

INFLUENCES OF WATER CHEMISTRY AND FLOW
CONDITIONS ON NON-UNIFORM CORROSION IN COPPER
TUBE

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ABSTRACT

Water chemistry and fluid velocity are factors that can perpetuate certain types of non-uniform pitting corrosion in copper tube, specifically in waters with high chlorine and a high pH. These two parameters can further act synergistically to alter pitting propensities in copper pipes subjected to this type of water.

A preliminary short-term experiment considered pitting propensity in copper pipe as a function of water chemistry. This study used a water chemistry that had been documented to promote and sustain pitting in copper tube that further developed into fully penetrating pinhole leaks. Modifications to this base water chemistry found that dosing a chloramine disinfect (rather than free chlorine) or the addition of silica greatly reduced corrosion activity and pitting propensity on copper pipes.

In another short-term experiment, copper pitting propensity was considered as a function of fluid velocity. A number of different fluid velocities were tested in several different pipe diameters using the same documented pitting water. Velocity was observed to significantly increase pitting propensity in all pipe diameters considered. At the highest fluid velocity tested (11.2 fps) a pinhole leak formed in ¼” tubing after only 2 months of testing. Larger pipe diameters were also found to increase the likelihood of forming deeper pits on the pipe surface at the same fluid velocity.

Chlorine was a driving factor in corrosion for preliminary tests conducted using this pitting water. The reduction of chlorine to chloride is believed to be the primary cathodic reaction limiting the overall rate of corrosion in this type of water. As such, a subsequent study considered the relationship between the rate of chlorine reduction and corresponding corrosion activity. Chlorine reduction or demand rates were found to be good indicators for pitting propensity and corrosion activity for this particular type of water.

All preceding work led to the development and design of a large scale, long-term, copper pitting study. A matrix of 21 unique conditions tested various water chemistries, flow conditions, corrosion inhibitors, and galvanic connections of copper pipes to other metallic plumbing materials. The severity of pitting corrosion was observed to be dramatically decreased by lower free chlorine residual concentrations, high alkalinity, and sufficient doses of copper corrosion inhibitors such as natural organic matter, silica, and orthophosphate. Pitting severity was consequently observed to increase at a low alkalinity, indicating that this parameter has a significant effect on corrosion reactions.

Furthermore, the addition of aluminum solids to the base pitting water chemistry dramatically increased the formation of tubercle mounds on the inside of the copper pipes in contact with the water. Aluminum solids have been observed to be a vital constituent for sustaining pit growth in this specific water at lower pHs, however, the role of this constituent at the high pH levels tested in this study was previously unknown. From simple visual observation, aluminum solids appear to increase the aggressiveness of this water even at higher pHs.

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I would first like to thank Dr. Marc Edwards for his assistance in helping me understand and convey the material herein. His tireless efforts to improve environmental issues involving corrosion are remarkable and his steadfast devotion to his research and his students has greatly inspired me. I would not have been able to produce this work without his encouragement and wise counsel.

I would also like to thank Paolo Scardina for providing me with a wealth of knowledge on matters both theoretical and practical. His wise instruction on plumbing proficiency, his constant availability for questions, and his willingness to help me with whatever I needed has greatly assisted me in accomplishing this work.

Thanks also to Dr. Panos Diplas for providing me with a fundamental understanding of fluid mechanics and for his encouragement and support of this work.

Thanks to the entire Edwards research group for their friendship and camaraderie. I consider myself fortunate to have worked with such an amazing group of people, all of whom have graciously assisted me in my research and have provided an incredibly supportive environment for me.

I would like to give special thanks to Emily Sarver for her intelligent insight and advice that has improved the quality of this work. This work would not be possible if it weren't for the vast number of hours that she generously spent assisting me in the laboratory and for her willingness to oversee the final phase of some of the experiments presented herein.

I would like to thank my friends and family for their constant support and encouragement. I would also like to especially thank my wife, Tara Custalow, for her belief in me that has helped to give me the strength and resolve that I needed to produce this work.

Finally, I would like to thank the Powell Fellowship, the Copper Development Association, and the Water Research Foundation for their generous funding and support of this work.

DEDICATION

This thesis is dedicated to Dr. G.V. Loganathan and teaching assistant, Matthew Gwaltney, who were victims in the events that took place on April 16, 2007. By their example, both men inspired me to pursue knowledge and to aid others in the same pursuit. They are the finest teachers that I have ever had.

ATTRIBUTION

A number of colleagues aided in the research and writing of several chapters of this thesis. A brief description of their contributions is presented here.

Prof. Marc Edwards- Ph.D. (Department of Environmental and Water Resources Engineering, Virginia Tech) is the primary Advisor and Committee Chair. Prof. Edwards established the overall direction of this research and provided the guidance necessary to complete the different phases of the experiments presented herein. Furthermore, Prof. Edwards was heavily involved in the analysis of the experimental data, as well as the writing and presentation of this work.

Paolo Scardina- Ph.D. (Department of Environmental and Water Resources Engineering, Virginia Tech) was an advisor in the author's group. He contributed to the discussion of the electrochemistry of copper pitting and the discussion on mechanisms by which flow can influence pitting reactions in chapter 1. He provided an extensive amount of assistance in both the construction and maintenance of the experiments presented in all three chapters. Furthermore, he was instrumental in defining the overall structure of this thesis and shaping the figures presented in this work.

Prof. Panos Diplas- Ph.D. (Department of Environmental and Water Resources Engineering, Virginia Tech) was an advisor in the author's group. He contributed to the discussion on the effects of various flow parameters on pitting propensity in chapter 1. He also helped with the discussion on the synergistic effects of oxidant availability and delivery rate on pitting reactions discussed in chapter 2.

Emily Sarver- M.S. (Department of Environmental and Water Resources Engineering, Virginia Tech) was a student in the author's group and contributed during her graduate studies to this chapter in terms of developing a method for quantifying the chlorine demand of a pipe network which was used as an indicator of pitting propensity in chapters 2 and 3. She was an incredible assistance in maintaining the large experiments that make up the bulk of this work. She was also involved in the conceptualization and design of the water matrix experiment and is overseeing the continuation of this study.

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AUTHOR'S PREFACE

All three chapters of this thesis are based upon laboratory studies at Virginia Tech that investigated copper pitting corrosion in potable water plumbing systems. Chapter 1 is comprised of two separate studies that investigated the effects of both water chemistry and flow conditions on copper pitting corrosion. The first study presented in chapter 1 considered water chemistry modifications to a water known to promote and sustain pitting corrosion. The second study exclusively examined the effects of different flow rates and velocities through several different pipe diameters. Chapter 2 examines the relationship between copper pitting corrosion and chlorine reduction as it occurs in this particular pitting water. In this chapter, chlorine reduction rates are compared to other conventional forms of corrosion measurement to evaluate the ability of chlorine reduction to indicate corrosion or pitting activity. In Chapter 3, preliminary results are presented for an ongoing study concerning pitting propensity in copper tubing that tests a matrix of different water chemistries, flow conditions, corrosion inhibitors, and galvanic connections of copper pipes to other metallic plumbing materials.

Chapter One: Influence of Water Quality and Fluid Velocity on Copper Pitting Corrosion

Benjamin Custalow, Marc Edwards, Emily Sarver, Paolo Scardina

ABSTRACT

Copper pitting and associated pinhole leaks are synergistically influenced by specific water chemistries and fluid velocity through the tubing. Various modifications of a particular water known to cause copper pitting (high pH and high level of chlorine) were tested in this research. Pitting propensity was dramatically reduced whenever either silica or a chloramine disinfectant were present. Pitting propensity was also found also to be strongly influenced by fluid velocity and moderately influenced by pipe diameter. A high fluid velocity of 11.2 fps in a ¼” diameter copper pipe produced two fully penetrating pinholes in less than two months of testing under continuous flow at hot water temperatures.

INTRODUCTION

Pinhole leaks originating from pitting corrosion in copper tubing can be influenced by both water chemistry and flow conditions. Certain water chemistries have been observed to promote and sustain pitting corrosion (Marshall, 2004) while other water chemistries have been shown to be relatively harmless to copper pipes. Additionally, flow conditions have been observed to play an influential role in accelerating corrosion rates or enhancing corrosion activity, such that specific combinations of water chemistry and flow can create an optimally aggressive situation for pitting, leading to the premature failure of a copper pipe.

For example, prior research by Marshall showed that water with high chlorine and high pH could produce fully penetrating pinholes in copper pipes in less than 12 months under continuous flow (Marshall, 2004). Further research by Murray-Ramos observed variable pitting rates as a function of water chemistry when the Marshall water was modified to test a range of common parameters (Murray-Ramos, 2006). Murray Ramos found that high levels of orthophosphate or natural organic matter markedly reduced pitting severity; whereas, the addition of iron solids or higher levels of chloride seemed to exacerbate pitting compared to baseline conditions.

Water flow patterns also have an influence on pitting corrosion. In the Marshall study (2004), the most extensive pitting occurred under continuous flow rather than intermittent flow, and the severity of pitting increased with the duration of flow. A follow-up study by Lattyak found stronger evidence for a relationship between fluid flow and pitting in this water (Lattyak 2007). Specifically, Lattyak found higher fluid velocities increased pitting (i.e. Marshall, 2004).

Lattyak also found water quality to be a driving factor in relation to this velocity effect, in that additions of phosphate corrosion inhibitors significantly reduced and possibly eliminated pitting activity. There was also an observed link between velocity and water chemistry in a study by Murray-Ramos (2006). In that test, at 7 fps, the chlorine levels were maintained approximately every other day instead of continuously, such that the chlorine concentrations were lower on average over the course of the study than in the Marshall (2004) or Lattyak (2007) studies. Although the study by Murray-Ramos was conducted for a longer duration (15 months) than the Marshall study (12 months), pinhole leaks did not form in the pipes. Even though there were higher fluid velocities in this study compared to the Marshall study, limited available chlorine was most likely the more controlling factor in pitting corrosion rates.

Given the strong evidence that both water quality and fluid velocity synergistically drive some pitting corrosion reactions, two separate short-term studies were designed to examine effects of water chemistry and flow. The goal of the study was to examine how water chemistries and flow conditions influence pitting propensity.

METHODS AND MATERIALS

In an effort to examine some water chemistries previously tested by Murray-Ramos at higher levels of chlorine, as well as some new conditions, an experiment was conducted using six different variations to the aggressive, high chlorine, high pH water used by Marshall (Table 1 – 1). This experiment used 100 L plastic bins as a reservoir and a submersible pump that circulated water at 3 fps through 2” long, ½” diameter, type K, copper coupons (Figure 1 – 1). The pipe sections were physically separated by vinyl tubing and electrically connected by external copper wires that could easily be removed for electrochemical measurements with a handheld multimeter. The external electrical connections between the separate copper coupons ensured that they behaved electrochemically as a single, larger unit.

Table 1 – 1: Conditions Considered in the Water Quality Study

Water Quality	Description
<i>Control</i>	Marshall Water (pH = 9.2, Cl ₂ = 4 mg/L)
<i>Al Solids</i>	Marshall Water with 2 mg/L Al Solids
<i>No Hardness</i>	Marshall Water with No Calcium and 2 mg/L Al Solids
<i>Silica</i>	Marshall Water with 5 mg/L Si and 2 mg/L Al Solids
<i>Low Conductivity</i>	1:10 Dilution of Marshall Water
<i>Chloramines</i>	Marshall Water with 6 mg/L Chloramines and 2 mg/L Al Solids

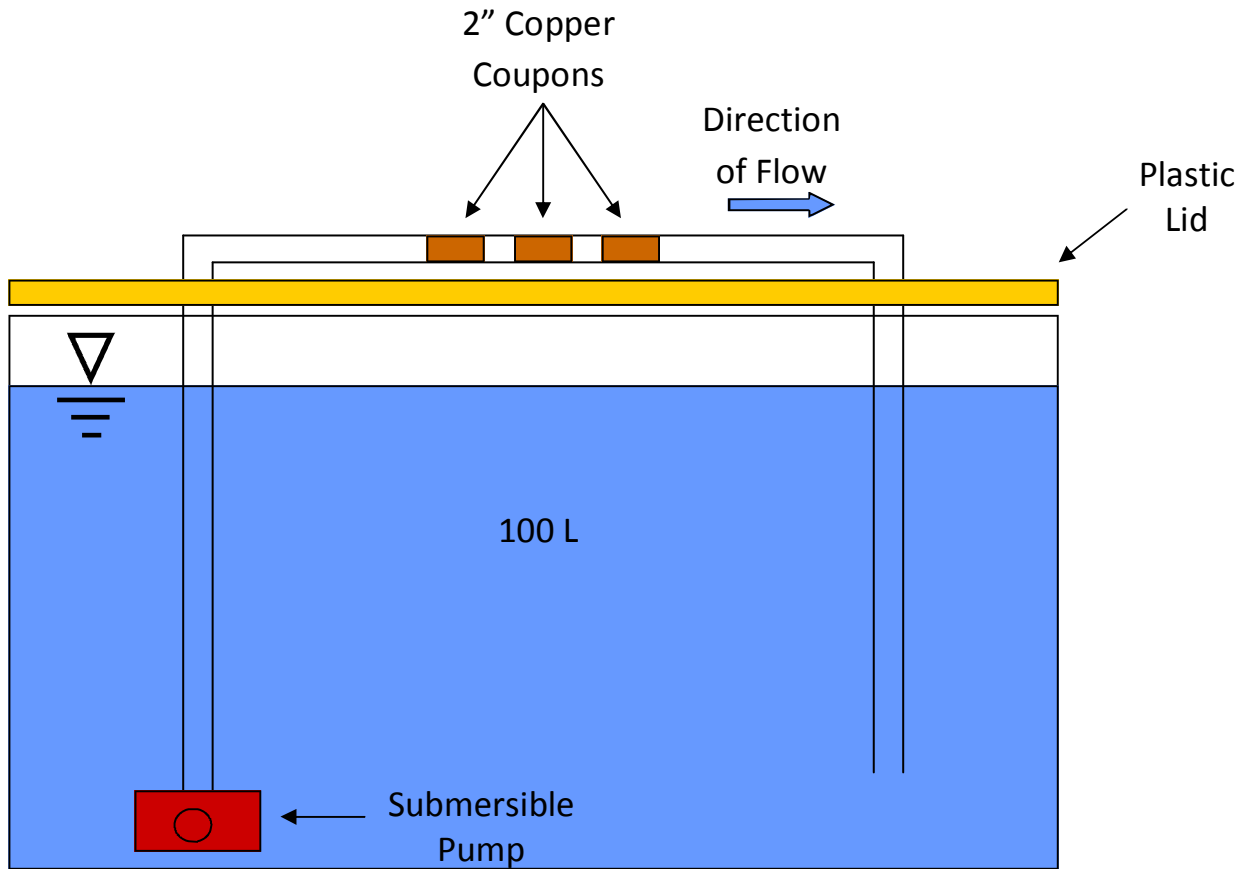


Figure 1 – 1: Water Chemistry Study Experimental Setup

The base water chemistry used for each of the individual conditions was the same recipe used in the Marshall study (2004), but without addition of aluminum solids. This synthesized potable water was made by adding 4.1296 g of CaCl₂ di-hydrate, 2.5 g of CaSO₄ di-hydrate, and 5.685 g of NaHCO₃ to 100 liters of de-ionized water. Sodium hypochlorite and sodium hydroxide were added to this water to reach a target chlorine concentration of 4 mg/L and pH target of 9.2. Preformed aluminum solids were added to some of the water chemistries at a concentration of 2 mg/L as Al.

Each water quality contained the same levels of calcium, chloride, and alkalinity, except for the low conductivity water which was a 1:10 dilution of the control condition. Chlorine and pH were allowed to naturally drift (decrease) overnight for each of the six test conditions. Both of these parameters were adjusted daily to their target values of 4mg/L Cl₂ and a pH of 9.2 for all conditions except for the condition with chloramines which had a pH of 9.2 and a chloramine concentration was 6 mg/L (Cl₂:NH₃ ratio of 4:1). This experiment was conducted for four weeks, after which the coupons were cut lengthwise and visually inspected to compare the amount of pitting for each section and each water quality.

Flow and Velocity Study

In the Lattyak study (2007) one experiment considered the effects of different fluid velocities on pitting corrosion. A high level of corrosion activity (indicated by electrochemical data) occurred at a fluid velocity of 2.8 fps which was very close to the velocity used in the Marshall study that produced fully penetrating pinhole leaks in less than 12 months. Therefore, a matrix of fluid velocities were selected for different pipe diameters based upon this reference condition of 2.8 fps in ¾” tubing (Table 1 – 2). A total of eight unique conditions were tested with the goal of determining whether velocity, flow rate, or Reynolds number was the key parameter that controlled rapid pitting corrosion. This experiment was conducted by continuously circulating the same water used by Lattyak (2007) and Marshall (2004) through multiple sections of copper pipe for a duration of 2 months (the same water chemistry designated “Al Solids” for the water chemistry study listed in Table 1 – 1).

Table 1 – 2: Fluid Parameters Considered in the Flow Study

Condition	Pipe Diameter	Velocity (fps)	Flowrate (lpm)	Reynolds Number
1	<i>3/4"</i>	0.7	3.7	5,600
2		2.8	14.6	22,400
3		7.7	40.0	61,400
4	<i>1/2"</i>	1.6	3.7	8,500
5		2.8	6.5	15,000
6		4.2	9.7	22,400
7	<i>1/4"</i>	2.8	0.9	5,600
8		11.2	3.7	22,400

Each condition utilized three vertically-oriented 1' sections of copper pipe that were physically separated by vinyl tubing and electrically connected externally by copper wires (Figure 1 – 2). The copper used for this experiment was type L for the 3/4" and 1/2" pipes while the 1/4" pipe was conventional refrigeration tubing. Six different centrifugal pumps were used in various configurations to deliver the desired flow rates and in-line ball valves were used to more precisely regulate the flow to meet the desired conditions for each set of pipes (i.e. Table 1 – 2). The ball valves were located after the last pipe section in flow to minimize the likelihood of cavitation damage to pipes during the study.

