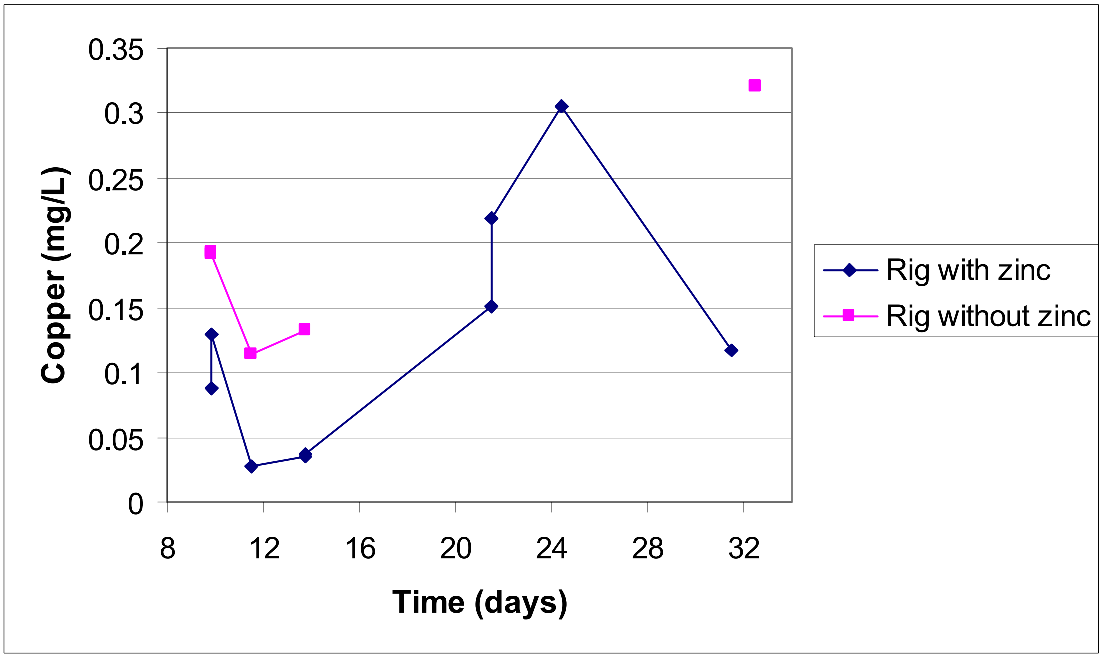


Figure 2-39. Copper concentration measured in short term pitting rigs.

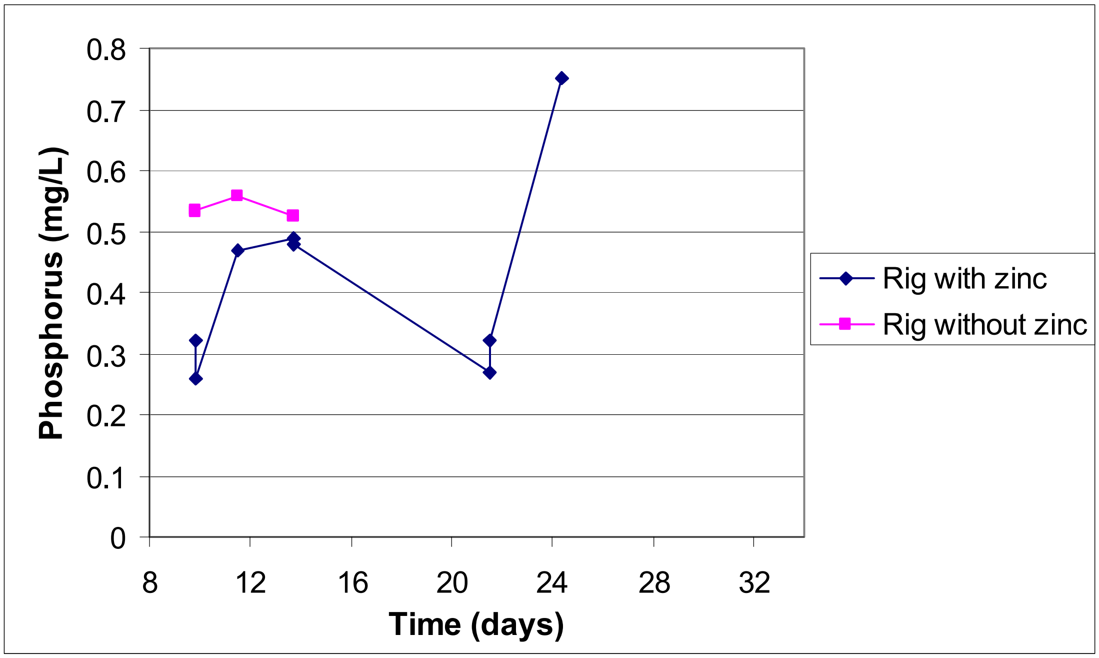


Figure 2-40. Phosphorus concentration measured in short term pitting rigs.

Chapter 3: Case Study of Copper Pitting Corrosion – Iowa Utility

Gregory Sheffer, Marc Edwards, and Paolo Scardina

ABSTRACT

Effects of disinfectant type (chlorine versus chloramines) and corrosion inhibitor type (orthophosphate versus zinc polyphosphate) on copper pitting propensity were examined at a utility in Iowa. Electrochemical methods, chlorine decay kinetics and surface analyses were used to evaluate the effectiveness of each condition on copper pitting inhibition. This study determined that no benefits, and probably some detriments, could occur from dosing orthophosphate to this water in the presence of high free chorine or chloramines at pH 8.5. Several of the electrochemical testing methods indicated that zinc polyphosphate may decrease pitting propensity, especially in free chlorine systems. The presence of zinc polyphosphate decreased chlorine decay rates, decreased E_{Corr}, and caused more rapid reductions in pitting currents.

INTRODUCTION

Treated water at the subject utility was produced by conventional softening and filtration processes applied to local groundwater. The raw water is initially passed through an upflow clarifier where it is mixed, flocculated, and settled using lime, sodium aluminates, and polymer at pH 10.5. Following clarification, the water is sent to a recarbonation tank where pH is dropped to 8.1 using CO_2. Thereafter, a mixed oxidant is added to the water to remove naturally high levels of ammonia. The water is then passed through sand/GAC dual media filters. Finally, fluoride and sodium hypochlorite solutions are added to the water prior to distribution. The target effluent pH is 7.8 and total maximum water production is 3.5 MGD.

Historically the utility has used chloramines at a target concentration of 3 mg/L as Cl_2 as a secondary disinfectant due to naturally high ammonia concentrations in the raw water. In July 2001, the utility exceeded the maximum contaminant level of nitrites (1.0 mg/L) by 0.01 mg/L due to an excess of ammonia in the distribution system. In order to bind the excess ammonia and prevent the formation of nitrites, the utility increased the total chlorine dose to 6 mg/L as Cl_2. Although this method effectively reduced the formation of nitrites, this solution was only temporary because 2004 drinking water regulations established maximum residual disinfectant levels for free chlorine and chloramines at 4.0 mg/L as Cl_2. Consequently, in August 2004, the utility began adding MIOX, a mixed oxidant product, to lower the free ammonia concentrations to a level which still allowed the formation of chloramines, but eliminated excess ammonia. Shortly thereafter, the utility experienced erratic behavior in finished water quality caused by dosing the mixed oxidant. In March 2005, the utility decided to initiate breakpoint chlorination and use free chlorine as a residual disinfectant at 1.5 mg/L as Cl_2.

Although historical accounts vary depending on the source, it is generally agreed that at least some level of copper pinhole leak activity has always existed in the area. However in 2004, customers experienced an outbreak of copper pinhole leaks without parallel to previous occurrences. This prompted the utility to seek assistance for a case study. Results of the study are reported herein based on data collected from October 2005 until January 2006.

Specifically, this study was aimed at identifying the effectiveness of orthophosphate and zinc polyphosphate as corrosion inhibitors in reducing the pitting propensity of the water. Surface analyses, chlorine decay kinetics and electrochemical methods including E_{Corr} measurements were applied in the experimental approach. E_{Corr} has been correlated to the formation of pinhole leaks and it is generally believed that water changes that decrease E_{Corr} will reduce the severity of copper pitting (Marshall, 2004). Greater rates of chlorine decay are indicative of higher rates of reduction reactions at cathodic surfaces, which are a key factor driving copper pitting (Chapter 1). Given the history of the utility regarding secondary disinfection methods and the uncertainty as to which disinfectant would be more efficient in terms of reducing pitting severity, the relative effects of using free chlorine or chloramines were explicitly considered.

In addition, an innovative approach in this work attempted to create live pits. In this method, attempts were made to develop pitting wires that allow pitting current, potential, and resistance of artificial pits to be measured with a simple multimeter as described in Chapter 1.

Orthophosphate was tested due to its popularity as a corrosion inhibitor, as well as for the fact it had recent success alleviating pitting problems at another water utility (Nguyen, 2005). Zinc polyphosphate, also referred to as zinc metaphosphate or zinc hexametaphosphate, was used considering the promising results in recent laboratory pitting studies at a Florida utility (Chapter 2).

MATERIALS AND METHODS

The 75 day study used four 55 gallon reservoirs operating in a continuously circulated mode located in the chemical feed room of the water utility. Each rig circulated water at 2 gpm using a submersible pump in the 55 gallon reservoir upwards thru four 2” Type L soft copper coupons and three feet of ¾” Type L soft copper pipe to a 90° CPVC bend, horizontally across six inches of ¾” CPVC, and then back down three feet of ¾” Type L soft copper pipe (Figure 3-1). The outer surface of the soft copper pipe protruded only a few inches into the reservoir and the surface was protected by plastic tubing and sealed with silicone sealant. Thus, only the inner surface of the copper was exposed to the water. Recirculating pumps rated at 18 gpm were installed and turned on when chemical adjustments were made to hasten distribution of chemicals.

Among the four reservoirs, two were used as controls dosing free chlorine or chloramines and contained no inhibitor. The remaining two rigs were used to investigate the effectiveness of inhibitors in the presence of each disinfectant. Orthophosphate was dosed at 2 mg/L as P into each of these reservoirs from Day 7 until Day 43. Thereafter, zinc polyphosphate was dosed at 0.4 mg/L as P and 0.1 mg/L as Zn into the same rigs previously containing orthophosphate. This phase occurred for the remaining 32 days of the experiment (Day 43 to Day 75). The target free chlorine concentration was 8.5 mg/L as Cl_2 and was maintained within 2 mg/L of this value. The target chloramine concentration was 12.5 mg/L as Cl_2 and was maintained within 5.0 mg/L. The target pH was 8.5 and was maintained between 8.0 and 9.0.

During the first week of operation (Day 1 to Day 7), all rigs circulated product water containing free chlorine at 10 mg/L as Cl_2 at pH 9.5 in order to initiate pitting and establish baseline data. High chlorine and high pH have both been shown to increase pitting propensity (Marshall, 2004). During this time, E_{Corr} was measured as an indication of pitting propensity among the rigs.

Water quality was maintained every two to three days at a minimum, although adjustments were typically made daily. Total chlorine concentrations were recorded to determine chlorine decay kinetics. Samples were taken at the end of the experiment and analyzed for total metal concentrations using inductively coupled plasma mass spectroscopy (ICP-MS).

Real Time Electrochemical Measurements

Corrosion potential (E_{Corr}) and pitting current measurements were continuously collected for periods of the experiment using a Gamry ECM-8 multiplexer in a zero resistance ammeter mode. A positive current indicates that the pitting wire is anodic relative to the pipe and it is actively pitting, whereas a negative pitting current indicates that the pipe is anodic relative to the pit. Of these a positive current on the pit is deemed worse with respect to pitting propensity, and the magnitude of the current is proportional to the magnitude of the problem.

In general, higher E_{Corr} indicates increasingly aggressive water. Ag-AgCl reference electrodes, used to measure E_{Corr}, were maintained regularly to ensure accuracy.

Pitting Current, Potential, and Resistance

Pitting wires were made by inserting 18g electrical grade bare copper wire into teflon sleeving (ID = 1/16”, OD = 1/8”) and sealing both ends with silicone sealant. The end of the pitting wire which would be exposed to the water was sanded to a smooth, circular copper surface using a small handheld sanding tool with a 60 grit sanding band. The other end of the pit wire was electrically connected to the copper pipe via alligator clips, insulated copper wire and battery clamps. On Day 4, relay boxes which established an electrical connection between the pitting wires and the pipe were installed for ease of measurements (Figure 3-1). When measurements were not being made, pitting wires maintained an electrical connection to the copper pipe via the relay box and the current was allowed to flow naturally. The pitting wires had about the same cross sectional area (1 mm^2) as real pits found in the system. The general idea is that anodic activity on the tips of pitting wires could produce a detectable current which is directly related to the rate of pit growth. Two pitting wires from each rig were continuously measured using a Gamry ECM-8 multiplexer with a potentiostat in a zero resistance ammeter mode.

Tips of some pitting wires were exposed to water in areas of high velocity, whereas others were installed in areas of low velocity, since it is believed that differential water velocity on copper pipe surfaces can act to initiate pitting in at least some waters (Marshall, 2004). Pits exposed to high flow conditions (high flow pits) were placed directly into the copper pipe effluent, pits exposed to low flow conditions (low flow pits) were placed 10" from the copper pipe effluent where the water was quiescent, and pits exposed after 90° bends (90 degree in-flow pits) were placed into the horizontal CPVC section connecting upstream and downstream copper pipes (Figure 3-2).

Ultimately, nearly all of the pits died and results of the pitting wire tests cannot be deemed to have replicated 'live' pits as had been anticipated. This indicates that pits could not reproducibly be formed on the pitting wires in question, and that some factor other than low or high water flow is involved in getting pits started in this particular water, at least with a high degree of reproducibility. However, relative pitting current comparisons among experimental conditions is still deemed a measure of pitting propensity in these tests, since it is believed that factors which tend to oppose separation of anodic and cathodic areas on pipe is a key factor that helps to stop copper pitting.

It is noteworthy to mention that low flow pits sustained the highest pitting currents among all pit wire locations, followed by high flow pitting wires and 90° in-flow pitting wires, respectively. Thus, pitting current results of the low flow pits were used for all comparisons among the experimental conditions.

The pitting current and potential was measured between the pitting wires and the pipe using a Fluke 189 True RMS Digital Multimeter in conjunction with a relay box. Higher current and potential are deemed indicative of greater levels of corrosion. The resistance between the pitting wire and the pipe was also measured using the same instrument. Since the resistance of the water is relatively low, the high electrical resistance indicates that a protective film is forming on the copper surfaces and indicative of the ability of the film to reduce corrosion. In general, higher resistance is believed to indicate a more protective pipe scale.

Surface Analysis of Copper Coupons

Each rig incorporated four ¾" Type M copper coupons. Each coupon was 2" in length. Coupons were weighed both before and after the experiment to quantify any scale formation and/or weight loss due to corrosion. Perhaps more significantly, these coupons were examined for visual indications of pitting. A scanning electron microscope (SEM) equipped with electron dispersive spectrometry (EDS) was used to identify elements present on the interior surface of each coupon down to a depth of 1 μm.

RESULTS AND DISCUSSION

The testing was conducted in three phases including baseline conditions, orthophosphate inhibitor testing, and zinc polyphosphate inhibitor testing. After discussing test results of each phase, results of surface analyses of coupons are described, and then key conclusions are reviewed.

Baseline Data

During the baseline exposure, all copper samples were exposed to the same water containing free chlorine at 10 mg/L as Cl_2 at pH 9.5 and no inhibitor. Analysis of E_{Corr} data indicated that two of the conditions were higher than the other two, perhaps due to slight differences in the copper used for the rig (Table 3-1). Specifically, average E_{Corr} (with standard deviation) was 92 +/- 6 mV in Rig 1 and 97 +/- 12 mV in Rig 2. These two conditions were equal at greater than 90% confidence. Rig 1 and Rig 2 later contained free chlorine without and with inhibitor, respectively. Similarly, Rig 3 and Rig 4 had average E_{Corr} values of 101 +/- 13 mV, and 105 +/- 8 mV, respectively, and were also equal at greater than 90% confidence. Rig 3 and Rig 4 were later exposed to chloramines with and without inhibitor, respectively. Henceforth, each rig is referred to by its experimental condition and not by rig number.

Orthophosphate Inhibition Results

Free Chlorine Systems

In the free chlorine systems, the addition of orthophosphate seemed to increase pitting propensity on the basis of E_{Corr} and pitting currents. Specifically, E_{Corr} was 20 mV higher in the system with orthophosphate relative to the system without orthophosphate (Figure 3-3). Although this system was 5 mV higher at the start of the test and before orthophosphate was added (Table 3-1), the increase is still believed significant. Higher E_{Corr} after dosing orthophosphate was also observed in the pitting experiments of Chapter 2, for which full-scale data confirmed that dosing orthophosphate indeed made pitting worse (Edwards, 2005).

Pitting currents also suggested that orthophosphate was increasing the pitting propensity of the water. The two pits measured in the free chlorine system with orthophosphate supported higher currents than the two pits measured in the free chlorine system without inhibitor (Figure 3-4). Interestingly though, paired t-tests at 79% confidence determined the chlorine decay rate in the system without inhibitor was greater than the system containing orthophosphate. Specifically, the average chlorine decay rates in the free chlorine systems were 0.13 and 0.23 mg Cl_2/L/day for systems with and without orthophosphate, respectively. This suggests that the orthophosphate may have reduced the cathodic rate of the reaction between chlorine and copper, which overall should have some benefits on pitting propensity. Further, since E_{Corr} rose, this indicates that orthophosphate also tended to decrease the rate of the anodic reaction. Generally, this reduction of anodic and cathodic reaction rates is desirable as overall pitting activity is decreased. However, the possibility exists that the decrease in the cathodic reaction rate is greater than the decrease in anodic activity. If this occurred, corrosion would proceed on a smaller number of anodic pitting sites, but these remaining sites would corrode at a greater intensity.

Chloramine Systems

In the systems dosed with chloramines, E_{Corr} rose substantially with time, consistent with a water having a high pitting propensity. The addition of orthophosphate had no significant effect on pitting propensity on the basis of E_{Corr} or pitting currents. For the first 18 days of orthophosphate dosing, E_{Corr} of the chloramine system without inhibitor was approximately 5 mV higher than the system with orthophosphate (Figure 3-5). However over the following 18 days, the trend switched and E_{Corr} in the chloramine system without inhibitor became 5 mV lower than the one containing orthophosphate. Overall, paired t-tests at 90% confidence determined that E_{Corr} for the system dosed with orthophosphate was greater than the system without inhibitor. Regardless, differences in E_{Corr} were relatively low and no clear benefits due to orthophosphate occurred in systems dosed with chloramines.

Pitting currents produced similar results and indicated the addition of orthophosphate produced no benefits. In fact, the two pits measured in the chloramine system with orthophosphate supported higher currents than the two pits measured in the chloramine system without inhibitor (Figure 3-6). The average chlorine decay rates were nearly identical at 0.12 and 0.11 mg Cl_2/L/day for systems with and without orthophosphate, respectively, and no differences in chlorine decay rates could be determined using t-tests at 90% confidence. This further supports the general idea that dosing orthophosphate was not influencing pitting reactions in the presence of chloramines.

Zinc Polyphosphate Inhibition Results

After failing to identify a combination of disinfectant and corrosion inhibitor that would decrease pitting propensity, supplemental testing was conducted in an attempt to find a promising alternative.

Free Chlorine Systems

Upon adding zinc polyphosphate, E_{Corr} of the free chlorine system previously dosed with orthophosphate dropped from 20 mV higher than the E_{Corr} of the system without inhibitor to only 5 mV higher (Figure 3-7). In time, E_{Corr} of the system dosed with zinc polyphosphate became roughly equal to the system without inhibitor. In fact, from Day 58 to Day 62, E_{Corr} of the system dosed with zinc polyphosphate was actually less. Thus, the addition of zinc polyphosphate did not increase E_{Corr} relative to the system without inhibitor as did the addition of orthophosphate. Although t-tests confirmed with 90% confidence that E_{Corr} of the system with zinc polyphosphate was still greater than the system without inhibitor, E_{Corr} of the systems were significantly closer relative to E_{Corr} trends during the addition of orthophosphate (Figure 3-3). Further, given that the test time was relatively short and E_{Corr} trends were promising, it is very possible that with time the addition of zinc polyphosphate would have significant benefits. Increasing benefits with time were realized when dosing zinc polyphosphates in pitting experiments for another utility (Chapter 2).