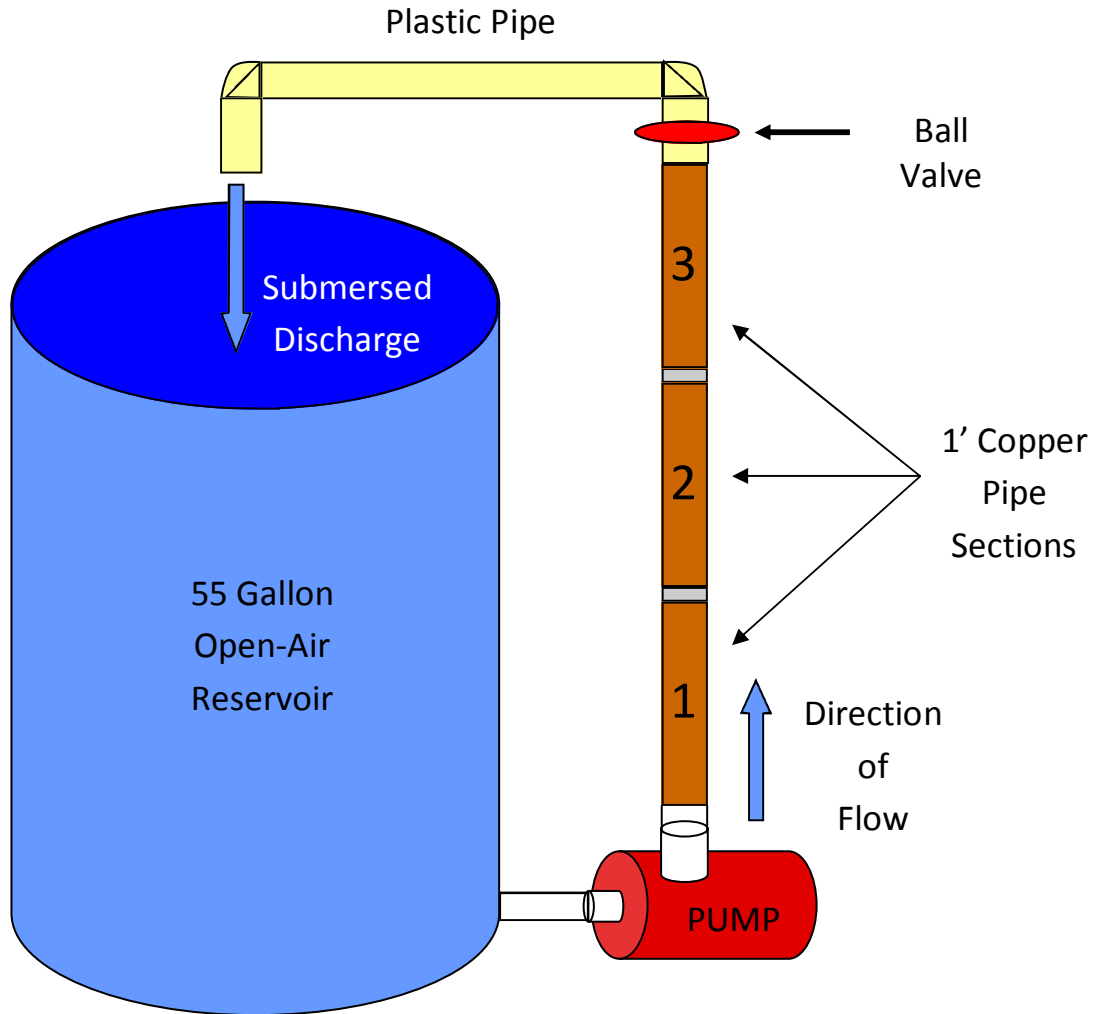


Figure 1 – 2: Flow Study Experimental Setup.
There Were a Total of 8 Loops Using the Water From a Single Barrel.

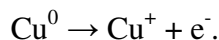
One 55 gallon barrel was used as a reservoir to hold the bulk water used in this experiment. The chlorine and pH for this common reservoir were maintained throughout the experiment at 4.0 mg/L and 9.2, respectively, by an external feed pump that continuously delivered a concentrated solution of sodium hypochlorite and sodium hydroxide. Water quality was assessed daily, and the hydraulic parameters were checked weekly in order to keep the conditions as close to the target as possible. The water in the reservoir was completely changed once a week.

The six pumps used in this study released a considerable amount of energy to the reservoir. For example, after changing the reservoir water, the typical water temperature was approximately 20 °C. The water temperature then increased to about 45 °C over the next two days and

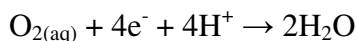
remained constant at this temperature for the rest of the week. This temperature is representative of hot water recirculating lines in American homes.

Evaluating Corrosion: Electrochemical Measurements

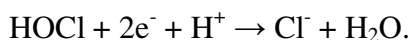
Pitting corrosion involves two separate redox half reactions. At the site of active corrosion (i.e. the pit), an anodic reaction proceeds where copper is oxidized:



The electron produced at the anode (pit or corrosion site) flows through the copper pipe where it is then consumed at the cathode by either dissolved oxygen or chlorinated disinfectants present in the bulk water:



or



All electrons produced at the anode are consumed at the cathode, creating an electrical current through the metal. In a normal situation with a continuous section of pipe, it is impossible to physically measure the resulting electrical corrosion current. If the anode and cathode are physically separated by vinyl but electrically connected via an external wire, then a simple handheld ammeter can be inserted in-line between wires from the separate pipe sections, and the current can be measured. The flowing DC current might represent anywhere from 0 up to 100% of the non-uniform corrosion activity on the pipe surface. In this study, corrosion currents were measured with a Fluke 189 True RMS Multimeter several times during the week and always after the chlorine and pH were confirmed to be at their target values. The external wires were temporarily disconnected to insert/remove the multimeter, and the external wires remained electrically connected at all other times.

The configuration of the multimeter leads and the sign of the corresponding data are significant in that they indicate which section of copper pipe is anodic relative to another section. The following convention was used (Figure 1 – 3), where current measurements were collected between the first pipe in the flow sequence relative to the other sections. Consistent with the findings of Lattyak (2007), when this pitting water flows through a sequence of copper pipes, the first pipe section typically becomes the most anodic compared to the other pipe sections. A

positive sign convention in all data indicates the location of the anode and the active site of corrosion. For example, electrons flowing from Section 1 to Section 2 would be considered a positive current, whereas electrons flowing from Section 3 to Section 2 would be considered a negative current (Figure 1 – 3). The data is presented in terms of anodic current density which is the current flowing from the first copper pipe in flow to the last copper pipe in flow divided by the surface area of the first copper pipe.

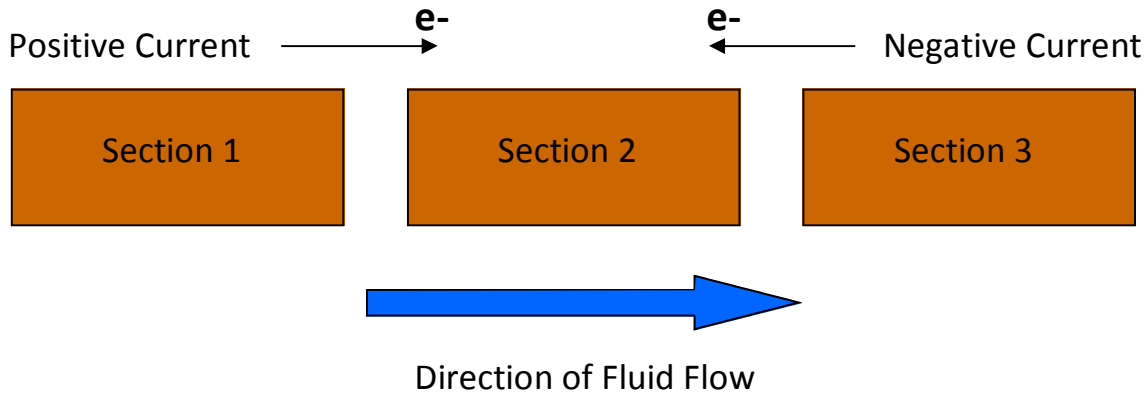


Figure 1 – 3: Sign Convention for Current Measurements

On rare occasions, the sign of the current was observed to change direction: the upstream copper section became the cathode and the downstream coupon became the anode. This change in current direction only consistently occurred in the presence of chloramines. Hence, with the exception of the chloramines condition, the few data points that exhibited this anomalous short-term behavior were removed from the figures in this chapter. All data is therefore presented as anodic current flowing from upstream sections of copper pipe to downstream sections.

RESULTS

The results of the two corrosion studies are presented in sequence. A brief discussion section follows that elaborates on the significance of these results.

Short-Term Water Quality Study

The electrochemical data gathered from this water chemistry study shows a profound difference in the extent of corrosion activity in the waters containing either silica or chloramines when compared to the other conditions (Figure 1 – 4). Specifically, the addition of silica decreased the

currents flowing between the copper pipe sections by nearly a factor of 40. Similarly, the water quality containing chloramine also significantly decreased the currents by a factor of about 10.

Interestingly, using chloramine as the disinfectant rather than free chlorine appeared to reverse the sequencing of anodic behavior along that flow path that was observed in waters with chlorine. That is, the data indicated that the first pipe section was cathodic relative to the last section (i.e. the location of the anode and active corrosion). This data would suggest that both chloramines and silica have the tendency to reduce or decrease non-uniform corrosion tendencies for this particular water quality, although, as mentioned earlier, current is at best an indirect measure of actual copper pitting corrosion tendencies. The remaining four conditions had no statistical difference in terms of corrosion activity compared to the control pitting water without aluminum solids (Figure 1 – 4).

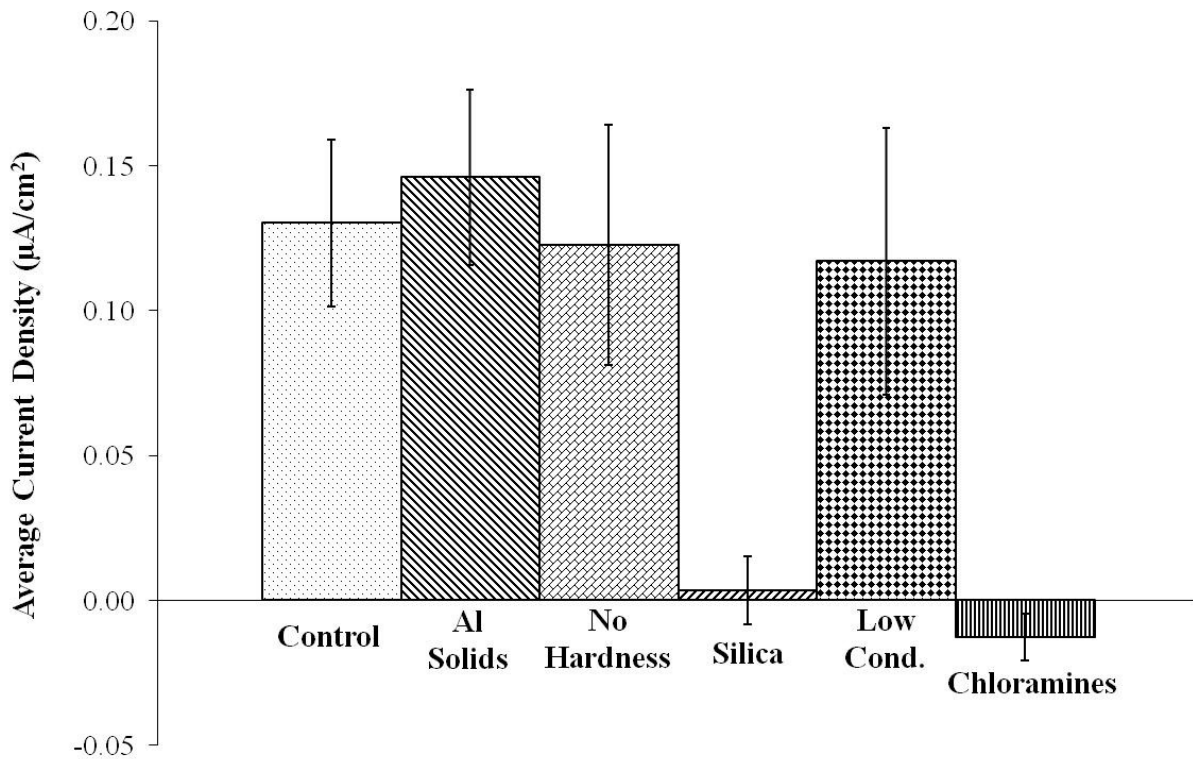


Figure 1 – 4: Average Current Densities for Different Water Chemistries. Error Bars Represent 95% Confidence Assuming a Normal Distribution

Visual inspection of sectioned pipes at the end of the experiment confirmed the electrochemical data trends. The copper tubing exposed to the control water (without aluminum solids) and the water with aluminum solids had corrosion scale covering nearly the entire pipe surface, and there were also indications of raised mounds of byproduct scale, known as tubercles, which usually reside overtop of active pits. In contrast, the copper pipe exposed to the water with silica and the water with chloramine formed essentially no scale and visually looked like brand new copper tube.

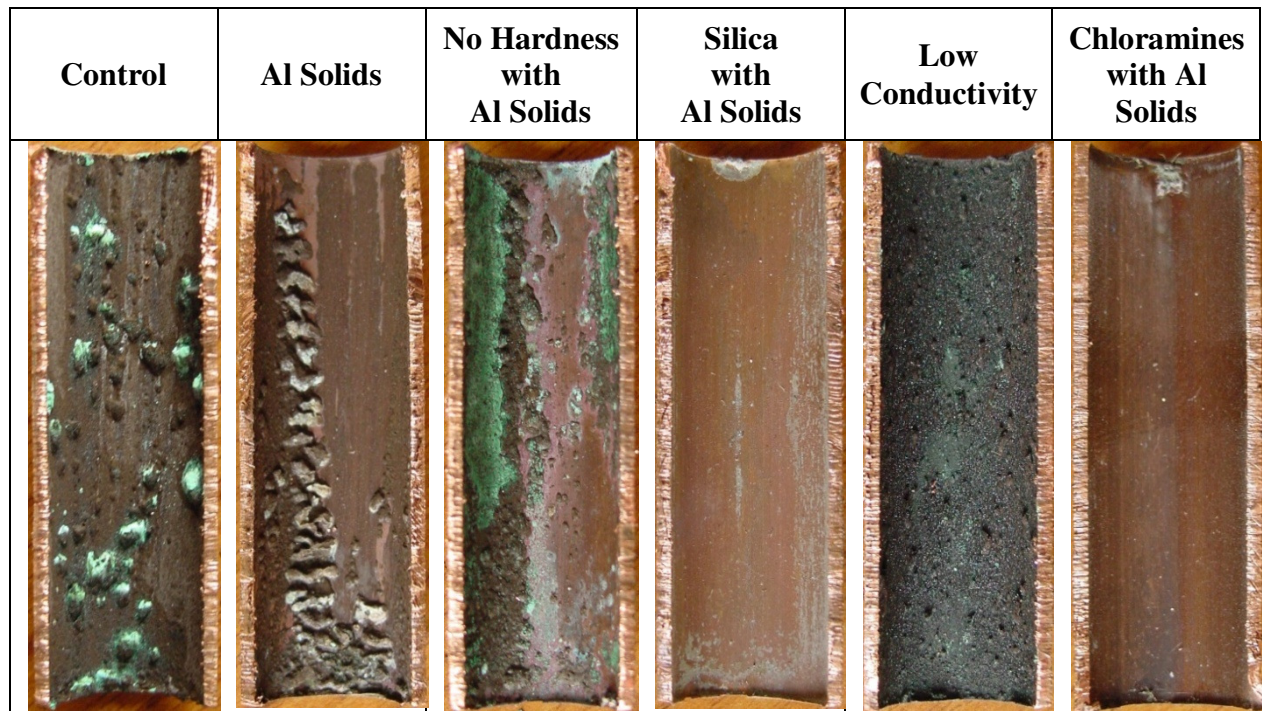


Figure 1 – 5: Scale Formation for Different Water Chemistries

After the coupons had been photographed and visually inspected, the scale was carefully removed and the pipes were examined for pits (Table 1 – 3). Only two of the water qualities formed pits while the other four had completely smooth pipe walls once the scale was removed. Pits were observed in the control water as well as the low conductivity water. The pits for the control were more numerous and deeper on average than the pits for the water with low conductivity, although both contained a fair number of pits with significant pit depths for only four weeks of testing.

Table 1 – 3: Pit Depths for Different Water Chemistries

<i>Water Chemistry</i>	Control	Al Solids	No Hardness	Silica	Low Conductivity	Chloramines
<i>Maximum Pit Depth (% Penetration of 1/2" Type M Copper Tube)</i>	37%	No Pits	No Pits	No Pits	30%	No Pits

It is interesting to note in this very short term experiment, that the two water chemistries to form pits were the only two that were not dosed with aluminum solids. Aluminum solids play a vital role in pit propagation and growth at pH levels around 8 in this particular water chemistry, however, their role in causing pit propagation and growth at pH 9.2 remains unclear. Since this experiment lasted only four weeks it would be premature to arrive at any conclusions on the role of aluminum solids in pitting corrosion at this pH, although the results do confirm the prediction of Marshall (2004) that pitting in this water would occur in the absence of aluminum solids. Further testing would be necessary to more fully understand the effects of this constituent on the initiation and propagation of pitting in this type of water at this specific pH.

Flow and Velocity Study

The electrochemical data gathered during the flow study suggests that, in general, corrosion activity increases with water velocity (Figure 1 – 6). This trend was observed for each of the three pipe diameters tested. Pipe diameter also appeared to be influential, since for a given velocity, both the electrochemical activity and corresponding pit depths increased with larger pipe diameters (Figure 1 – 6, Bottom).