Pitting current measurements indicated that one of the two pits tracked in the free chlorine system with zinc polyphosphate "died" immediately (Figure 3-8). Although the other pit exposed to zinc polyphosphate was relatively unaffected, this result is considered promising as propagation of one of two pits was instantly stopped. Pitting is a statistical phenomenon and while it would be desirable to have results for hundreds of pits to make predictions with confidence, this short term result is still noteworthy.

Chlorine decay rates also indicated the addition of zinc polyphosphate produced beneficial effects. The chlorine decay rates in the free chlorine systems with and without zinc polyphosphate were 0.17 and 0.47 mg Cl_2/L/day, respectively. In addition, t-tests confirmed that chlorine decay rates were greater in the system without zinc polyphosphate at 90% confidence as opposed to the trend established during orthophosphate testing which confirmed the result at only 79% confidence. This result indicates that zinc polyphosphate dramatically reduced the extent of the cathodic reaction between copper and chlorine. Thus, the zinc polyphosphate may be effectively functioning as a cathodic inhibitor.

Although leaching of copper is not related to pitting, total copper concentrations were 0.22 and 0.24 mg Cu/L for systems with and without zinc polyphosphate, respectively. This result indicates that use of the zinc polyphosphate will probably not increase copper leaching.

Chloramine Systems

Upon adding zinc polyphosphate, E_{Corr} of the chloramine system previously containing orthophosphate continued to rise but then abruptly dropped by 60 mV after roughly ten days (Figure 3-9). Previously, E_{Corr} of the system containing orthophosphate was slightly higher than the system without inhibitor. Although the E_{Corr} of the chloramines system without inhibitor also experienced an abrupt drop, the decrease was not as great in magnitude, and E_{Corr} quickly returned to within 15 mV of its previous value. Further, from Day 51 to Day 58, E_{Corr} of the system with zinc polyphosphate was lower relative to the system without inhibitor. Thus, zinc polyphosphate decreased the relative corrosivity of the water in comparison to the system without inhibitor. Furthermore, it can be stated with at least 95% confidence that the addition of zinc polyphosphate decreased E_{Corr} of the system relative to measurements during the presence of orthophosphate. From this perspective zinc polyphosphate performance was very positive.

The benefits of the zinc polyphosphate extended to pitting current measurements as well. Previously, pitting currents were around 1.3 μA in the presence of orthophosphate, but dropped by 1 μA (77%) during exposure to zinc polyphosphate for seven days. The pitting currents in the system without inhibitor also dropped during the same time period, but only by 35% (Figure 3-10).

Chlorine decay rates in the system with chloramines were 0.37 and 0.77 mg Cl_2/L/day in the systems with and without zinc polyphosphate, respectively. This is quite a significant outcome given that results were previously indistinguishable when comparing the orthophosphate condition to the control system. In other words, the orthophosphate did not decrease the reaction rate of chlorine decay, whereas zinc polyphosphate did. In addition, t-tests confirmed that chlorine decay rates were greater in the system without zinc polyphosphate at 81% confidence.

Total metals results provided additional support for zinc polyphosphate as copper concentrations were twice as high in the system without inhibitor. Concentrations were measured at 0.25 and 0.49 mg Cu/L for the systems with and without zinc polyphosphate, respectively.

Surface Analysis of Copper Coupons and Sections of Copper Pipe

Four 2” copper pipe coupons were incorporated into each rig (Figure 3-1). Water recirculating through the rig contacted the coupons first and then passed through the remaining copper pipe before exiting back into the reservoir. Coupons were labeled A – D on each rig and were consistently positioned such that water flowed through Coupon D first, and then through the remaining coupons in decreasing letter sequence. At the end of the experiment, coupons and pipe sections were disassembled and the interior pipe scale was examined. While absolute conclusions cannot be determined due to the relatively short time of exposure, inspection of these coupons still produced valuable information.

Visual Examination of Copper Coupons and Sections of Copper Pipe

Visual examination discovered distinctive differences in comparing *sets* of coupons between different experimental conditions as well as differences among the four *individual* coupons of a given experimental condition. Interesting differences were observed among individual coupons of each experimental condition. Specifically, the coupons first receiving flow (Coupon D) consistently produced the most pronounced corrosion scale (Figures 3-11, 3-12, 3-13, and 3-14). The amount or degree of corrosion gradually decreased across the remaining three coupons in the direction of flow such that the last coupon receiving flow (Coupon A) was subject to the least amount of corrosion. This trend suggests that coupons first receiving flow became more anodic relative to latter coupons. This same trend occurred on copper coupons in the pitting tests of Chapter 2 and similar observations were also observed by Marshall (2004), where copper pitting occurred predominantly at the entrance of pipe sections. Given that Coupon D experienced the greatest degree of corrosion in each system, these coupons were selected for comparative coupon analyses between experimental conditions.

When examining Coupon D from each experimental condition, the free chlorine control system appeared to be the most heavily corroded based upon scale abundance and the formation of tubercles indicative of non-uniform corrosion (Figure 3-15). In fact, no tubercles were found on coupons from the remaining test conditions. However, a potentially non-aggressive uniform corrosion scale predominantly formed on Coupon D from the remaining conditions. Specifically, Coupon D from the chloramine system with inhibitor seemed to have the most abundant scale among the remaining conditions (Figure 3-16) and the scale on Coupon D from the chloramine control system and the free chlorine system with inhibitor were qualitatively similar (Figures 3-15 and 3-16).

The three foot copper pipe sections which supported flow were also examined. Visual interpretations were consistent with that of the coupons. Specifically, the pipe section from the free chlorine control system seemed to have the most pronounced corrosion, even though no tubercles or other indications of pitting were observed (Figure 3-17). Accordingly, pipe sections from the chloramine system with inhibitor had the next greatest indications of corrosion, followed by the pipe section from the chloramine control system (Figures 3-18 and 3-19). The pipe section from the free chlorine system with inhibitor appeared to have the least amount of visible corrosion (Figure 3-20).

Scale Accumulation and Weight Loss of Copper Coupons

The mass of scale accumulation on coupons confirmed visual observations as the greatest amount of scale (corrosion activity) was produced on the coupons from the free chlorine control system (Figure 3-21). Respectively, the chloramine system with inhibitor and the chloramine control system produced the next greatest amount of scale. The least amount of scale production was consistently measured on the coupons from the free chlorine system with inhibitor.

In addition, the total weight loss due to corrosion was determined after completely removing the scale on all coupons. Although results slightly varied among the different coupon positions, the trends of Coupon D established that the greatest weight loss (corrosion activity) occurred in the free chlorine control system and the least weight loss occurred in the free chlorine system with inhibitor (Figure 3-22). Again, intermediate measurements resulted in the chloramine systems with and without inhibitor.

SEM-EDS Analysis of Copper Coupons and Sections of Copper Pipe

Portions of the interior coupon pipe scale were removed for surface analysis with the SEM-EDS. Attempts were made to select portions of scale which were more pronounced and indicative of areas which were subjected to greater amounts of corrosion. Analysis determined that greater percentages of zinc and phosphorus existed on the surface of coupons from systems dosed with corrosion inhibitors, indicating the precipitation of zinc and phosphorus (Table 3-2). More specifically, greater amounts of zinc and phosphorus were found on the coupons from the free chlorine system with inhibitor relative to coupons from the chloramine system with inhibitor. Zin et al. (2004) and Olesen et al. (1998) have noted a synergistic effect between zinc and phosphate in other precipitation applications. Analysis confirmed significantly less zinc and phosphorus on the coupons from the systems without inhibitor, as would be expected.

In order to determine if the presence of phosphorus effectively reduced copper corrosion at the pipe surfaces, the raw energy data collected by the SEM-EDS in the form of energy counts per second was evaluated for all surface sites measured. Given the scatter inherent in heterogeneous surfaces such as corrosion scales, a trend line was applied to the plot of the copper and phosphorus raw energy data from the two systems with inhibitor (Figure 3-23). Consistent with the visual observations and scale accumulation data, increasing phosphorus on the surface correlated to a decrease in copper in the free chlorine system with inhibitor and actually caused an increase in copper in the chloramine system with inhibitor (Figure 3-23). In other words, the phosphorus from the inhibitors may have reduced the extent of copper corrosion in the free chlorine system.

Although it is not known if this apparent benefit of phosphorus was due to the addition of orthophosphate or zinc polyphosphate (or both), the electrochemical data suggested that greater benefits occurred during zinc polyphosphate addition and that orthophosphate produced no benefits and may have even increased pitting propensity (Figures 3-3, 3-4, 3-7, and 3-8). Further, additional raw energy measurements confirmed a net decrease in copper at the surface for systems in which the zinc inhibitor was dosed (Figure 3-24). Further research would be needed to determine whether zinc exclusively produced benefits with respect to copper corrosion or performed synergistically to increase the precipitation of phosphorus.

Again, these results can not provide definitive conclusions regarding pitting propensity and inhibition solely from visual inspections, especially given the significant amount of uniform corrosion scale observed in each system. However, it does appear that the most aggressive corrosion occurred in the free chlorine system without inhibitor; which was the only system where tubercles resembling pitting were observed. The free chlorine system with inhibitor appeared to have the least amount of corrosion.

CONCLUSIONS

- The addition of orthophosphate did not produce any benefits in terms of copper pitting inhibition in either free chlorine systems or chloramine systems based on electrochemical measurements. In fact, in free chlorine systems, the addition of orthophosphate may even encourage copper pitting.
- In free chlorine systems, zinc polyphosphate may reduce copper pitting propensity, as pitting currents dropped to low levels in one of two pitting wires and the chlorine decay rate was less than half of the rate measured in the system without zinc polyphosphate. Results from surface analyses also provided indications that zinc polyphosphate performed as an effective copper pitting inhibitor.
- In chloramine systems, zinc polyphosphate may reduce copper pitting propensity as all pitting currents measured died, and chlorine decay rates and soluble copper concentrations were both lower than measurements in the system without zinc polyphosphate.
- In comparing all systems, general corrosion appeared to be the worse in the free chlorine system without inhibitor according to methods including surface analyses. Corrosion appeared to be inhibited most effectively in the free chlorine system with zinc polyphosphate inhibitor.

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Table 3-1. Baseline Data - Average E_{Corr} values through Day 7.