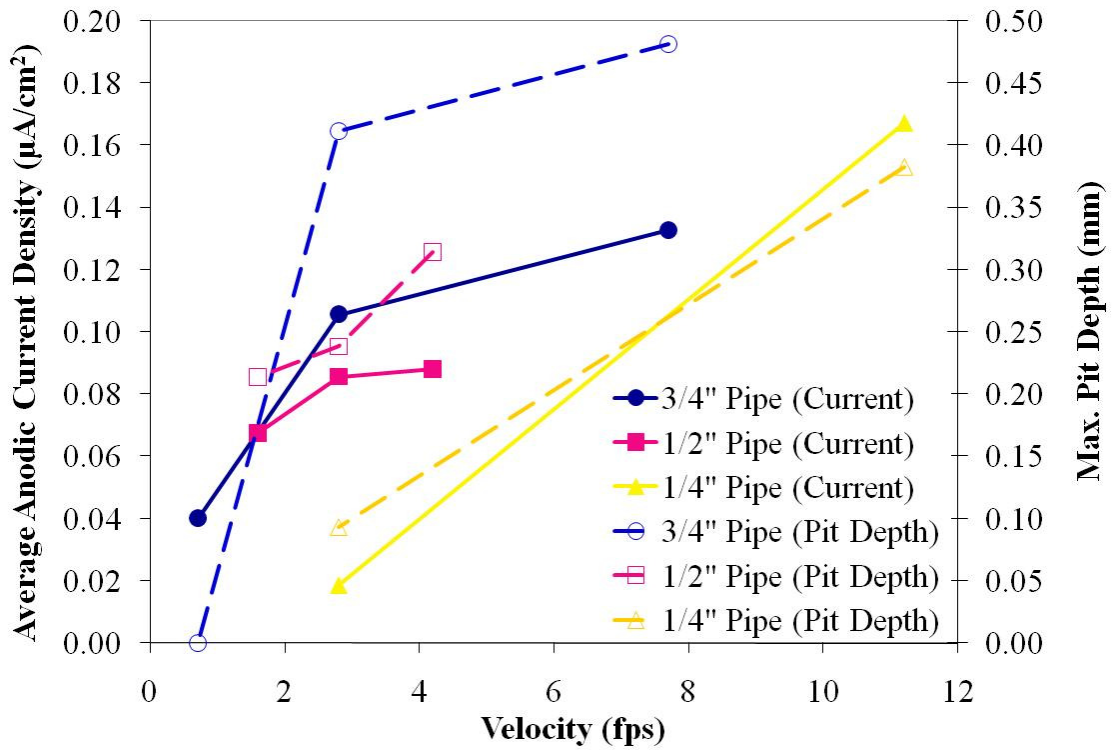
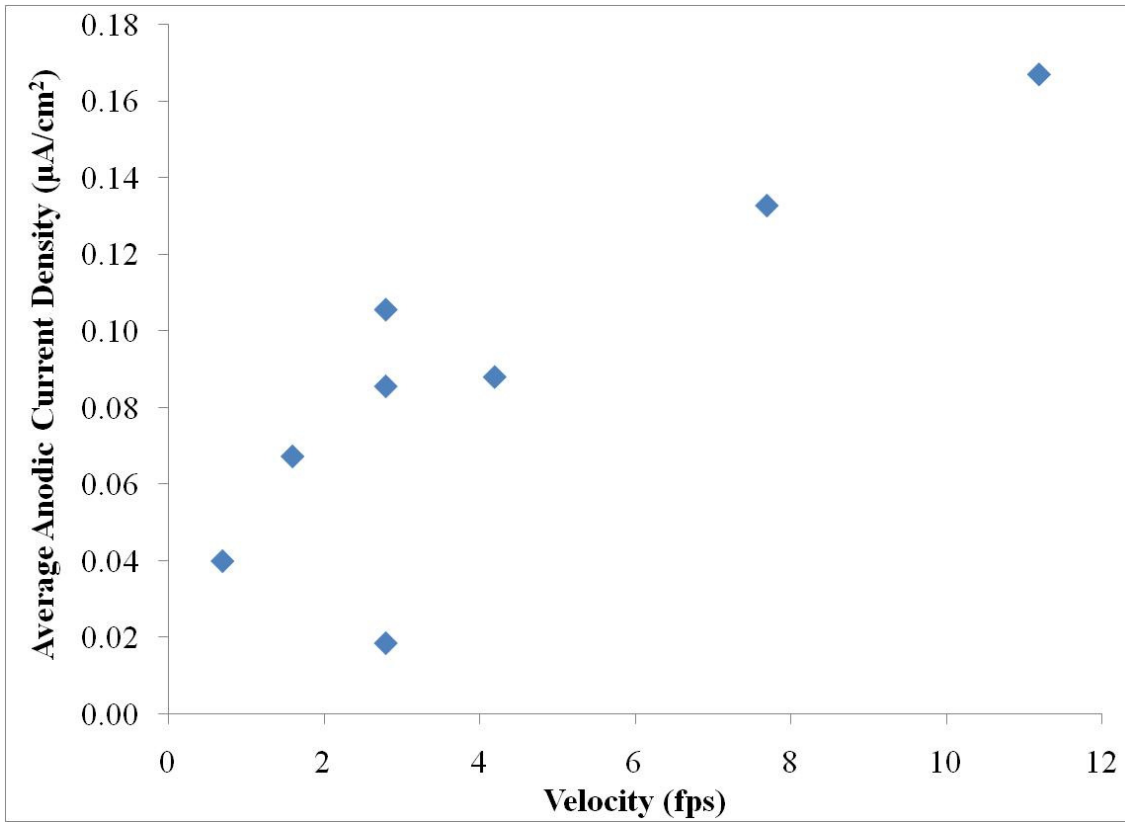


Figure 1 – 6: Electrical Current Density as a Function of Velocity: All Conditions (Top) and Specific Pipe Diameters with Corresponding Pit Depths (Bottom)

The pipes were disassembled/sectioned at the end of the study to visually inspect the interior corrosion. Some unique patterns were observed with variation in velocity as well as location in flow sequence. Specifically in some pipes, there was a thicker amount of scale as well as more tubercles on the first copper pipe in the flow sequence compared to the last copper pipe in the sequence (Figure 1 – 7). This is consistent with expectations given that this section tended to be relatively anodic versus downstream sections of pipe. There was also a significant variation in scale and tubercle formation between the entrance and exit of a given pipe section (Figure 1 – 8). This pattern was apparent for most conditions, except for the higher fluid velocities which formed thick scale across the entire surface of all the pipes.

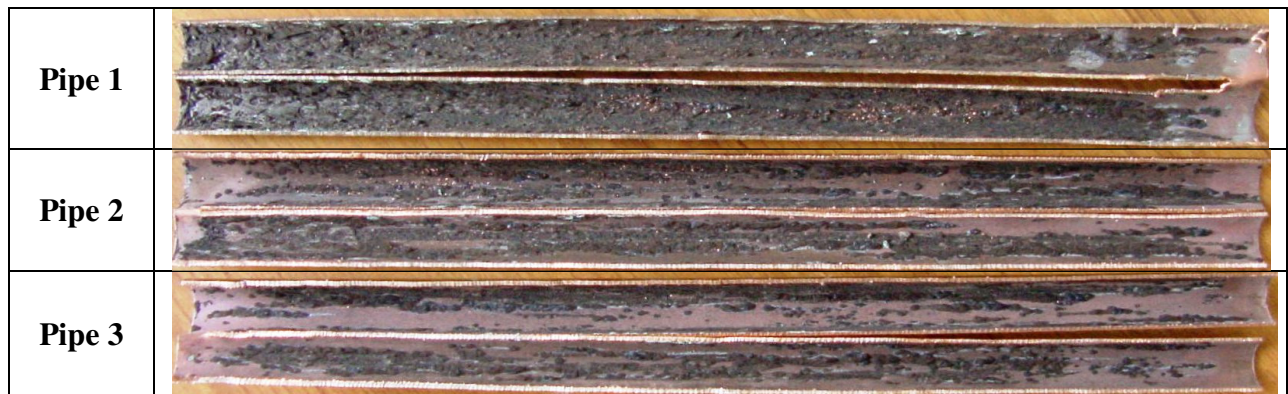


Figure 1 – 7: Differing Scale Development with Position in Flow (1/2” Pipe at 1.7 fps). There Was Much More Scale and Pitting on the First Pipe in the Flow Sequence.

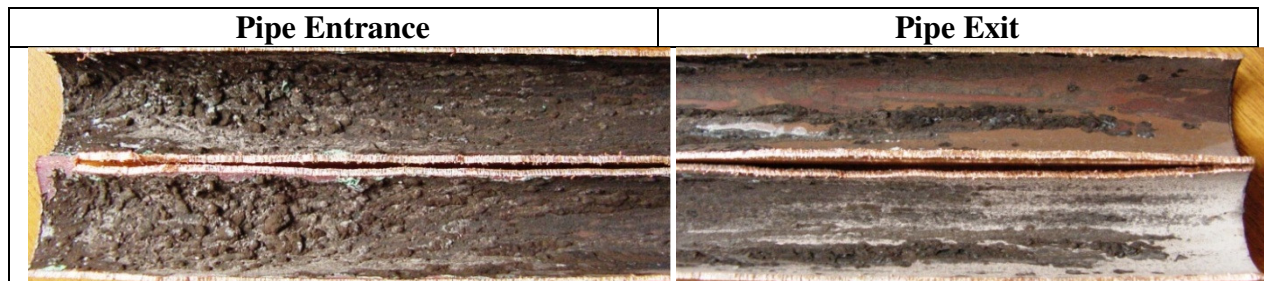


Figure 1 – 8: Differing Scale Development in Relation to Location on the Same Pipe (3/4” Pipe No. 1 at 0.7 fps). The First Part of the Pipe Surface to Contact the Flowing Water Was Relatively Anodic Versus the Last Section of the Pipe Surface.

Furthermore, the corrosion scale thickness as well as size and number of tubercles on the copper pipe surface visually appeared to increase with velocity (Figure 1 – 9). This observation is in agreement with the indication of corrosion rates from the electrochemical data (see Figure 1 – 6). Pipes that were subjected to higher fluid velocities had significantly more scale and more tubercles covering the copper surface than pipes that were subjected to lower velocities. Large tubercle mounds covered a majority of the pipe surface at velocities greater than 4 fps. In contrast, very few and very small tubercles were observed and only covered part of the surface area of the copper pipe for velocities less than 2 fps.



Figure 1 – 9: Effects of Velocity on Scale and Tubercle Formation on the Third Pipe in Flow for ¾” Diameter Tube

After the pipes had been photographed the scale was carefully removed and each pipe was inspected for pits. All significant pit depths were measured with a standard micrometer and the pipes were evaluated for the deepest pit. The pit depth data is in agreement with all other observations. The penetration of pits during this short-term test increased with higher velocity (Figure 1 – 6, Bottom). Two fully penetrating pinhole leaks developed in the ¼” diameter tubing at the highest velocity of 11.2 fps in just two months (Figure 1 – 10). While this is indeed significant, it is acknowledged that this particular diameter tubing has a much thinner wall (0.015 in.) compared to the other conventional plumbing tubing (0.050 in. and 0.062 in. for ½” and ¾” Type L, respectively). The depth of pit penetration in the ¾” tube at 7.7 feet per second also exceeded 0.015 in.

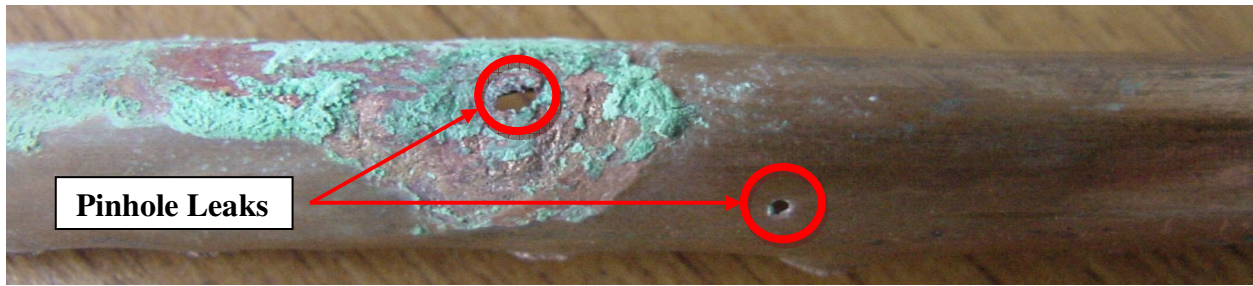


Figure 1 – 10: Pinhole Leaks in ¼” Tubing with Velocity of 11.2 fps

At a given velocity, the depths of the deepest pits on each of the three pipes in the flow sequence were observed to increase with pipe diameter (Figure 1 – 11). This may indicate that velocity is not the only flow parameter influencing pitting corrosion. Since tube diameter seemed influential, the Reynolds number (Re) was considered since this dimensionless parameter is a product of both velocity (V) and pipe diameter (D):

$$Re = \frac{\rho VD}{\mu}$$

Both the pitting data and the electrochemical data were observed to increase with Reynolds number suggesting that pitting corrosion may be influenced by turbulence (Figure 1 – 12). However, for a given Reynolds number, the electrochemical data as well as pit depths were often observed to decrease with pipe diameter (i.e. more corrosion at higher velocities for the same Reynolds number). This suggests that velocity is a much more influential parameter on pitting corrosion than pipe diameter.

It is likely, however, that both the increase in pit depths and electrical current for larger pipe diameters are attributable to the variable surface area of copper on each pipe. The ¾” diameter pipe had 44% more surface area than the ½” pipe, and over 300% more surface area than the ¼” diameter pipe. Consequently, for the same fluid velocity of 2.8 fps, the average anodic current for the ¾” pipe was 23% greater than the ½” pipe and about 450% greater than the ¼” pipe. Given that these ratios of surface area and corrosion activity are very similar, it appears that more corrosion occurred when a greater copper surface area was present (i.e. larger pipe diameter) which in turn increased the probability of developing deeper pits.

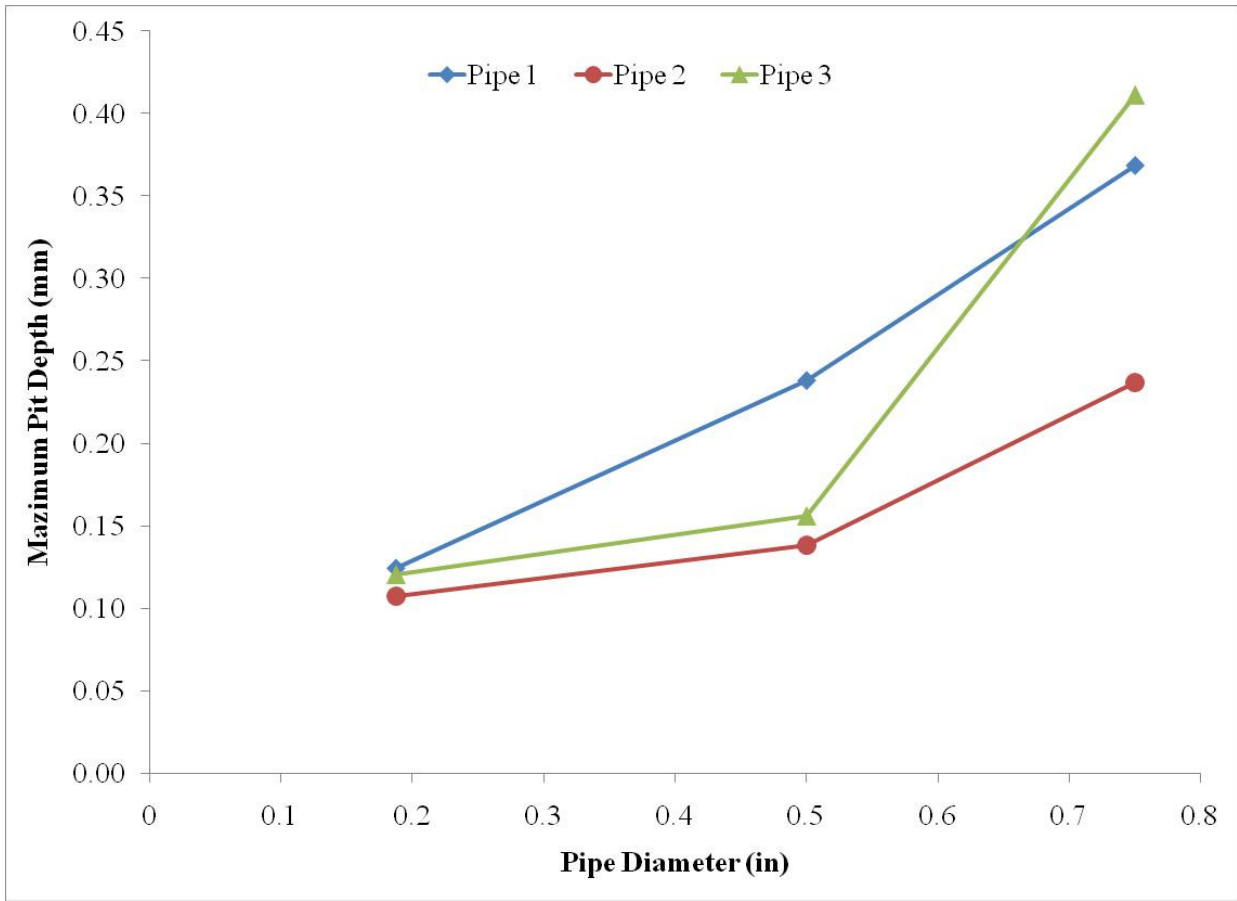


Figure 1 – 11: Effects of Pipe Diameter on Pit Penetration at a Constant Velocity of 2.8 fps

Given the short nature of this study and the heterogeneity of a phenomenon like pitting corrosion, it is difficult to determine the influence of a parameter like pipe diameter. Further research testing a wider range of velocities and pipe diameters for a greater duration of time would be necessary in order to understand the effects of each parameter individually. Regardless of whether increased turbulence (i.e. higher Reynolds numbers) or a greater available surface area for pitting is the influencing factor behind the observed increase in pitting for larger diameter pipes, the results from this study show that pitting corrosion increases dramatically with velocity and moderately with pipe diameter.