	Average E_{Corr} (mV)
Rig 1 (Free Chlorine Control)	92
Rig 2 (Free Chlorine with Inhibitor)	97
Rig 3 (Chloramine with Inhibitor)	101
Rig 4 (Chloramine Control)	105

Table 3-2. Elemental Percent Abundance (% by mass) of interior coupon surface.

Element	**Free Chlorine Control System**			**Free Chlorine System with Inhibitor**			**Chloramine Control System**			**Chloramine System with Inhibitor**		
O	31.3	±	6.4	23.9	±	8.2	21.5	±	3.9	25.3	±	7.8
Na	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Mg	0.7	±	0.4	0.3	±	0.3	0.2	±	0.2	0.4	±	0.2
Al	0.1	±	0.1	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Si	13.2	±	5.2	0.4	±	0.2	1.9	±	0.4	0.3	±	0.1
P	0.1	±	0.0	4.8	±	1.8	0.1	±	0.0	3.4	±	0.4
S	0.2	±	0.1	0.3	±	0.1	0.5	±	0.4	1.2	±	0.3
Cl	0.1	±	0.0	0.1	±	0.0	0.1	±	0.1	0.2	±	0.1
K	0.1	±	0.0	0.1	±	0.0	0.1	±	0.0	0.1	±	0.0
Ca	0.6	±	0.2	1.8	±	0.6	0.7	±	0.2	0.9	±	0.2
Cu	53.2	±	11.1	66.7	±	10.6	74.5	±	4.4	67.6	±	7.8
Zn	0.3	±	0.1	1.7	±	1.0	0.4	±	0.1	0.7	±	0.3

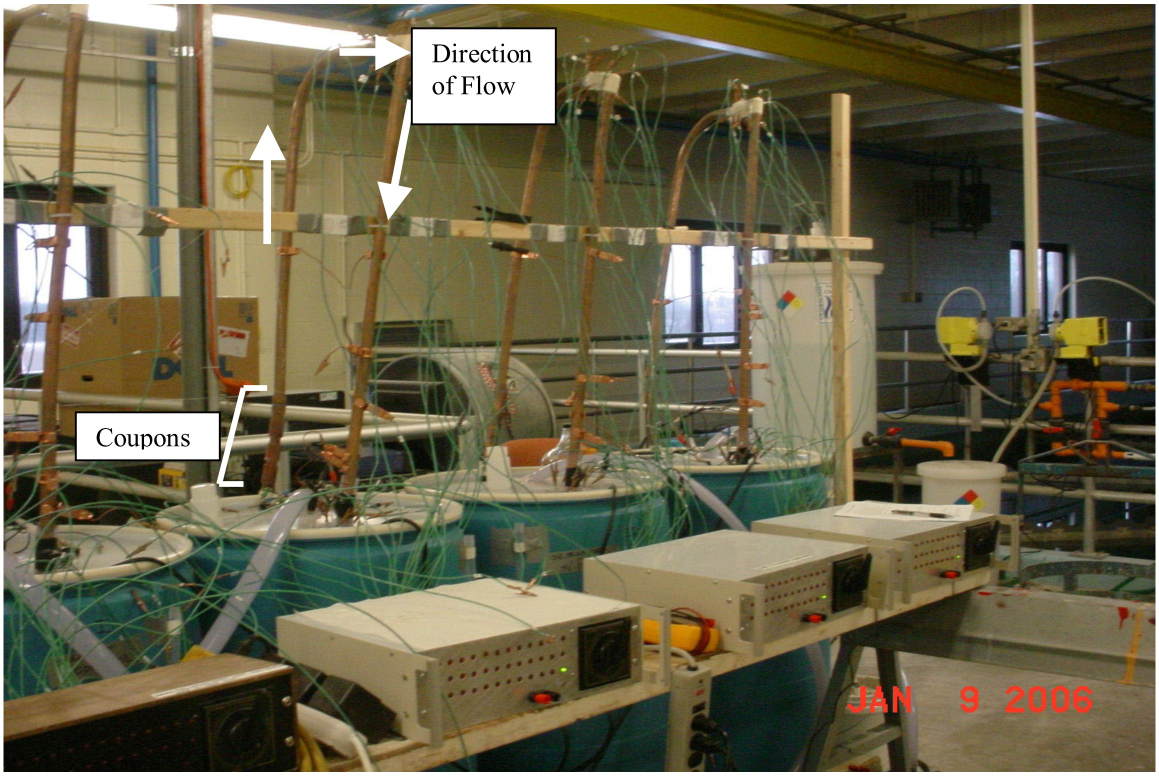

Figure 3-1. General pitting rig experimental setup with relay boxes.

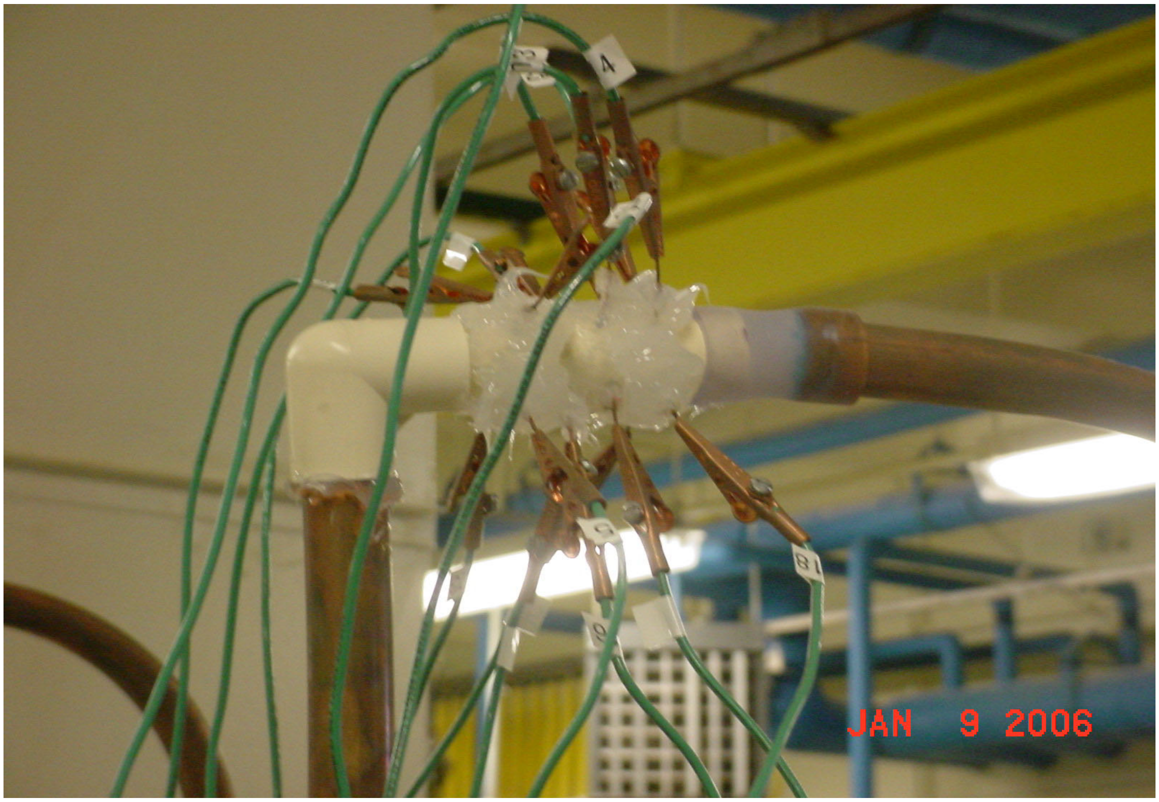

Figure 3-2. 90 Degree in-flow pit wires.

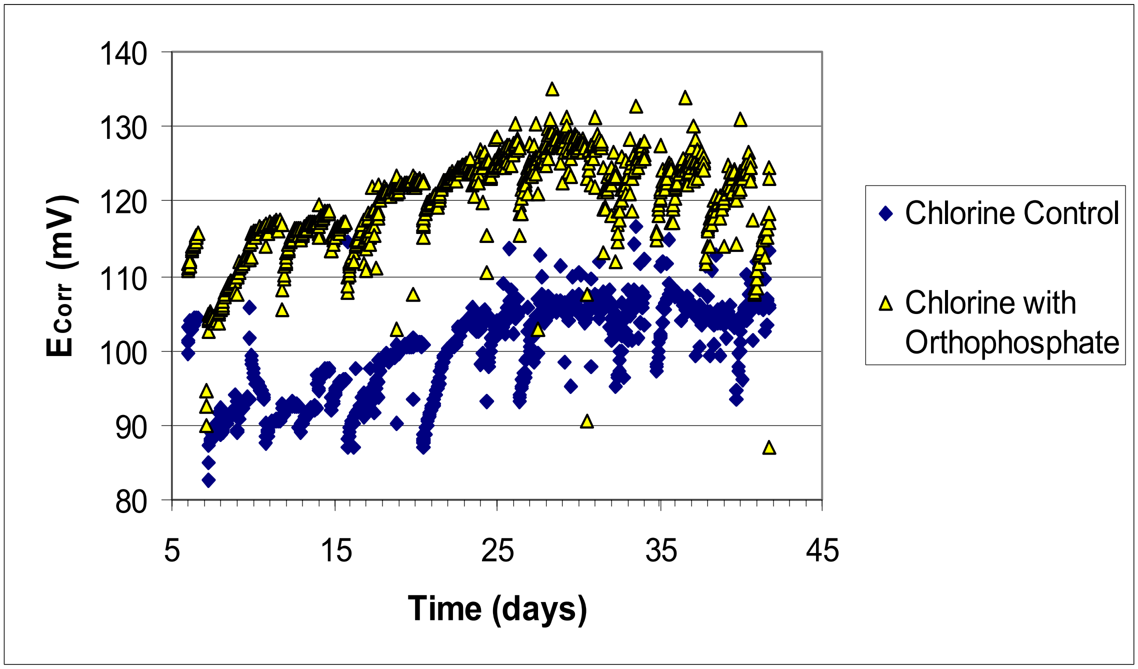

Figure 3-3. E$_{Corr}$ measurements in free chlorine systems with and without orthophosphate.