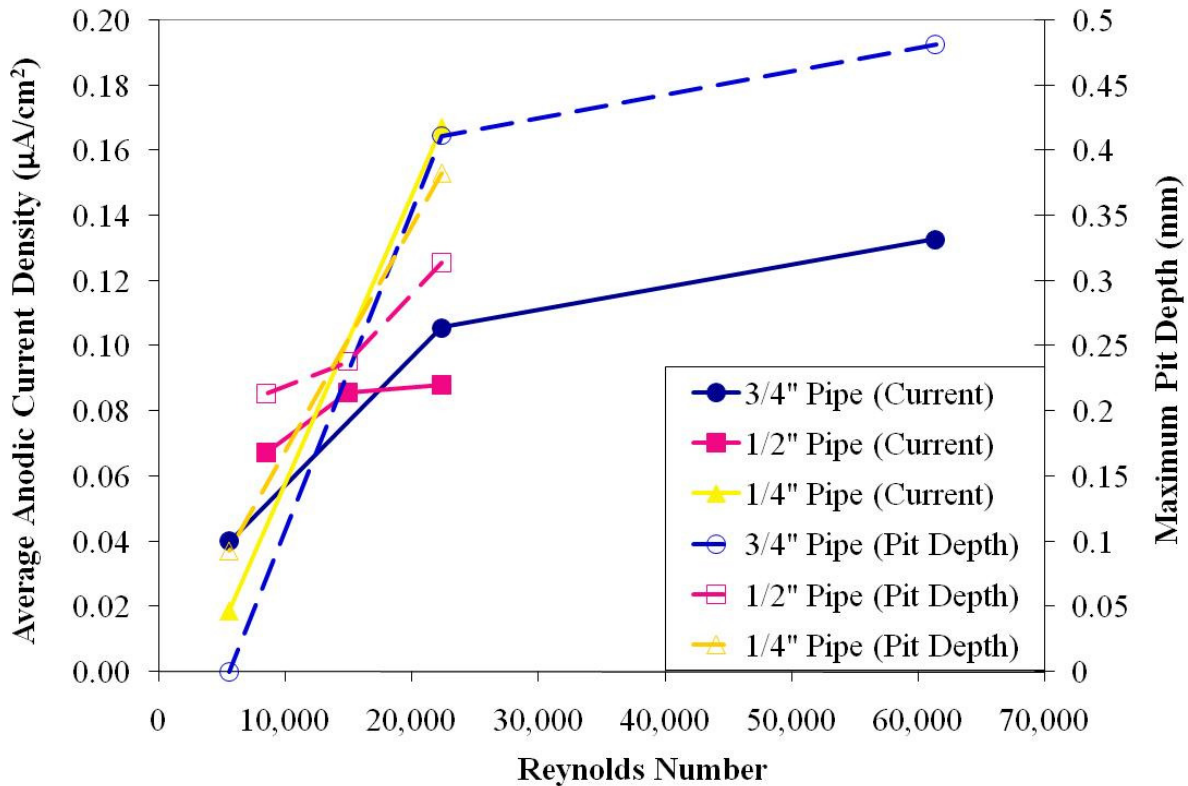


Figure 1 – 12: Corrosion Current and Pit Depth as a Function of Reynolds Number

DISCUSSION:

The results from the water chemistry study clearly show that modifications to the chemistry of this pitting water have a significant effect on non-uniform corrosion. This relationship between water chemistry and pitting propensity had been observed in previous research by Rushing (2002), Murray-Ramos (2006), and Lattyak (2007). The results from this water chemistry study show that high concentrations of silica or the use of chloramines instead of free chlorine severely inhibits the extent of corrosion in the same type of water tested by previous researchers.

Additional observations found that aluminum solids possibly delayed the onset of pitting. From this large body of work between multiple researchers testing different modifications to this specific pitting water, it is clear that subtle changes in water chemistry are a controlling factor in determining whether pitting corrosion occurs or not.

While specific water qualities have long been considered as an influential factor that controls pitting corrosion, the relative significance regarding the role of fluid flow or velocity is more

recent. For example, in the initial study by Marshall (2004), fully penetrating pinhole leaks only developed in the pipes experiencing continuous flow. Follow-up work by Lattyak (2007) found definitive correlations between pitting propensity and fluid velocity. Observations from this work also demonstrate the influential role of velocity on pitting corrosion, in that higher fluid velocities were observed to increase corrosion currents as well as the extent of pitting at hot water temperatures. Thicker corrosion scale, more tubercles, and deeper pits formed in the conditions at higher fluid velocities for all pipe diameters tested. There also seemed to be a correlation between pitting and the pipe diameter, since pit propensity increased with tube diameter for a given fluid velocity (i.e. Figure 1 – 11).

Furthermore, the pitting and corrosion patterns that developed on some of the pipes (i.e. Figure 1-7) were consistent with those observed recently by other researchers (Lattyak, 2007; Edwards et al., 2009). Specifically, an additional mechanism known as flow electrification is believed to have been prevalent and to be an influencing factor on pitting propensity in these experiments.

Flow electrification, also known as streaming current, can induce corrosion when a fluid passes along a metallic surface such as a pipe. Since the corrosion scale layer that naturally develops on a metallic surface is typically believed to produce an overall negative surface charge at this pH, counter balancing positively charged cations dissolved in the bulk solution are preferentially drawn close to the scale surface (i.e. electrical double layer). This concentration of unfixed cations is swept along the pipe surface during fluid flow.

Given that the negative charges on the pipe scale surface are fixed, another source of electrons is necessary in order to satisfy electroneutrality and balance the concentrated positively charged cations sweeping along the pipe surface. These electrons are produced via corrosion reactions ($\text{Cu}^0 \rightarrow \text{Cu}^+ + \text{e}^-$) within the metallic piping. The electrons resulting from this corrosion flow along the metallic piping following the imbalance of positive cations flowing in solution until the electrons are consumed by cathodic reactions with either dissolved oxygen or chlorine.

Consequently, water flowing along a metallic pipe creates active anodic and cathodic corrosion reaction sites on the pipe that further creates a voltage drop along the pipe length between the anode and cathode. In other words, fluid flow induces, or can further enhance existing corrosion activity on a metal pipe.

Flow electrification has been studied extensively within the petroleum industry because of its implications in creating explosions in petroleum pipelines. However, the effects of this phenomenon were considered negligible for higher conductivity aqueous fluids such as potable water since relatively low voltages (millivolts) developed across pipe lengths, compared to the hundreds or thousands of volts that were observed to develop across petroleum pipelines. However, Lattyak (2007) showed that the development of a few hundred millivolts could induce or enhance non-uniform corrosion in a copper pipe. Lattyak (2007) observed that flow electrification influenced pitting corrosion and that velocity had a significant impact on flow electrification currents. Lattyak (2007) further observed that fluid flow typically forced the first pipe in the flow sequence to be anodic relative the subsequent pipes, with the last pipe in sequence typically developing into the strongest cathode. This latter observation is consistent with the conventional model, where the most active site of corrosion occurs for the copper that first contacts the water flow.

Flow electrification most likely manifested in this work. For example, all aspects of corrosion activity increased with higher flow and velocity. Furthermore, corrosion patterns developed that are indicative of flow electrification, where the first pipes in the flow sequence were typically anodic relative downstream pipes and demonstrated the most visually apparent corrosion (i.e. Figure 1 – 7). The corrosion currents that result from flow electrification, and which are measured via an ammeter, are an acceleration to baseline corrosion rates for sections of pipe located first in the flow path. Sacrificial effects (or a deceleration to the base rate) are observed for sections of copper located last in the flow path.

Water chemistry can effectively reduce the flow electrification effect, as was observed for the waters containing silica and chloramine. Therefore, the flow electrification phenomenon depends on factors other than velocity alone. Further research is needed in order to more fully evaluate the relationship between fluid velocity and water quality induced corrosion(s). However, whether by direct or indirect means, higher fluid velocity increases pitting corrosion in this type of water.

CONCLUSIONS

- Pitting corrosion is a function of both water quality and fluid velocity
- The addition of silica, as well as the use of chloramines instead of free chlorine, effectively eliminated copper pitting corrosion in this particular water.
- Aluminum solids were observed to delay the onset of pitting for the first four weeks of exposure to this water.
- Corrosion currents and pitting severity were observed to increase with velocity at hot water temperatures.
- Pipe diameter was found to influence corrosion, but did not have as strong of an impact as fluid velocity.

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Chapter 2: The Role of Chlorine Reduction in Copper Pitting Corrosion in High pH Waters

Benjamin Custalow, Marc Edwards, Emily Sarver, Paolo Scardina

ABSTRACT:

Copper pitting in certain water qualities with high pH levels has been found to be largely driven by reactions with free chlorine. The overall rate of chlorine reduction has been shown to be a good indicator of pitting propensity in this type of water and has been observed to be controlled by water chemistry. In this work, overall chlorine reduction rates were decreased by low chlorine concentration, the use of chloramines instead of free chlorine, low alkalinity, and sufficient concentrations of copper corrosion inhibitors such as natural organic matter, silica, and orthophosphate. Chlorine was most rapidly consumed in waters with high chlorine concentrations, low alkalinities, and waters that contained iron coagulant solids.

INTRODUCTION:

Chlorine is a common constituent in U.S. drinking water because of its desirable properties as both a strong disinfectant and oxidant. Chlorinated disinfection has substantially improved water quality and has been cited as a major contributor to the dramatic decrease in the frequency of waterborne illnesses. Unfortunately, in at least some cases, chlorine can also promote or participate in undesired reactions such as the corrosion of metallic plumbing materials. In the case of premise plumbing where copper is still the preferred residential plumbing material, chlorine accelerates pitting corrosion in at least some water chemistries.

Copper corrosion is an electrochemical process driven by two independent redox reactions. The first reaction, also referred to as the anodic reaction, is the oxidation of copper metal (Cu^0) to its ionic form (Cu^+). The electron released by this anodic, corrosion reaction flows through the pipe wall to the site of the second reaction, where the electron(s) are consumed at the cathode by a reduction reaction with oxidants like dissolved oxygen or chlorinated disinfectants.

Chlorine that participates in corrosion reactions is reduced to chloride, resulting in a corresponding loss or decay of the disinfectant. This supplements chlorine loss from normal auto-decomposition. Previous observations found a correlation between chlorine decay and

corresponding pitting propensity in certain waters. This relationship was explored in greater detail in this work using a water known to initiate and sustain pitting in copper tubing.

BACKGROUND: The Role of Chlorine in Pitting Corrosion

Marshall (2004) showed that a synthetic potable drinking water with a high level of free chlorine (> 2 mg/L Cl₂) coupled with high pH and aluminum solids could cause extensive pitting leading to pinhole leaks in less than 12 months in copper pipes subjected to continuous flow. Murray-Ramos (2006) modified this pitting water to test a number of different treatment strategies, corrosion inhibitors, and other natural parameters on pitting corrosion. Although that study was unable to produce pinhole leaks, Murray-Ramos observed severe pitting in several of the different water chemistries tested. He found that pitting corrosion rates varied between the different water chemistries, as did the rate of chlorine reduction. Water chemistries that had higher chlorine reduction rates were observed to have more pits and deeper pits on average than water chemistries with lower chlorine reduction rates. Murray-Ramos even found that some water chemistries with very low chlorine reduction rates did not form any significant pits in 15 months of testing under continuous flow. This strong correlation between these two parameters suggests that chlorine reduction rates can be a good indicator of pitting corrosion rates in this type of water.

Quantification Methods

There are several different methods that can be used to determine the rate of chlorine reduction due to corrosion reactions. Murray-Ramos quantified chlorine reduction rates by measuring chlorine decay. In this study, the chlorine concentrations in the test waters were allowed to decay overnight and were adjusted back to their target levels every morning. The rate at which chlorine disappeared varied for the different water chemistries tested and was termed chlorine decay. Chlorine decay is defined as the change in chlorine concentration of the bulk water, normalized for the water volume, as well as the time period considered. This parameter has units of mass over time and is determined by the following formula:

$$1. \text{ Chlorine Decay} = [(IC - FC) * V] \div TP$$

Where:

IC = Initial Chlorine Concentration in the Bulk Water (mg/L)

FC = Final Chlorine Concentration in the Bulk Water (mg/L)

V = Bulk Water Volume (L)

TP = Time Period Between the Initial Measurement and Final Measurement (hr)

Another method very similar to chlorine decay was used to determine chlorine reduction rates in a short term water chemistry study. Instead of measuring the chlorine decay over a period of time, the daily required chlorine addition necessary to maintain free chlorine residuals was used to quantify reduction rates. Chlorine addition is defined as the amount of chlorine spiked every day to a given water chemistry in order to bump the chlorine concentration of the bulk water back up to its target level. This method is a cumulative measurement of all of the chlorine spikes for a given week and is reported in units of mass over time. Chlorine addition is determined by the following formula:

$$2. \text{ Chlorine Addition} = \left\{ \sum_{i=1}^7 DA_i * SC \right\} \div TP$$

Where:

DA = Daily Addition of Chlorine Stock Solution Spiked to the Bulk Water in Order to Raise the Chlorine Concentration Back to Its Target Value (L)

SC = Chlorine Stock Solution Concentration (mg/L as Cl_2)

TP = Time Period Between Water Changes (hr)

These two methods (chlorine decay and chlorine addition) are useful for quantifying overall chlorine reaction rates. However, in other systems where chlorine is maintained at a constant level, another method is required to determine reduction rates. In these systems it is necessary to determine the chlorine demand since the chlorine concentration in the water is not allowed to decay.

In one study presented in this work, chlorine concentrations were constantly maintained by a chemical feed pump that delivered a concentrated solution of sodium hypochlorite to the bulk water at a very slow rate. Chlorine demand data is therefore presented for this study and is

defined as the chlorine feed rate to the system that is required to continually maintain the bulk water chlorine concentration at its target level. Chlorine demand has units of mass over time and is determined by the following formula:

$$3. \text{ Chlorine Demand} = [(\text{CFV} * \text{FC}) + (\text{CBWCC} * \text{BWV})] \div \text{TP}$$

Where:

Change in Feed Volume (CFV) = Initial Feed Solution Volume Minus Final Feed Solution Volume (L)

Feed Concentration (FC) = Chlorine Concentration of Feed Solution (mg/L)

Change in Bulk Water Chlorine Concentration (CBWCC) = Initial Bulk Water Chlorine Concentration Minus Final Bulk Water Chlorine Concentration (mg/L)

Bulk Water Volume (BWV) = Volume of Bulk Water (L)

Time Period (TP) = Time Elapsed Between Final Measurements and Initial Measurements (hr)

The accuracy of this formula for determining chlorine reduction rates was evaluated by comparing chlorine demand data to chloride increase data. The two measurements are expected to be nearly identical since the only reaction involving chloride in this water is the reduction of chlorine. The change in chloride concentration was monitored over the course of the week by taking ICP samples before and after every water change. The two independent sets of data were found to match up very well, indicating that the method used for quantifying chlorine demand in this study was indeed accurate (Appendix A1, Figure A – 3).

Differences between the two approaches of measuring and maintaining target chlorine levels can be important. Specifically, because the rate of chlorine reduction is heavily influenced by bulk water chlorine concentration, there will be significantly higher reaction rates (and possibly more pitting) if chlorine is maintained at higher concentrations than at lower concentrations (i.e. Figure 2 – 1). Therefore, when a system is maintained at a given chlorine concentration, the rate of chlorine demand will always be higher than the corresponding rate of chlorine decay for similar starting conditions and unit reaction times.

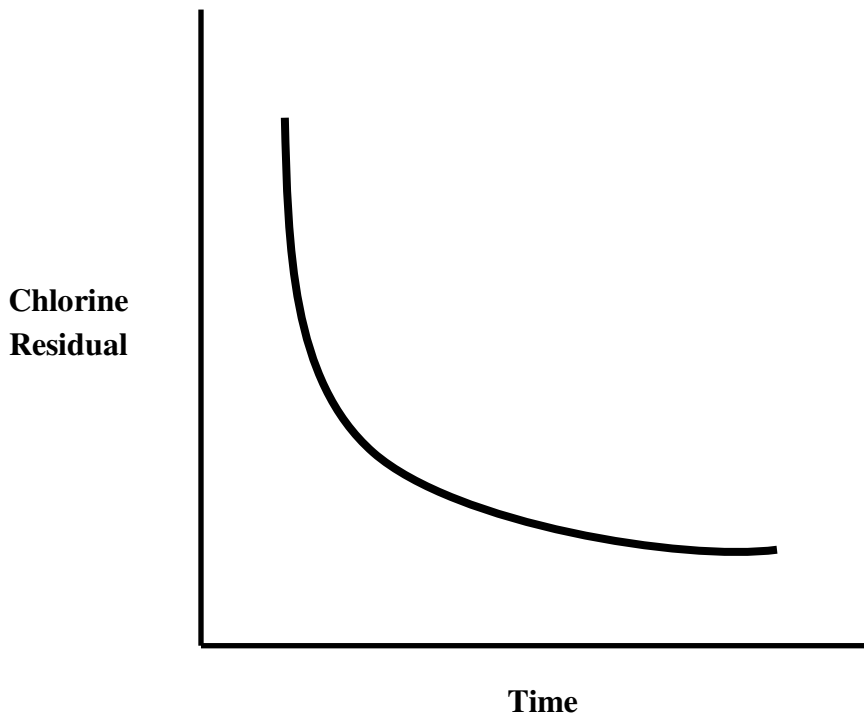


Figure 2 – 1: Chlorine Decay Curve

In addition to the expectation of increased corrosion activity for systems that maintain high chlorine residuals, high chloride level in the bulk water resulting from rapid chlorine decay would also be expected for these types of systems. That is to say that copper plumbing systems that experience accelerated corrosion due to reactions with chlorine will subsequently develop high chloride concentrations if the system recirculates the water. These elevated levels of chloride may further influence corrosion rates in some waters.

To summarize, chlorine is a key factor that drives pitting corrosion in many waters. It is suspected that reactions with chlorine are in some cases the rate limiting step in the overall corrosion or pitting activity. In these cases, there may be a direct relationship between chlorine levels, chlorine consumption, and pitting propensity.

METHODS AND MATERIALS:

Two different experiments were conducted to examine the relationship between pitting propensity in different water chemistries and associated chlorine reduction rates while maintaining high chlorine residuals. One experiment was a short term study that tested six

different water qualities at a constant flow rate. The second study examined a larger matrix of water qualities, flow conditions, corrosion inhibitors, and galvanic connections to other metals. All of the water chemistries tested in these two studies were based off the recipe of the pitting water used by Marshall (2004) that produced pinhole leaks in copper pipes under continuous flow. This water is referred to as “pitting water” throughout this chapter. An additional goal of these experiments was to examine the relationship between pitting rates and chlorine reduction rates as observed in the previous study by Murray-Ramos (2006). The two experimental studies are summarized below and are followed by a more detailed discussion of the results.

Short Term Water Chemistry Study

A simple experiment testing six different water chemistries was set up using a submersible pump to continually circulate water through 2” long, ½” diameter, type K, copper coupons at a velocity of 3 fps (Figure 2 – 2). All three copper coupons were electrically connected by copper wires to allow electrons to flow freely from one coupon to another. Chlorine and pH were both adjusted daily to their respective targets for each water chemistry (Table 2 – 1). Similar to the study by Murray-Ramos (2006), chlorine was allowed to decay overnight from the target concentration and was adjusted the following morning, but the 100 L reservoirs of water for each condition were changed every week to keep corresponding chloride levels in check. The experiment was run for a duration of four weeks, after which the pipes were evaluated for evidence of pitting corrosion.

Table 2 – 1: List of Water Chemistries

Water Quality	Description
<i>Control</i>	Pitting Water (pH = 9.2, Cl ₂ = 4 mg/L)
<i>Al Solids</i>	Pitting Water with 2 mg/L Al Solids
<i>No Hardness</i>	Pitting Water with No Calcium and 2 mg/L Al Solids
<i>Silica</i>	Pitting Water with 5 mg/L Si and 2 mg/L Al Solids
<i>Low Conductivity</i>	1:10 Dilution of Pitting Water
<i>Chloramines</i>	Pitting Water with 6 mg/L Chloramines and 2 mg/L Al Solids (Cl ₂ :NH ₃ ratio of 4:1)

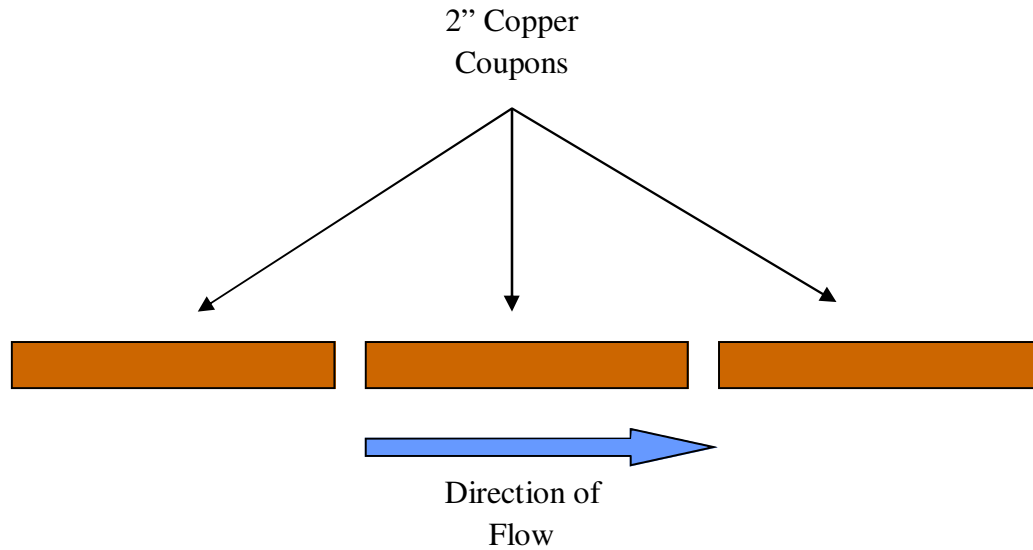


Figure 2 – 2: Experimental Setup for Water Quality Study

Long Term Water Matrix Study

A long term study was devised to test a matrix of different flow conditions, water chemistries, corrosion inhibitors, as well as galvanic connections to less noble metals in relation to copper pitting corrosion. The pitting water was used as a base water chemistry for this study, and all the

different waters tested were variations of this water (Table 2 – 2). The goal of this study was to determine what conditions enhanced or inhibited pitting corrosion. The study tested twenty-one unique conditions in total and utilized an experimental pipe network system that consisted of in-flow and out of flow components.

Table 2 – 2: List of Conditions for Long Term Water Matrix Study

Condition	Description	Condition	Description
<i>Low Q</i>	Pitting Water at a Lower Fluid Velocity of 1.6 fps in a Pipe Loop without a Copper Tee	<i>Low Alkalinity</i>	Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃
<i>No Tee</i>	Pitting Water in a Pipe Loop without a Copper Tee	<i>High Alkalinity</i>	Pitting Water with an Alkalinity of 150 mg/L as CaCO ₃
<i>Control</i>	Pitting Water (pH = 9.2 Cl ₂ = 4 mg/L)	<i>Low Chlorine</i>	Pitting Water with a Total Chlorine Concentration of 0.4 mg/L
<i>Al Solids</i>	Pitting Water with 2 mg/L Al Solids	<i>Low NOM</i>	Pitting Water with 0.01 mg/L Humic Matter
<i>Fe Solids</i>	Pitting Water with 2 mg/L Fe Solids	<i>High NOM</i>	Pitting Water with 0.1 mg/L Humic Matter
<i>pH 10</i>	Pitting Water at pH 10	<i>Low Conductivity</i>	1:10 Dilution of Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃
<i>Low Silica</i>	Pitting Water with 0.5 mg/L Silica	<i>No Hardness</i>	Pitting Water with No Calcium
<i>High Silica</i>	Pitting Water with 5 mg/L Silica	<i>Brass Tee (Connected)</i>	Pitting Water in a Pipe Loop with a Brass Tee
<i>Low Phosphate</i>	Pitting Water with 0.1 mg/L Phosphate	<i>Brass Tee (Disconnected)</i>	Pitting Water in a Pipe Loop with a Brass Tee Electrically Disconnected from the Copper Pipes
<i>High Phosphate</i>	Pitting Water with 1 mg/L Phosphate	<i>Brass Tee (CPVC)</i>	Pitting Water in a Pipe Loop with a Brass Tee and CPVC Pipes
-	-	<i>Iron Tee</i>	Pitting Water in a Pipe Loop with an Aged Iron Tee

The experimental setup consisted of a centrifugal pump used to circulate water at 4.5 fps through a pipe network that consisted of ¾” diameter tubing. Each condition tested had a 94 L plastic

reservoir that was used to house the test water. The pipe network was made up of a 1' section of CPVC followed by a CPVC tee with a 2" long Type M copper pipe section oriented downward and located "out of flow". This "out of flow" section is referred to as a "tee" throughout this chapter. The tee was plugged with a silicon stopper that could be easily removed for measurements of the local water. Following the CPVC tee, there were three 1' sections of the same type of copper pipe, in the path of flow with two, CPVC, ninety degree bends located between the first and second copper pipes (Figure 2 – 3). Two of the experimental conditions did not have copper tees, four conditions had either brass or iron tees, and one condition had only CPVC pipes along the path of flow (Table 2 – 2). All metal sections were electrically connected by external copper wires unless otherwise stated.

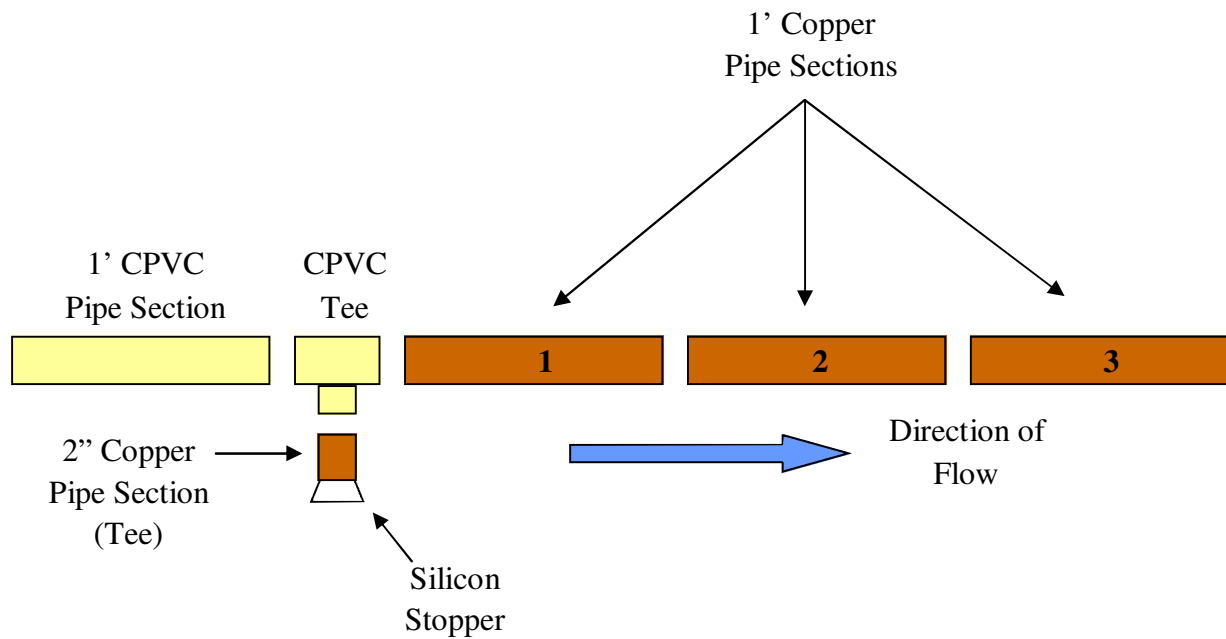


Figure 2 – 3: Experimental Setup for Water Matrix Study

Chemical feed pumps were used to slowly feed a highly concentrated solution of sodium hypochlorite and sodium hydroxide to each of the twenty-one conditions in order to keep the chlorine and pH at their target values. Chlorine demand was measured for each condition every week by the previously mentioned method (Formula 3). The bulk water was changed every week for all conditions for the first eight weeks, after which the waters were changed either

every week, every other week, or every third week, based on chloride increase rates in the bulk water.

Previous research (see Chapter 1) has demonstrated the importance of flow in relation to pitting in this particular water (Marshall, 2004; Lattyak, 2007). Consequently, most of the copper pipes in this study were subjected to continuous flow at a velocity of 4.5 fps. However, in order to mimic conditions in real, residential plumbing systems where some pipes experience more frequent flow than others, this experiment was designed to contain both “in-flow” and “out of flow” sections. The “in-flow” sections were subjected to continuously flowing water, while the “out of flow” sections contained relatively stagnant water. Fundamentally different water chemistries were expected to develop between the stagnant water and the continuously flowing water that was believed to further influence corrosion activity. The general theory was that the water settling inside of the downward oriented, out of flow copper tee (stagnant water) would have a lower chlorine concentration, a lower pH, higher levels of copper, and higher levels of chloride compared to the water passing through the in-flow copper sections. This differential water quality between the different sections of copper was considered to possibly drive pitting reactions at this out of flow copper section.

RESULTS AND DISCUSSION:

Data indicating the correlation between chlorine reduction rates and pitting propensity will be presented for each of the recent copper studies. Thereafter, a short discussion section will consider the implications of this mechanistic parameter.

Short Term Water Quality Study

In the short term water quality study, chlorine reduction rates were assessed by chlorine addition, since the chlorine level was adjusted daily via a manual addition (Equation 2). The chlorine addition data for the short term water quality study showed significant differences between water chemistries. In other words, specific water qualities consumed and required more chlorine than others. Chlorine consumption is a function of both chlorine auto-decomposition and direct chlorine reduction at the surface of the copper pipe wall.

Chlorine consumption was observed to vary over the four week test period for all of the different water chemistry conditions, which would be expected since the activity of the copper surface changes due to the development of surface scale layers. Chlorine reduction rates would therefore be expected to change with time until the system reaches a relative steady state. Given the nature of this short term study, the system did not reach a steady state. These results are representative of new plumbing systems prior to sufficient aging. Nevertheless, clear trends were observed over the four weeks that the experiment was run (Figure 2 – 4).

In this particular experiment, higher chlorine addition values correspond to higher chlorine reduction rates. The required chlorine addition for the different waters could be grouped into three general categories: high, medium, and low. The control water, as well as the low conductivity water consistently, had very high chlorine reduction rates compared to the rest of the water qualities. In contrast, the waters with silica and chloramines started out with chlorine reduction rates very close to the other conditions, but then steadily decreased over the four week period, and, by the conclusion of the experiment, both conditions had very low reduction rates. The water with aluminum solids as well as the water with no hardness had chlorine reduction rates that remained fairly constant for the duration of this experiment. The chlorine reduction rates for these two conditions were significantly lower than the high reduction rates of the control water and the low conductivity water, but were also considerably higher than the rates of the water with silica and the water with chloramines.

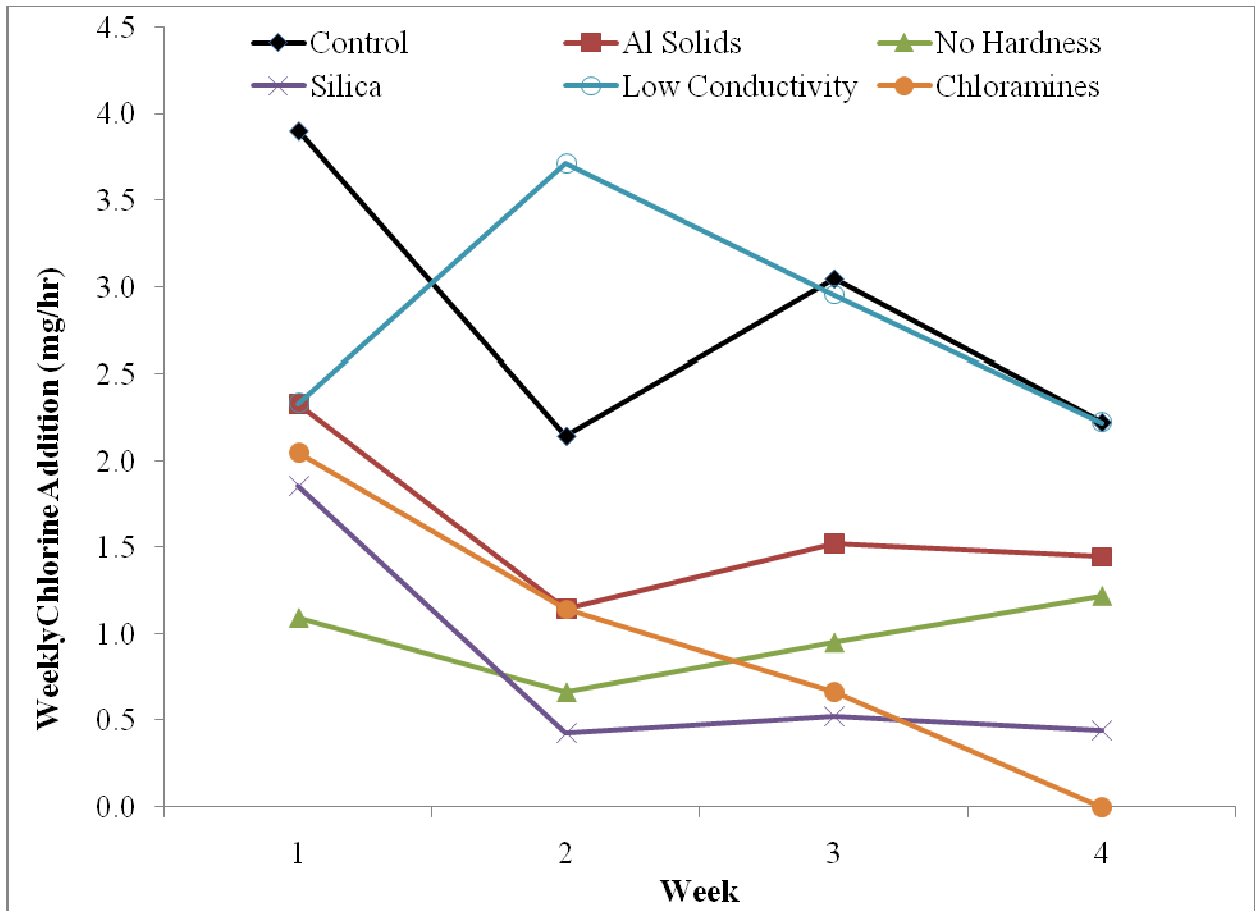


Figure 2 – 4: Chlorine Decay Rates for Water Quality Study

Visual inspection of the copper coupons at the conclusion of the experiment confirmed the trends given by the chlorine reduction data (Figure 2 – 5). The two water qualities with high chlorine reduction rates (Control and Low Conductivity) had coupons that were completely covered in corrosion scale and had begun to develop pits on the copper surface. The two water qualities with medium reduction rates (Al Solids and No Hardness) had a considerable amount of scale that had formed on the coupon surface, but did not have any measurable pits that formed beneath the scale. This is not necessarily surprising given the very short duration of this test. The two water qualities that had low reduction rates (Silica and Chloramines) did not have any scale form on the surface of the copper coupons and looked in appearance very much like brand new copper.