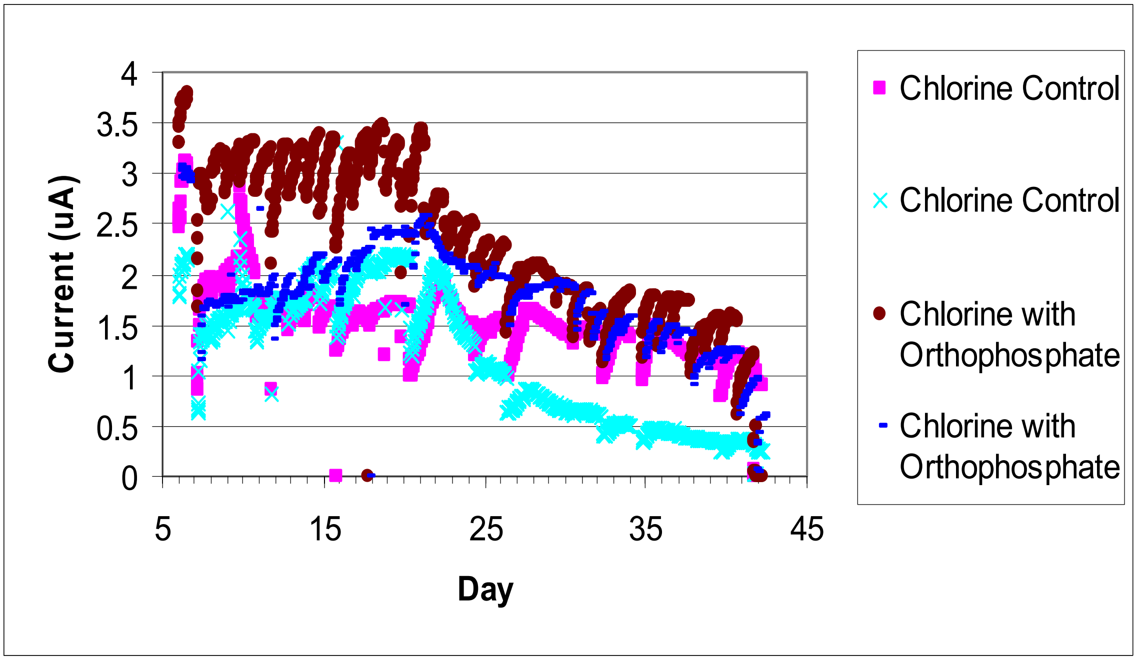

Figure 3-4. Pitting currents in free chlorine systems with and without orthophosphate.

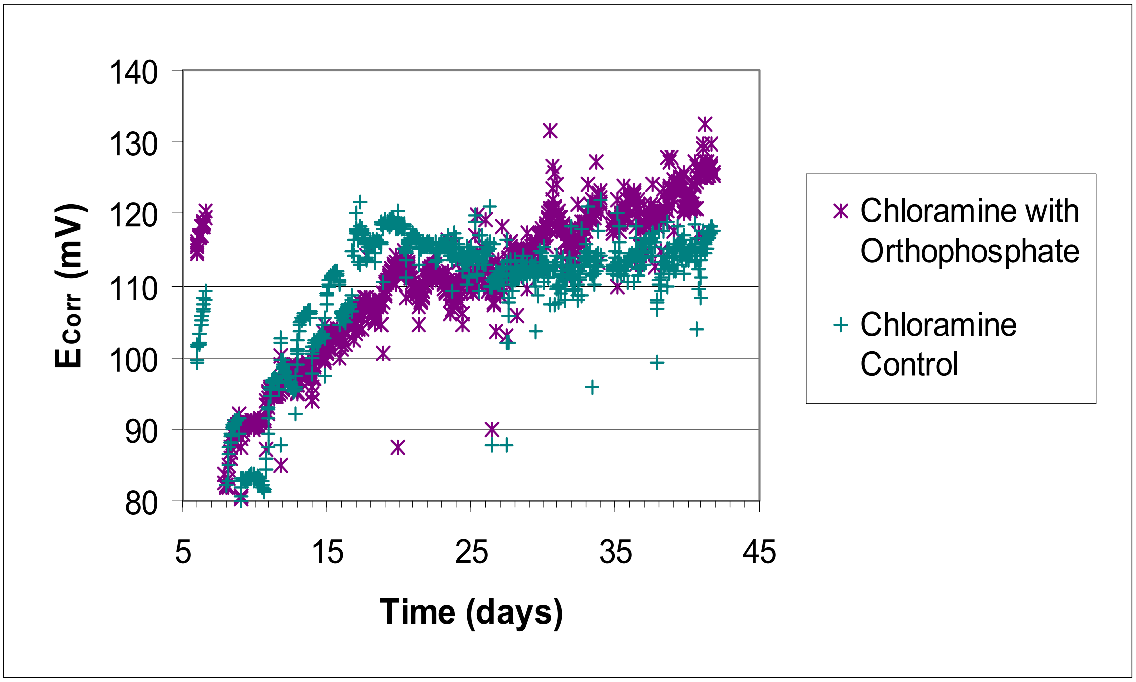

Figure 3-5. E_{Corr} **measurements in chloramine systems with and without orthophosphate.**

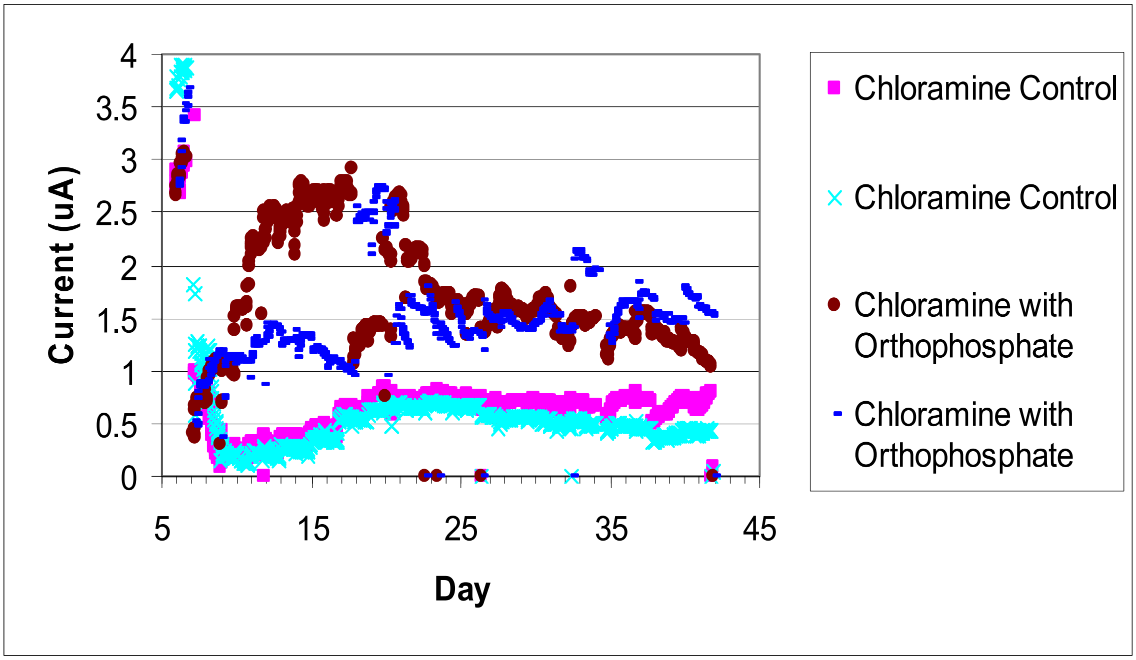

Figure 3-6. Pitting currents in chloramine systems with and without orthophosphate.

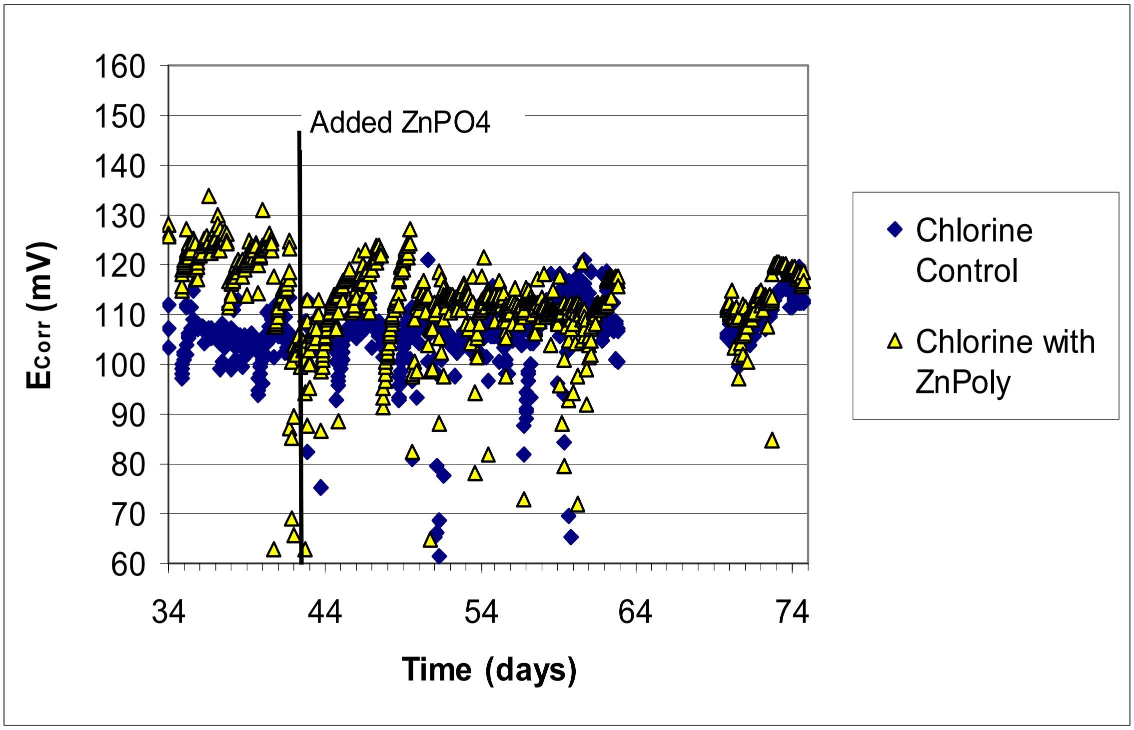

Figure 3-7. E_{Corr} measurements in free chorine systems with and without zinc polyphosphate.