Figure 2 – 5: Scale Formation on Copper Coupons

Although four of the conditions formed tubercles on the copper pipe surface, penetrating pits were only observed for the control and the condition with low conductivity. In just four weeks the control formed pits that correspond to a penetration of 37% of a ½” diameter type M copper pipe wall. Similarly, the low conductivity water formed pits that correspond to a 30% penetration of the same pipe wall. Both water chemistries produced an extensive amount of pitting for new copper pipes in only four weeks. These were also the two conditions with the highest chlorine reduction rates. In contrast, the two conditions in this study that did not form any scale or pits (Silica and Chloramines) had the lowest corresponding chlorine reduction rates. This generally confirms the hypothesis that chlorine reduction rates are a good indicator of both corrosion activity (scale formation) and pitting propensity for this particular type of pitting water.

Water Matrix Study

Given the experimental setup for the larger long term water matrix study, chlorine demand (Equation 3) was measured to quantify chlorine reduction rates, since each condition was maintained at a specified chlorine concentration via an external feed pump. Similar to the short-

term water chemistry study, chlorine reduction rates were observed to vary during the initial phase, such that when the copper was still relatively new the corresponding chlorine demand was low. However, after about forty days, the chlorine demand reached a relatively steady state, corresponding to a higher chlorine demand for most all of the conditions (Figure 2 – 6). As such, all tables and graphs presented in this work consider the data collected after forty days unless otherwise stated. Similar findings in this same type of water have been observed by Lattyak (2007).

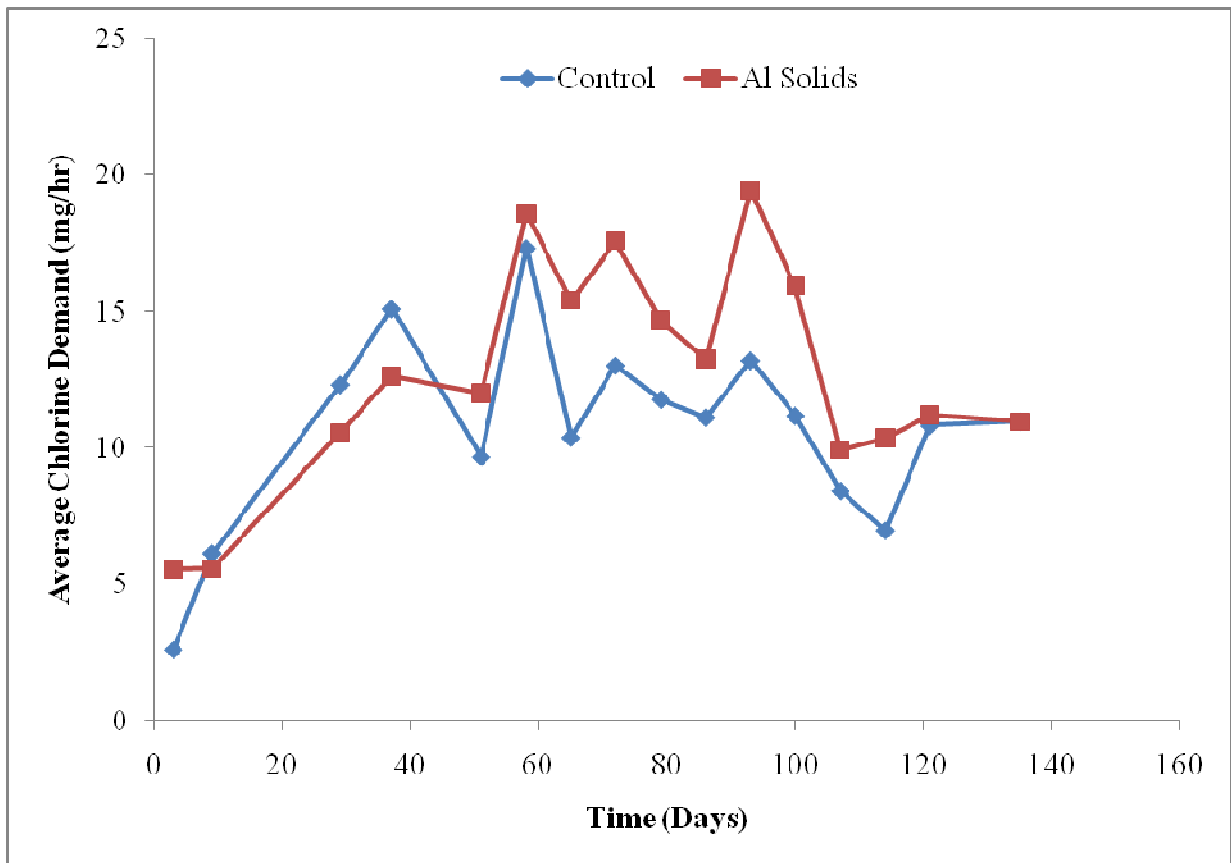


Figure 2 – 6: Chlorine Demand Over Time

The matrix of experimental conditions was grouped into different subsections: flow conditions, water chemistries, corrosion inhibitors, and galvanic connections. Results of this study will be presented in accordance to each experimental group.

Flow Conditions

Fluid velocity and flow configuration were observed to have a significant effect on chlorine demand (Figure 2 – 7). Two of the experimental conditions (labeled Low Q and No Tee) did not have an out of flow copper pipe section like the control water as per Figure 2 – 3. The low flow (Low Q) condition that had a fluid velocity of 1.6 fps had a chlorine demand that was almost half that of the same water chemistry in the same flow configuration (No Tee) but with a higher fluid velocity of 4.5 fps. This suggests that fluid velocity is an influencing factor affecting corrosion reaction rates. The presence of the out of flow tee, however, was not observed to significantly increase chlorine demand. Although the control, which had a section of copper out of flow (i.e. Figure 2 – 3), appeared to increase chlorine demand on average, it was not observed to have a statistically significant effect when compared to the same exact experimental condition without the out of flow copper (No Tee).

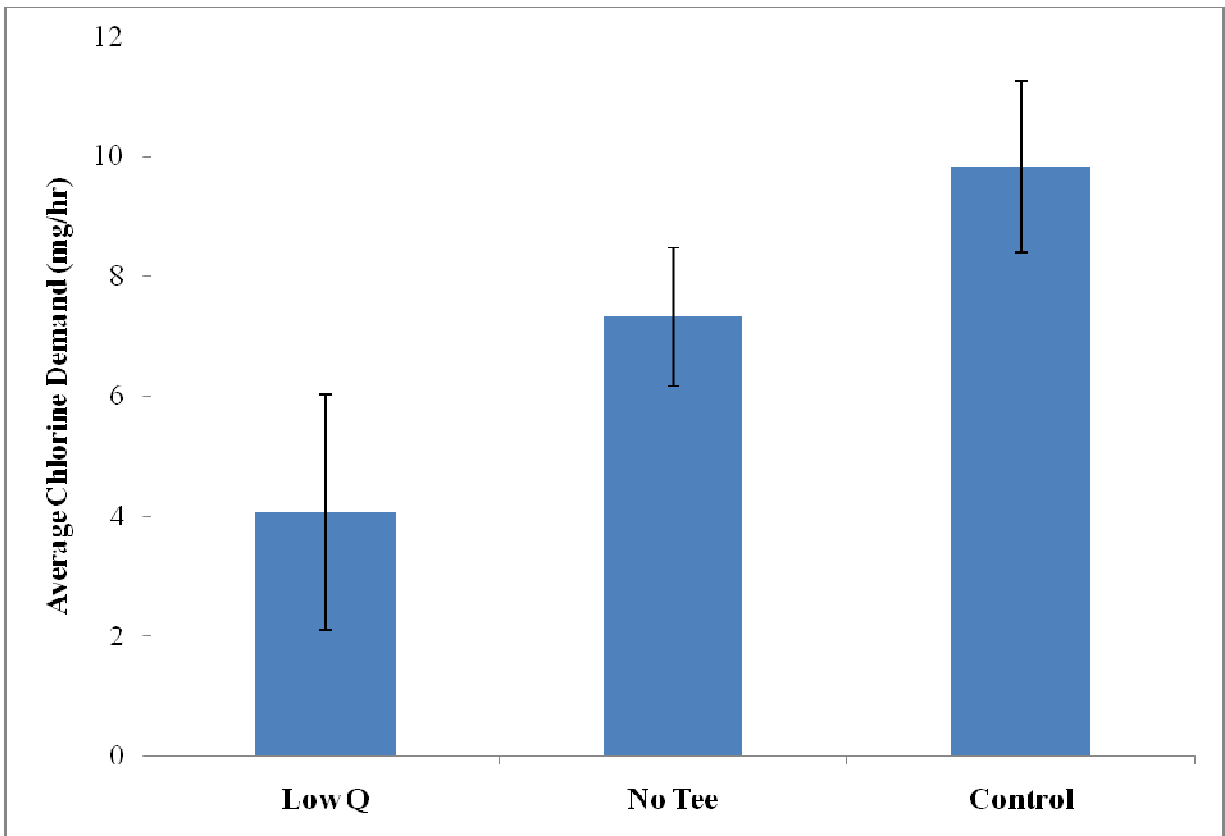


Figure 2 – 7: Average Chlorine Demand for Different Flow Conditions. Data Averaged From Weeks 12 Through 20 and Normalized for Differences in Copper Surface Area. Error Bars Represent 95% Confidence Assuming a Normal Distribution

In addition to the consideration of fluid velocity and flow configuration, the synergistic effects of flowrate and chlorine concentration on pitting corrosion were also considered. Chlorine mass loading rate (i.e. the concentration and rate at which chlorine is circulating through the pipe network) was considered in order to determine if the mass rate of oxidant delivery to the cathodic site was the primary factor driving the pitting reaction. The overall trend of the data from this study, as well as a previous study on the effects of velocity (Chapter 1), generally indicated that corrosion currents increased with mass loading rate. However, no definitive correlation suggesting that this phenomenon was purely as function of mass loading could be drawn (Appendix A, Figure A – 2).

Water Chemistries

Concurrent with the short-term study, chlorine demand was also observed to vary depending on the water chemistry (Figure 2 – 8). Fundamental water quality parameters like chlorine concentration and pH were found to influence the chlorine demand which is in turn expected to influence the pitting propensity. For example, the condition with 0.4 mg/L chlorine was observed to significantly reduce the chlorine demand of the system almost by 40 times compared to the condition with 4.0 mg/L chlorine concentration. This is consistent with expectations for this particular type of pitting, where pitting corrosion would be expected to increase when there is more chlorine available for the cathodic half reaction.

This particular pitting water had been found to be more aggressive at higher pHs around 9.2 in prior research (Rushing, 2002, Marshall, 2004). Yet, further increasing the pH to 10 appears to slightly decrease the chlorine demand compared to the same water at pH 9.2. The implications of this factor on pitting corrosion must be addressed in future research.

The addition of certain coagulant solids was found to increase chlorine demand in this type of water. Although the addition of 2 mg/L of aluminum solids had little effect on chlorine demand, the addition of 2 mg/L iron solids increased the chlorine demand by about four times compared to the control. This rapid loss of chlorine in copper tubing in the presence of iron solids had been observed in previous research by Murray-Ramos (2006). Murray-Ramos (2006) conducted a number of experiments examining the kinetics of chlorine decay and found that copper and iron

synergistically acted to catalyze chlorine reduction. His work showed that in this water, iron solids alone had virtually no chlorine demand when batch tests were performed, but when both iron solids and copper pipe were present, chlorine decay was accelerated such that concentrations would decay from 4mg/L Cl₂ to nearly 0 mg/L Cl₂ over the course of 24 hours.

Murray-Ramos (2006) found that, although copper pipe in the presence of iron solids dramatically increased chlorine reduction rates, it did not directly translate to pitting corrosion. In other words, this water chemistry with iron solids in copper plumbing systems induces rapid chlorine decay, but not all of the chlorine consumption is due to corrosion activity.

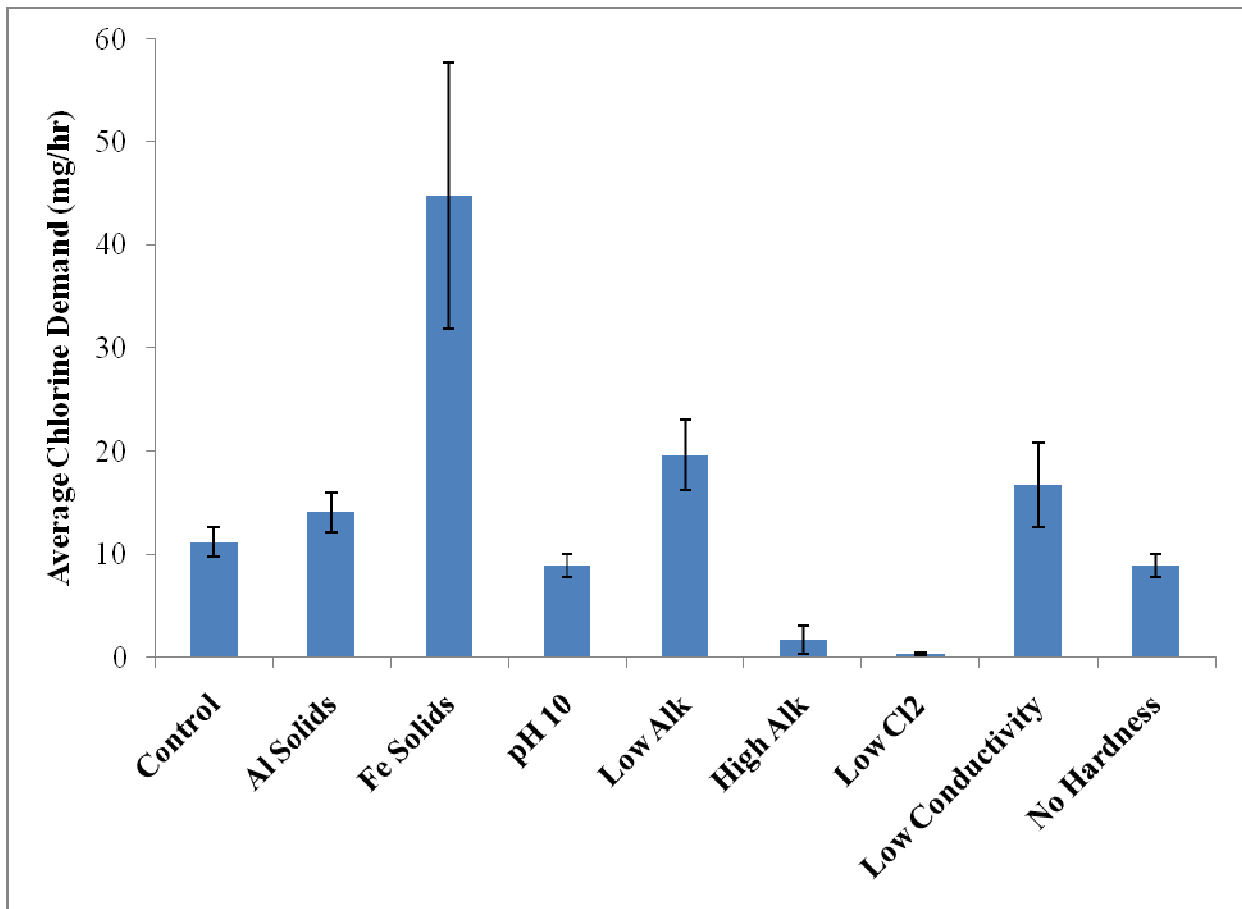


Figure 2 – 8: Average Chlorine Demand for Different Water Chemistries. Error Bars Represent 95% Confidence Assuming a Normal Distribution

Alkalinity was observed to have a tremendous impact on chlorine demand. For instance, a low alkalinity of 15 mg/L as CaCO₃ increased the chlorine demand by nearly a factor of 2 compared to the same water at an alkalinity of 30 mg/L as CaCO₃ (i.e. control water). A high alkalinity of 150 mg/L as CaCO₃, conversely, decreased the chlorine demand by a factor of 5 compared to the same water at an alkalinity of 30 mg/L as CaCO₃. Thus the difference in chlorine demand between the low alkalinity and high alkalinity conditions was about a factor of 10, suggesting that alkalinity has a significant effect on corrosion reactions in this type of water. Pitting corrosion in this type of water would therefore be expected to decrease with higher alkalinity and increase with lower alkalinity.

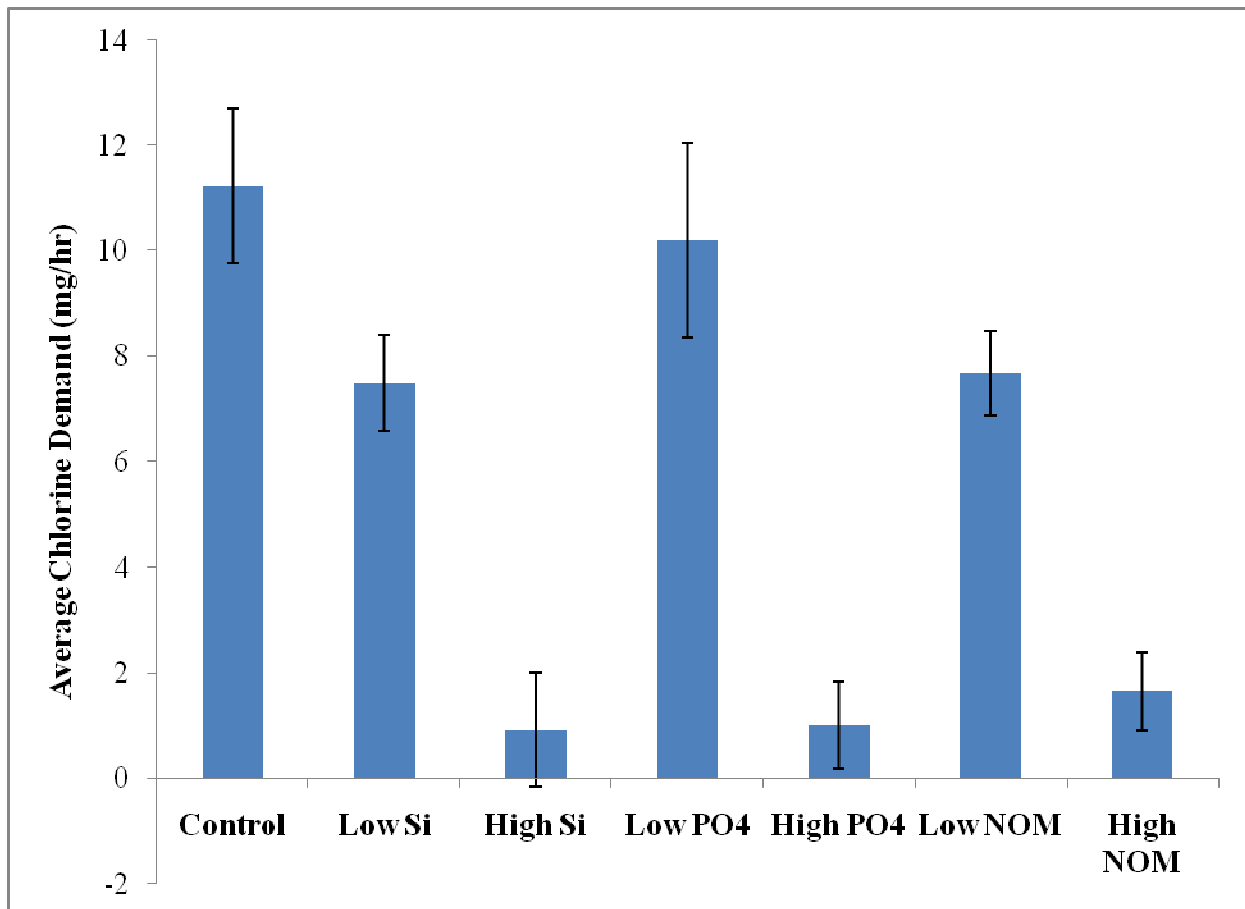
Conductivity and hardness had very little influence on chlorine demand compared to the control condition. The alkalinity of the low conductivity water was the same as the low alkalinity condition, which could explain why the two chlorine demand values were statistically similar. Thus, it appears that the high chlorine demand observed for the low conductivity water is due to alkalinity rather than conductivity. Although the water with no hardness was observed to slightly decrease chlorine demand compared to the control, neither parameter (hardness or conductivity) appears to be a driving factor in regards to chlorine demand and is therefore not expected to greatly influence subsequent pitting propensity.

Corrosion Inhibitors

Corrosion inhibitors were observed to have varying effects on chlorine demand depending on inhibitor concentration (Figure 2 – 9). All corrosion inhibitors were dosed once after every water change (i.e. the start of a “fresh” water). Higher levels of humic matter, orthophosphate, and silica were observed to dramatically decrease the chlorine demand of the system, whereas lower inhibitor concentrations did not have much effect on chlorine demand. For example, a concentration of 0.1 mg/L humic matter was observed to decrease chlorine demand by more than a factor of 5 compared to the control, which contained no humic matter. However, 0.01 mg/L of humic matter only slightly diminished the chlorine demand of the system compared to the control. Similarly, 5 mg/L of silica was observed to decrease chlorine demand by more than a factor of 10 compared to the control, whereas 0.5 mg/L of Silica only decreased the chlorine demand by about 30%. Also, 1 mg/L of orthophosphate was sufficient to reduce the chlorine

demand of the system by more than a factor of 10 compared to the control, however, 0.1 mg/L of orthophosphate had no statistically significant effect on chlorine demand.

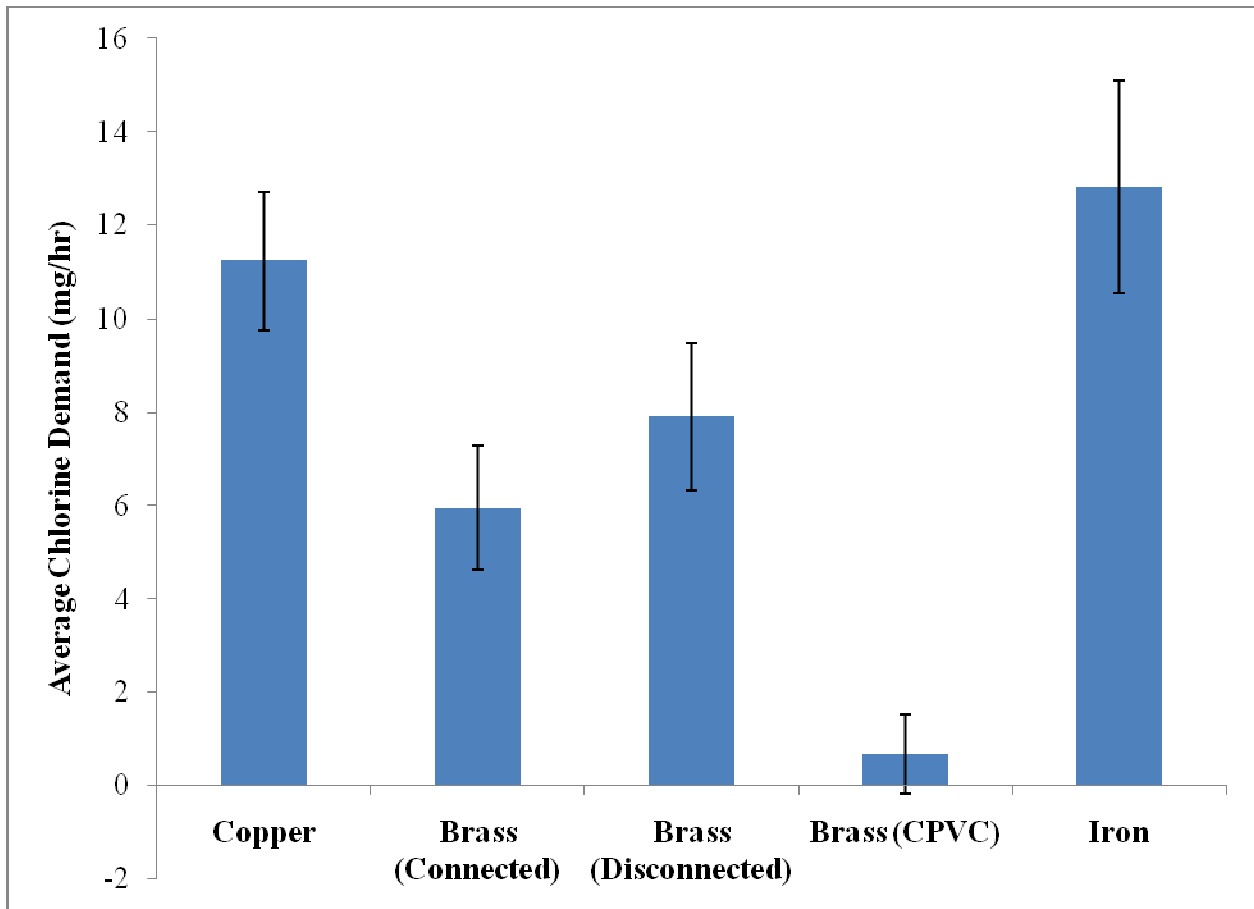
This data indicates that at high enough concentrations, each of these inhibitors are sufficient to protect copper pipes from excessive corrosion in this type of water. It would appear that 0.1 mg/L humic matter, 5 mg/L silica, and 1 mg/L orthophosphate have some protective abilities relative to copper pitting corrosion. However, this data also indicates that lower inhibitor concentrations provide little to no protection.



**Figure 2 – 9: Average Chlorine Demand for Different Inhibitor Concentrations
Error Bars Represent 95% Confidence Assuming a Normal Distribution**

Galvanic Connections

In addition to flow configuration, water chemistry, and corrosion inhibitors, the galvanic connection of copper to a less noble metal was also observed to have an effect on chlorine demand (Figure 2 – 10). By simply replacing the copper tee with a brass tee in the out of flow section, the chlorine demand was observed to decrease by nearly a factor of two on average. Whether electrically connected or disconnected, the presence of brass in the system at this out of flow location was shown to cut the chlorine demand nearly in half. This suggests that the presence of brass may act to decrease the corrosion rate of copper for this type of water. In contrast, the presence of an aged iron tee at this out of flow location had no statistically significant effect on chlorine demand.



**Figure 2 – 10: Average Chlorine Demand for Different Galvanic Connections
Error Bars Represent 95% Confidence Assuming a Normal Distribution**

As expected, chlorine demand was significantly lower for the condition with a brass section out of flow where all three 1' sections of copper pipe were replaced with CPVC pipe. This condition was designed to compare chlorine reduction rates in plastic pipe systems containing brass fittings to copper pipe systems. The data indicates that the majority of the chlorine demand in the systems tested in this study is due to reactions with the in-flow copper pipes, however, there is a small chlorine demand associated with the corrosion of the out of flow brass and auto-decomposition. On average the corrosion rate of the system with CPVC and brass was about 10 times less than the system containing copper and brass.

Overall, chlorine reduction rates were observed to vary with changes in water chemistry, flow conditions, inhibitor concentrations, and plumbing materials (Table 2 – 3). The conditions that had the strongest impact on chlorine demand were fluid velocity, alkalinity, inhibitor concentrations, chlorine concentration, chloramination as opposed to the use of free chlorine, and the presence of iron coagulant solids.

Table 2 – 3: Key Findings

FLOW CONDITIONS				
Condition	Description	Chlorine Demand (% Difference Compared to the Control)	Chlorine Demand Category	Comments
<i>Low Velocity, No Tee</i>	Pitting Water at a Lower Fluid Velocity of 1.6 fps in a Pipe Loop without a Copper Tee	61% Decrease	Low	Less Chlorine Demand at Lower Velocities
<i>High Velocity, No Tee</i>	Pitting Water at a Fluid Velocity of 4.5 fps in a Pipe Loop without a Copper Tee	27% Decrease	Moderate	Slightly Less Chlorine Demand Without the Out of Flow Tee
COAGULANT SOLIDS				
<i>Al Solids</i>	Pitting Water with 2 mg/L Al Solids	26% Increase	High	Slightly More Chlorine Demand with the Addition of Al Solids
<i>Fe Solids</i>	Pitting Water with 2 mg/L Fe Solids	299% Increase	Very High	Rapid Chlorine Decay Due to the Presence of Both Iron and Copper (Not All Decay is From Corrosion)
CHLORINE and pH				
Chloramines = 6.0 mg/L, pH = 9.2,	Pitting Water with 6 mg/L Chloramines (Cl ₂ :NH ₃ ratio of 4:1)	66% Decrease	Low	Significantly Less Chlorine Demand when Chloramines Are Used Instead Free Chlorine
Cl ₂ = 4.0 mg/L, pH = 10	Pitting Water at pH 10	20% Decrease	Moderate	Slightly Less Chlorine Demand at pHs greater than 9.2
Cl ₂ = 0.4 mg/L, pH = 9.2	Pitting Water with a Total Chlorine Concentration of 0.4 mg/L	97% Decrease	Very Low	Significantly Less Chlorine Demand at Low Chlorine Concentration
ALKALINITY				
<i>Low Alkalinity</i>	Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃	75% Increase	High	Significantly More Chlorine Demand at Lower Alkalinities
<i>High Alkalinity</i>	Pitting Water with an Alkalinity of 150 mg/L as CaCO ₃	85% Decrease	Very Low	Significantly Less Chlorine Demand at Higher Alkalinities

Table 2 – 3 (Continued): Key Findings

<i>CONDUCTIVITY</i>				
Condition	Description	Chlorine Demand (% Difference Compared to the Control)	Chlorine Demand Category	Comments
<i>Low Conductivity, Low Alkalinity</i>	1:10 Dilution of Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃	50% Increase	High	Increase in Chlorine Demand Due to Low Alkalinity, Not Low Conductivity
<i>HARDNESS</i>				
<i>No Hardness</i>	Pitting Water with a Calcium Hardness of 0 mg/L as CaCO ₃	20% Decrease	Moderate	Slightly Less Chlorine Demand at a Lower Hardness
<i>CORROSION INHIBITORS</i>				
<i>Low Silica</i>	Pitting Water with 0.5 mg/L Silica	33% Decrease	Moderate	Slightly Less Chlorine Demand with a Low Amount of Silica Present
<i>High Silica</i>	Pitting Water with 5 mg/L Silica	92% Decrease	Very Low	Significantly Less Chlorine Demand at Higher Silica Concentrations
<i>Low Phosphate</i>	Pitting Water with 0.1 mg/L Phosphate	9% Decrease	Moderate	No Statistically Significant Change in Chlorine Demand at Low Phosphate Doses
<i>High Phosphate</i>	Pitting Water with 1 mg/L Phosphate	91% Decrease	Very Low	Significantly Less Chlorine Demand at Higher Phosphate Doses
<i>Low NOM</i>	Pitting Water with 0.01 mg/L Humic Matter	32% Decrease	Moderate	Slightly Less Chlorine Demand with Low Amounts of Humic Matter Present
<i>High NOM</i>	Pitting Water with 0.1 mg/L Humic Matter	85% Decrease	Very Low	Significantly Less Chlorine Demand with Higher Levels of Humic Matter

Table 2 – 3 (Continued): Key Findings

<i>Galvanic Connections</i>				
Condition	Description	Chlorine Demand (% Difference Compared to the Control)	Chlorine Demand Category	Comments
<i>Brass Tee (Connected)</i>	Pitting Water in a Pipe Loop with a Brass Tee	47% Decrease	Moderate	Less Chlorine Demand When Copper is Electrically Connected to Brass
<i>Brass Tee (Disconnected)</i>	Pitting Water in a Pipe Loop with a Brass Tee Electrically Disconnected from the Copper Pipes	30% Decrease	Moderate	Slightly Less Chlorine Demand When Brass is Present in the Plumbing System
<i>Brass Tee (CPVC)</i>	Pitting Water in a Pipe Loop with a Brass Tee and CPVC Pipes	94% Decrease	Very Low	Significantly Less Chlorine Demand in Plastic Systems Compared to Copper Systems
<i>Iron Tee</i>	Pitting Water in a Pipe Loop with an Aged Iron Tee	14% Increase	High	No Statistically Significant Change in Chlorine Demand When Copper is Electrically Connected to Aged Iron

This study has shown that certain water chemistries under high flow conditions rapidly consume chlorine in corrosion reactions with copper pipe. This is a very undesirable reaction from two different standpoints. First, more rapid chlorine decay indicates that the copper pipe is corroding at a faster rate and is therefore more likely to fail prematurely. Second, increased chlorine decay rates deplete the chlorine level in the water that was intended to be available for disinfection. This increases the potential for microbial growth, especially in re-circulating systems since lower chlorine residuals provide a more conducive environment for bacteria and other potentially harmful pathogens to thrive. Furthermore, lower chlorine levels resulting from this rapid chlorine decay induced by copper corrosion can also lead to increased lead (Pb) leaching from brasses or leaded solder (Shock et al., 2001).

Chlorine safeguards public health by controlling microbial re-growth. When chlorine levels rapidly decay due to excessive corrosion reactions with metallic plumbing systems, water quality can be compromised.

CONCLUSIONS:

- Chlorine is a driving factor in pitting corrosion in this type of water as it readily forces the cathodic half reaction, which is a necessary mechanistic component to complete the corrosion reaction.
- Chlorine demand has been observed to be a good indicator of both total corrosion as well as pitting corrosion in particular in the type of water studied in this work. Certain limitations are expected when utilizing chlorine demand as a surrogate in other systems or with other types of pitting.
- Flow conditions, water chemistry, corrosion inhibitors, and galvanic connections all have a unique influence on chlorine demand.
- Plastic plumbing systems exert a significantly lesser chlorine demand than metallic plumbing systems.

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Chapter 3: The Effects of Water Quality, Flow Conditions, Corrosion Inhibitors, and Galvanic Connections on Copper Pitting Corrosion

ABSTRACT:

The severity of copper pitting corrosion in waters with high chlorine and a high pH has been observed to be dramatically affected by water chemistry, flow conditions, corrosion inhibitors and the presence of dissimilar metals. Similarly, the creation of concentration cells due to the development of dissimilar water chemistries on different sections of a copper pipe surface can further enhance existing corrosion. Using a water known to promote and sustain pitting corrosion as a base condition, this work tested a matrix of different representative water chemistries under flow conditions commonly encountered in real-world applications. In this work, pitting propensity was observed to significantly decrease with lower levels of free chlorine, high alkalinity, and sufficient doses of copper corrosion inhibitors such as natural organic matter, silica, and orthophosphate. A low alkalinity was observed to accelerate pitting corrosion in this type of water. This work was currently ongoing at the time of this publication and, therefore, only a preliminary presentation of the results is given herein.

INTRODUCTION:

Copper pitting corrosion is a costly phenomenon that affects many home owners across the United States. Although it has been studied for many years, pitting corrosion is still poorly understood due to its complex nature. Previous research by Marshall (2004) showed that water with high pH, high chlorine, and aluminum solids could produce pinhole leaks in copper tube in less than twelve months under continuous flow. A follow up study by Murray-Ramos (2006) observed pitting corrosion to vary with water chemistry in this type of water, since some modifications to the water chemistry used by Marshall were found to increase the extent of pitting, while other conditions were observed to nearly eliminate pitting. Further research by Lattyak (2007) showed that higher fluid velocities exacerbated pitting in this type of water.