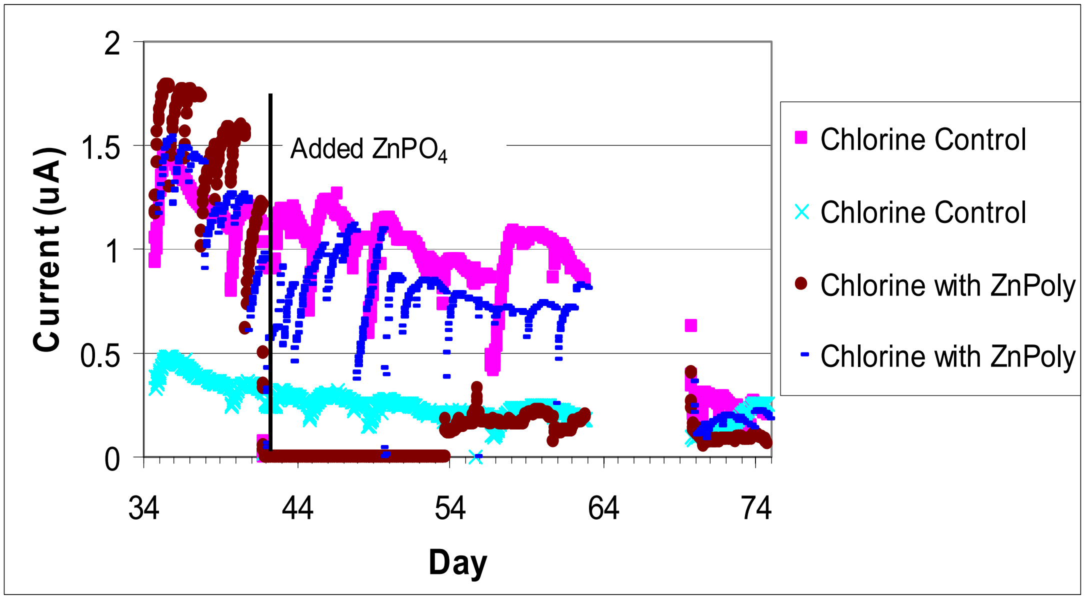

Figure 3-8. Pitting currents in free chorine systems with and without zinc polyphosphate.

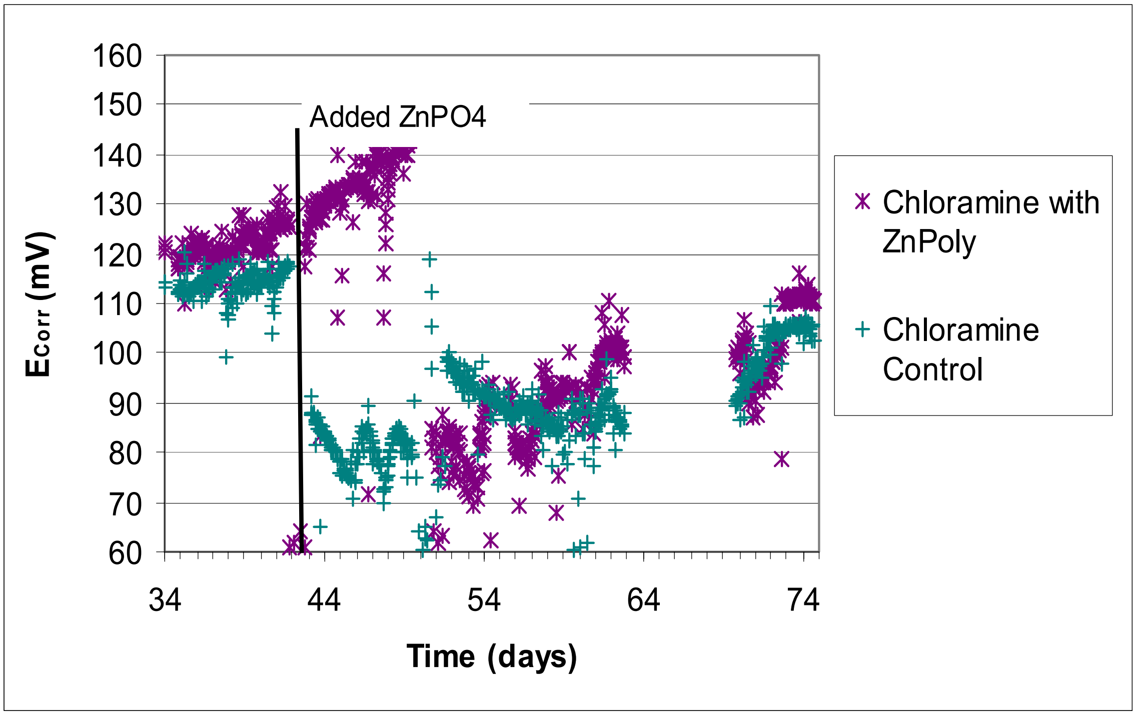

Figure 3-9. E_{Corr} measurements in chloramine systems with and without zinc polyphosphate.

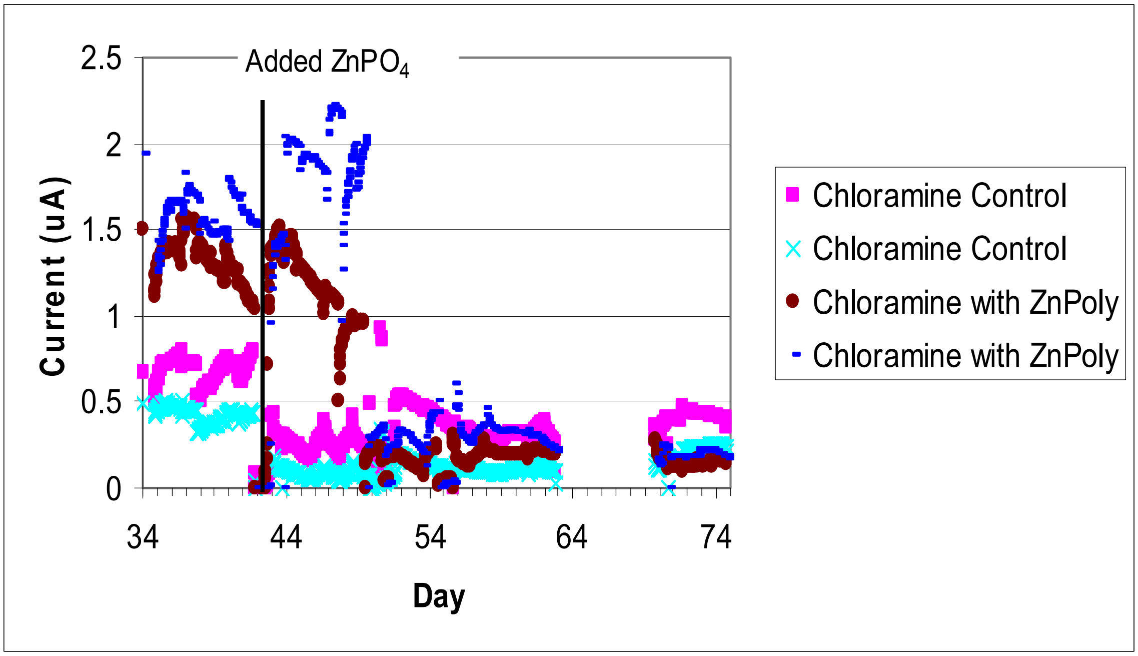

Figure 3-10. Pitting currents in chloramine systems with and without zinc polyphosphate.

Figure 3-11. Free Chlorine Control System - Coupons. Coupons A – D shown left to right.

Figure 3-12. Chloramine System with Inhibitor - Coupons. Coupons A – D shown left to right.

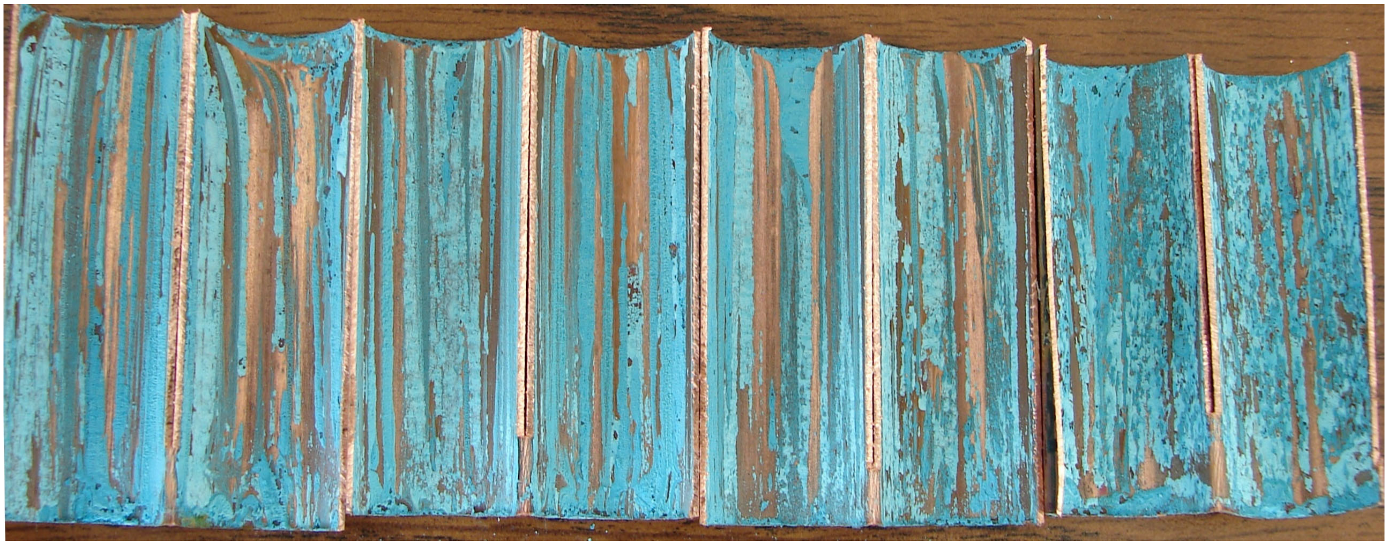

Figure 3-13. Chloramine Control System - Coupons. Coupons A – D shown left to right.

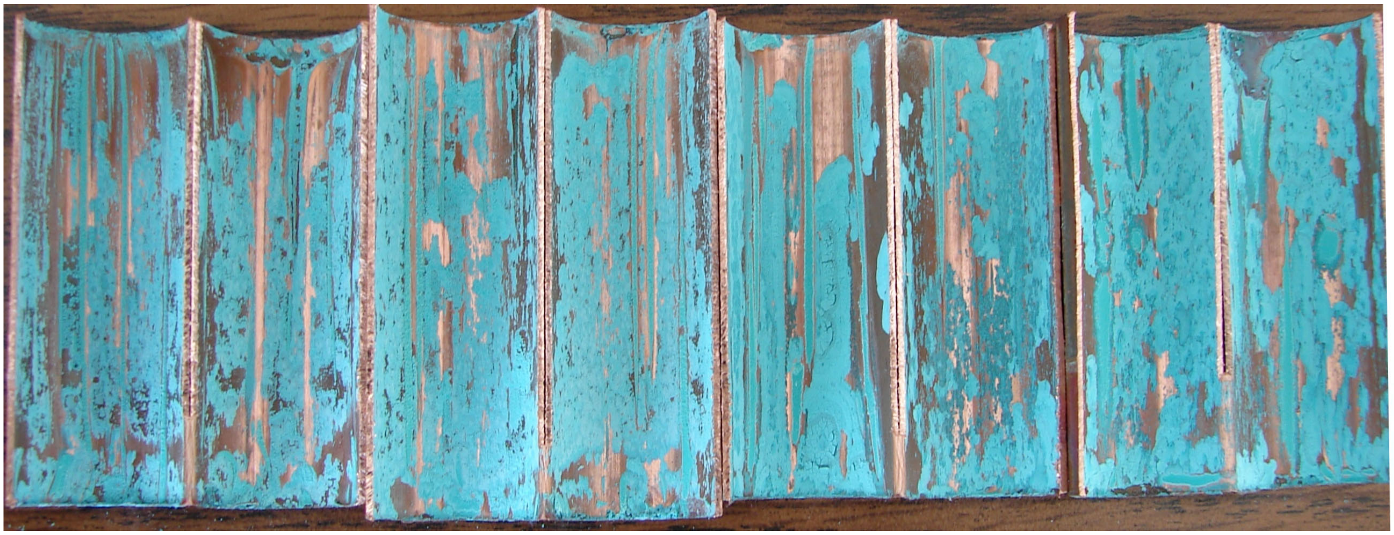

Figure 3-14. Free Chlorine System with Inhibitor – Coupons. Coupons A – D shown left to right.

Figure 3-15. Free Chlorine Systems – Coupon D Comparison. Free chlorine control system (left) and free chlorine system with inhibitor (right).

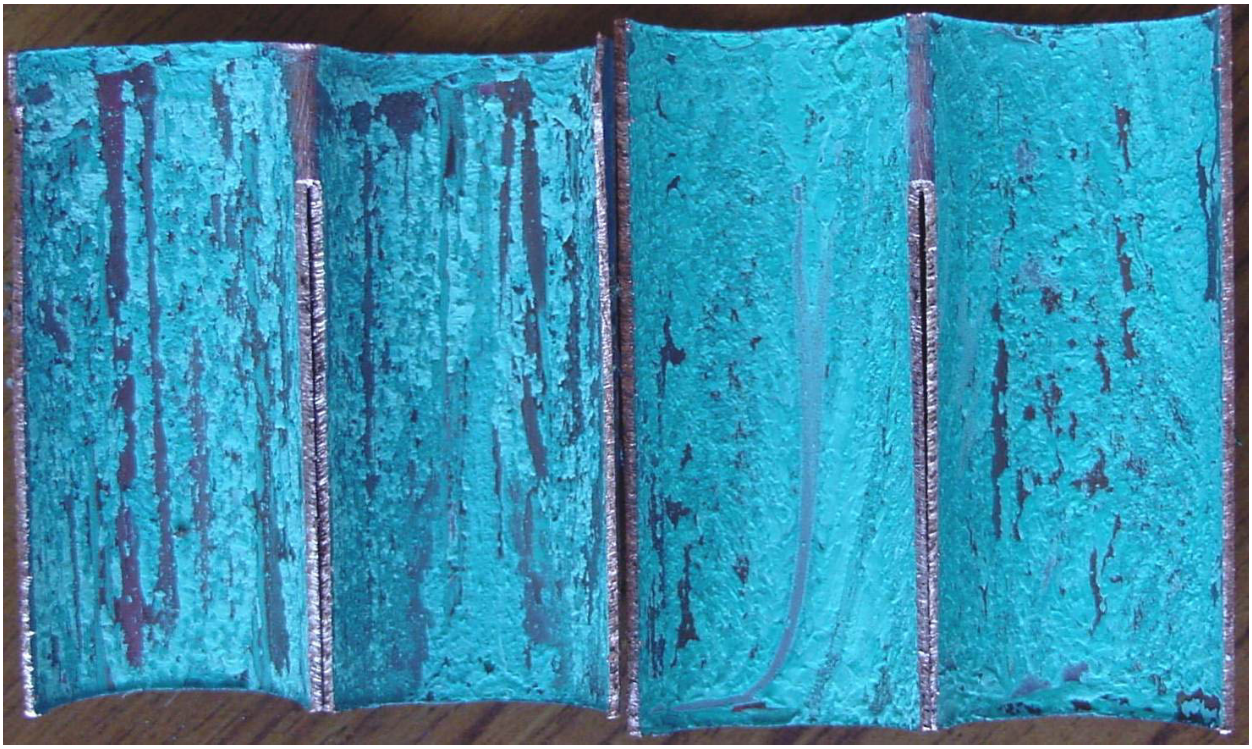

Figure 3-16. Chloramine Systems – Coupon D Comparison. Chloramine control system (left) and chloramine system with inhibitor (right).

Figure 3-17. Free Chlorine Control System – Pipe Section.

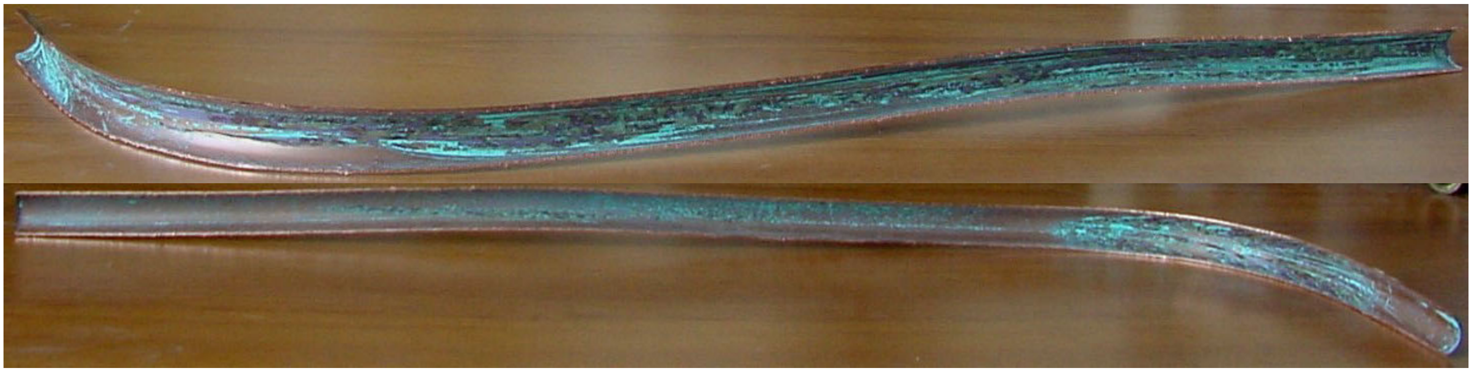

Figure 3-18. Chloramine System with Inhibitor – Pipe Section.

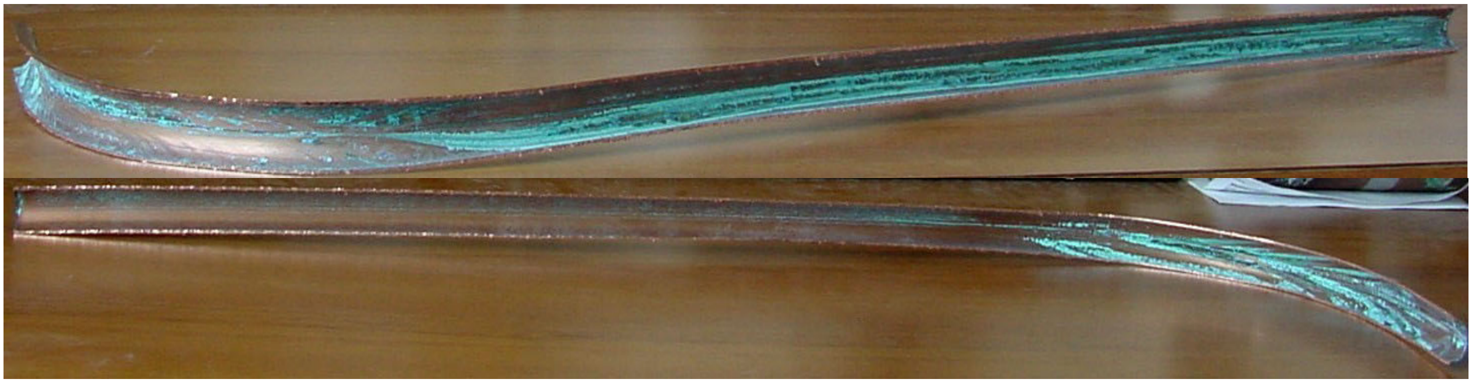

Figure 3-19. Chloramine Control System – Pipe Section.

Figure 3-20. Free Chlorine System with Inhibitor – Pipe Section.

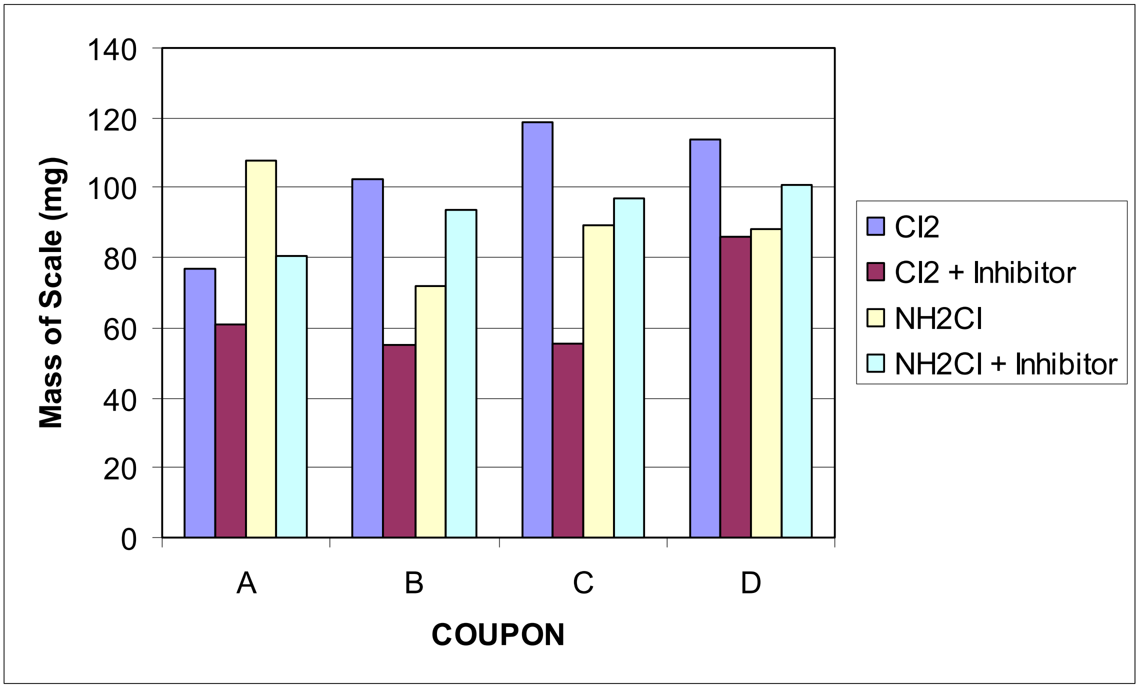

Figure 3-21. Mass of scale accumulation on coupons.

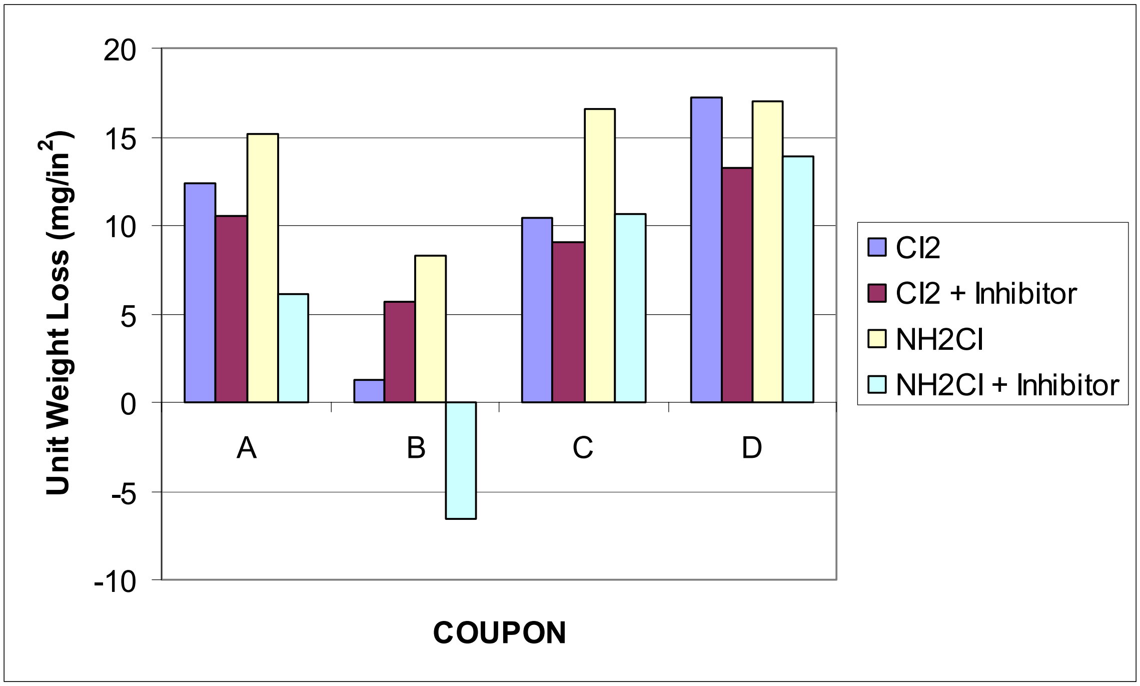

Figure 3-22. Unit weight loss of coupons.

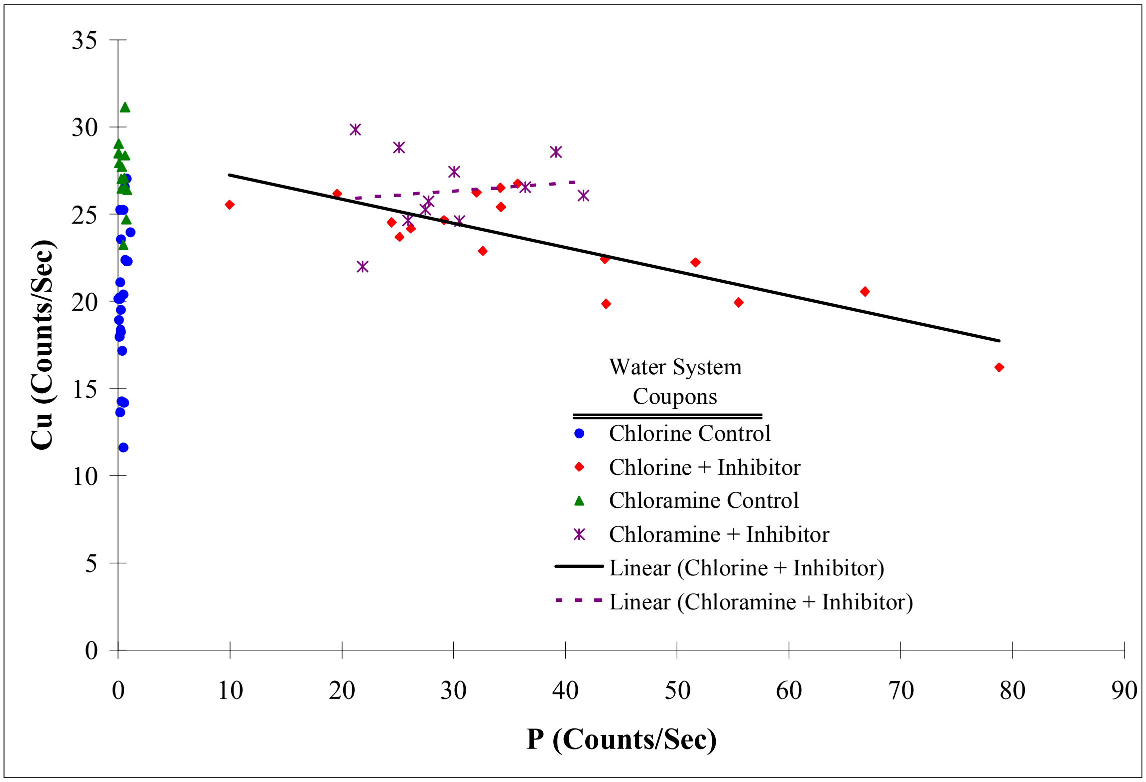

Figure 3-23. Raw Cu and P Data as collected by the SEM-EDS during surface analyses.

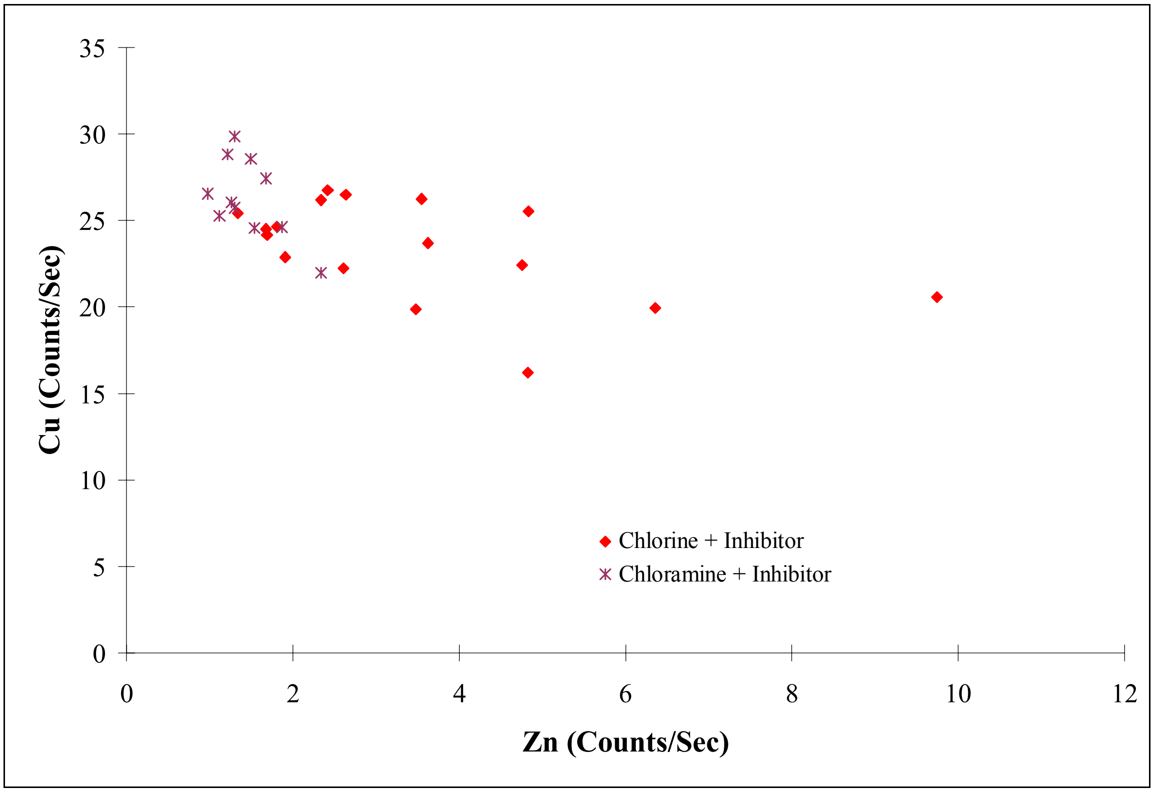

Figure 3-24. Raw Cu and Zn Data as collected by the SEM-EDS during surface analyses.