Although several factors have been shown to heavily influence copper pitting in this type of water, much remains unknown. When considering the seemingly infinite variability in potable water chemistries, it is evident that further research, testing a wide range of parameters, is needed to better understand this issue. This work tests a large number of common parameters and flow conditions on copper pitting corrosion in drinking water with high chlorine and high pH. The

goal of this study is to determine which conditions enhance pitting and which conditions inhibit this type of corrosion.

Background: Copper Pitting in High Chlorine High pH Waters

Conventional Pitting Model

Copper pitting in waters with high chlorine and high pH is conceptualized to consist of four fundamental steps (Figure 3 – 1). First, copper begins to actively corrode at the pit by an anodic reaction that releases an electron. Secondly, the electron travels through the pipe wall to a second location commonly referred to as a cathode. Thirdly, at this cathode, the electron is consumed in a cathodic reaction with common water constituents such as chlorinated disinfectants or dissolved oxygen. If the anode and cathode are physically separated by a dielectric, but electrically connected (i.e. external wire), an ammeter can be put in-line to measure the electron flow between these two locations due to corrosion. As this reaction continues to occur, a large amount of positively charged copper cations build up in the pit. This build up of positive charges initiates the fourth and final step that involves the migration of counterbalancing negatively charged anions into the positively charged pit. This imbalance in water chemistry between the water in the pit and the water at the cathode is believed to help sustain the pitting corrosion reaction.

A similar situation occurs in pipe networks that have flow configurations where a large amount of pipe area is subject to flow and a small amount of pipe area contains water that remains stagnant. The stagnant section retains the positively charged copper ions that are produced by corrosion while copper cations resulting from corrosion in the flowing section are continually swept away by the flow of water. This creates an imbalance in water chemistry similar to the above mentioned pit and cathode. The buildup of positive charges in the stagnant section of pipe would subsequently attract counterbalancing anions to this out of flow section.

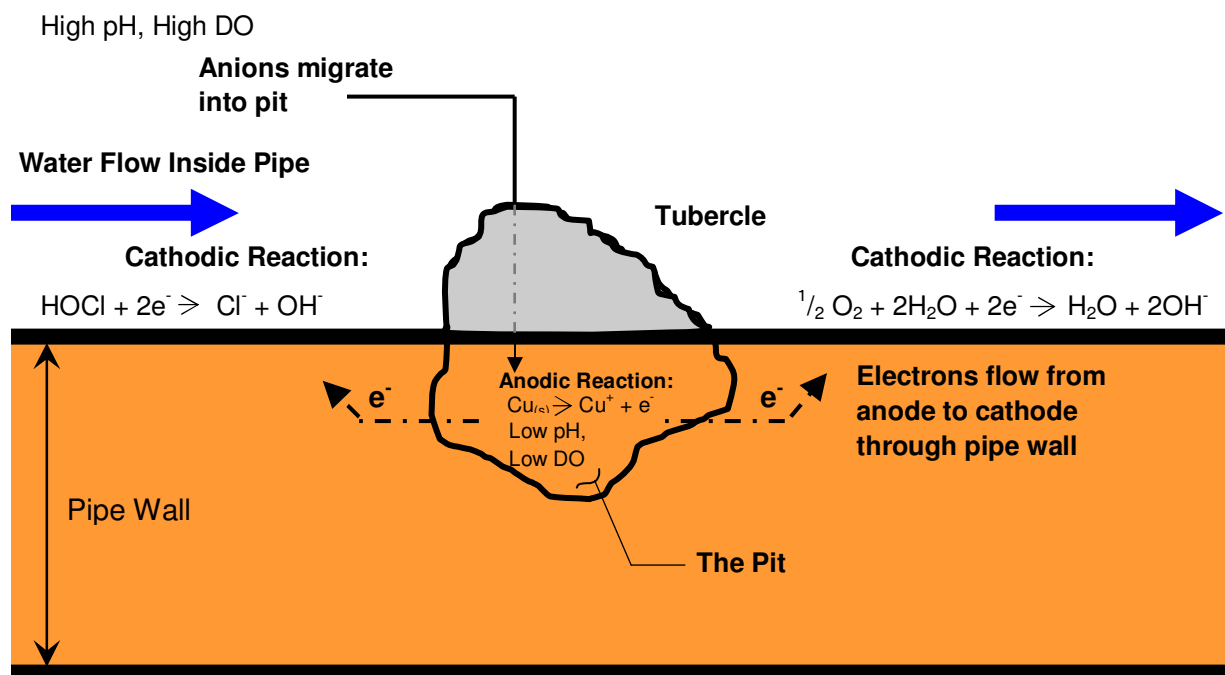


Figure 3 – 1: Conceptualized Pitting Reaction

Copper pitting reactions are believed to be dependent on all four fundamental mechanisms, regardless of the source initiating the pitting. There are a number of known and suspected causal factors that induce these pitting reactions which often lead to the formation of a pinhole leak. These factors can be loosely characterized as either aggressive water quality, microbial activity, or flow conditions. This particular work focused exclusively on a specific water quality (high pH, high Cl_2) that has been proven to induce pitting that develops into a pinhole leak (Marshall, 2004), and did not consider any possible microbial induced corrosion. Other studies have found that flow induced failure mechanisms like velocity (Lattyak, 2007) and concentration cells (Coyne, 2009) can influence and sometimes enhance this water's pitting propensity. The fundamental mechanisms of these two factors will be briefly reviewed, since they were considered to some extent in the experimental study presented herein.

Effects of Flow on Pitting Corrosion

Flow conditions in home plumbing systems are essentially varied and consist of different pipe diameters, fluid velocities, usage patterns, and network configurations. Pitting corrosion in waters with high chlorine and high pH has been observed to be heavily influenced by these

different flow parameters. Marshall (2004) observed pitting corrosion to increase with greater duration of flow when this type of water was circulated through new copper pipe under different flow cycles. Continuous flow was found to create the most aggressive condition for pitting in this study by Marshall (2004). Further research by Lattyak (2007) showed that fluid velocity had a dramatic effect on pitting corrosion subject to this specific water recipe under continuous flow.

Both of these previous studies considered only continuous sections of copper, all of which were subjected to the same fluid flow. Pipe network configurations that include both sections of copper pipe under continuous flow, as well as sections under stagnant conditions (out of flow) have not been investigated. Given that all real premise plumbing systems will inherently contain some copper sections under more frequent flow versus other sections that experience less flow, it is worthwhile to test such a scenario. This type of configuration is also important since prior research has shown evidence that a section of pipe under stagnant conditions connected to a section of pipe under flowing conditions may actually increase corrosion activity (Coyne, 2009).

Consideration of Real World Concentration Cells

When different systems conditions exist, a mechanism known as a concentration cell can help drive pitting corrosion reactions (Coyne, 2009). For example, when a chlorinated disinfectant decays in one section of tubing under stagnant conditions, the resulting byproduct of this decay is an increase in the concentration of chloride. However, in other pipe sections with more water usage, the amount of chlorinated disinfectant will be higher. Since there is an imbalance in chlorine speciation between the two locations, the system will move towards satisfying equilibrium. This often occurs at the expense of the copper tubing by initiating corrosion reactions to force the cathodic reaction, chlorine decay (Figure 3 – 1), to create more chloride at that location experiencing frequent flow. In other words, a higher concentration of certain dissolved species at one section of copper versus another can actually promote or enhance corrosion activity due to this concentration difference.

This type of flow can occur regularly in a home plumbing system (Coyne, 2009). For example, a kitchen sink would be expected to have much more water usage compared to an adjacent branch of pipe supplying a secondary (seldom used) bathroom sink. Since the two pipes sections are

electrically connected, corrosion currents that develop from differential system conditions can flow between the anode and cathode.

The previously mentioned example considered corrosion induced by chlorine imbalance due to chlorine decay, but existing pitting reactions can also subsequently induce a concentration gradient of chloride. As mentioned previously, counter balancing anions will migrate towards the pit which contains an over abundance of positive cations (Figure 3 – 1). Therefore, a concentration cell can develop around an existing anodic pit and cathode, further increasing pitting propensity. If the active pit is located in the section of premise plumbing with mainly stagnant water, then counterbalancing anions will migrate toward this area, creating a differential water chemistry that is high in copper, chloride, and sulfate, and low in pH, dissolved oxygen, and chlorine compared to a more refreshed water quality in the section subjected to more frequent, continuous fluid flow. Therefore, more aggressive conditions can develop where the stagnant “out of flow” becomes more susceptible to anodic reactions, while the water chemistry in the “in-flow section” is conducive to cathodic reactions.

The net result is that pitting propensity can be expected to change if some tubing is located in-flow and other tubing is located out of flow. Given the practicality of the formation of such a reaction mechanism in a real system, this type of configuration (out of flow copper vs. continuous inflow copper) was considered in this experimental study.

METHODS AND MATERIALS:

A large copper pitting experiment was conducted to test the effects of a number of different flow conditions, water chemistries, corrosion inhibitors, and galvanic connections of copper to less noble metals. The experiment consisted of twenty-one unique conditions in total, and there was an emphasis to mimic real potable water conditions, to the extent possible.

The benchmark water chemistry used in this study was the water used by Marshall (2004) that produced pinhole leaks in copper pipes in less than twelve months under continuous flow. Modifications to this water were made to test the impacts of several representative water chemistries on pitting corrosion. However, aluminum solids, which were part of Marshall’s aggressive water recipe, were only added to one condition in order to determine whether or not the presence of this coagulant solid enhanced pitting corrosion at the high pH levels tested. The

water without aluminum solids was used as the control in this study and is referred to as pitting water throughout this chapter (Table 3 – 1).

Table 3 – 1: Pitting Water Recipe

<i>Chemicals Added</i>	CaCl ₂ *2H ₂ O	CaSO ₄ *2H ₂ O	NaHCO ₃	Cl ₂	pH
<i>Concentration (mg/L)</i>	41.296	25	56.85	4.0	9.2

The water for each condition was housed in a 94 L plastic reservoir and was continuously circulated through a pipe network at 4.5 fps by an external, magnetic drive, centrifugal pump (Figure 3 – 2). A plastic lid was in full contact with the water surface to inhibit air and carbon dioxide exchange between the water and ambient atmosphere in order to maintain a relatively constant alkalinity throughout the experiment. Chemical feed pumps delivering a highly concentrated solution of sodium hypochlorite and sodium hydroxide were used to keep the chlorine and pH levels at their respective targets. The water was changed every week for the first eight weeks of the experiment, after which the water was changed either once a week, once every two weeks, or once every three weeks based upon chloride increase in the bulk water.

The base setup was comprised of ¾” diameter plumbing materials consisting of an initial 1’ section of CPVC pipe, followed a CPVC tee with a 2” section of type M copper pipe located downward and out of flow, three 1’ sections of type M copper pipe, and various lengths of vinyl tubing and CPVC fittings to complete the recirculating loop (Figure 3 – 2). The 2” section of out of flow copper was oriented downwards and was plugged with a silicone stopper that could easily be removed for sampling the localized water. This out of flow section of copper is referred to as a copper tee throughout this chapter. The 1’ CPVC section located before the copper was used in order to normalize entry effects for the entrance of the first copper pipe.

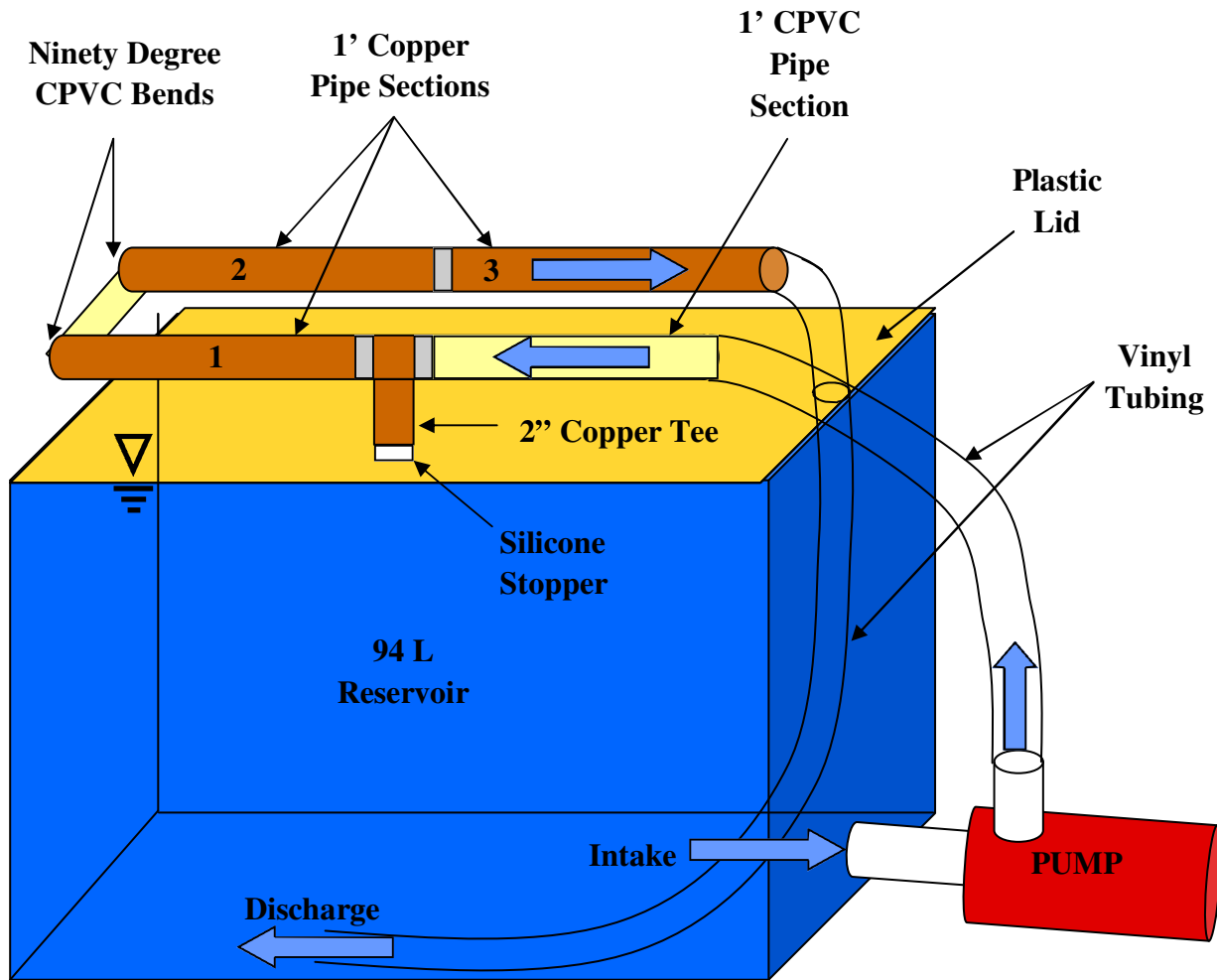


Figure 3 – 2: Control Experimental Setup

The pipe networks designed in this experiment varied from the control in either configuration or materials for six conditions (Table 3 – 2), and the remaining fourteen conditions had the exact same pipe network design as the control (Figure 3 – 2), but varied from the control in water chemistry (Table 3 – 2). Two of the conditions tested in this study did not have an out of flow copper tee, and one of these two conditions used a submersible pump instead of the external, centrifugal pump. The submersible pump delivered a fluid velocity of 1.6 fps in the $\frac{3}{4}$ " diameter pipe loop, compared to the 4.5 fps delivered by the external centrifugal pump. Three other conditions contained a different type of metal tee, but were identical to the control in every other respect: two of these conditions had a 1.75" brass tee (one electrically connected to copper and the other electrically disconnected) and one condition had a 2.12" aged iron tee located out of

flow. One final condition had a 1.75” brass tee connected to a pipe loop that consisted only of CPVC pipe.

The remaining experimental conditions considered variations to the base water recipe (Table 3 – 1) and tested a range of parameters including coagulant solids, pH, chlorine, alkalinity, conductivity, hardness, and corrosion inhibitors (Table 3 – 2). All but one condition was conducted at high fluid velocities since prior work observed pitting propensity to increase with velocity under continuous flow (i.e. Chapter One Figure 1 – 10).

Table 3 – 2: List of Test Conditions

Condition	Description	Condition	Description
<i>Low Q</i>	Pitting Water at a Lower Fluid Velocity of 1.6 fps in a Pipe Loop without a Copper Tee	<i>Low Alkalinity</i>	Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃
<i>No Tee</i>	Pitting Water in a Pipe Loop without a Copper Tee	<i>High Alkalinity</i>	Pitting Water with an Alkalinity of 150 mg/L as CaCO ₃
<i>Control</i>	Pitting Water (pH = 9.2 Cl ₂ = 4 mg/L)	<i>Low Chlorine</i>	Pitting Water with a Total Chlorine Concentration of 0.4 mg/L
<i>Al Solids</i>	Pitting Water with 2 mg/L Al Solids	<i>Low NOM</i>	Pitting Water with 0.01 mg/L Humic Matter Added
<i>Fe Solids</i>	Pitting Water with 2 mg/L Fe Solids	<i>High NOM</i>	Pitting Water with 0.1 mg/L Humic Matter Added
<i>pH 10</i>	Pitting Water at pH 10	<i>Low Conductivity</i>	1:10 Dilution of Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃
<i>Low Silica</i>	Pitting Water with 0.5 mg/L Silica	<i>No Hardness</i>	Pitting Water with No Calcium
<i>High Silica</i>	Pitting Water with 5 mg/L Silica	<i>Brass Tee (Connected)</i>	Pitting Water in a Pipe Loop with a Brass Tee
<i>Low Phosphate</i>	Pitting Water with 0.1 mg/L Phosphate	<i>Brass Tee (Disconnected)</i>	Pitting Water in a Pipe Loop with a Brass Tee Electrically Disconnected from the Copper Pipes
<i>High Phosphate</i>	Pitting Water with 1 mg/L Phosphate	<i>Brass Tee (CPVC)</i>	Pitting Water in a Pipe Loop with a Brass Tee and CPVC Pipes
-	-	<i>Iron Tee</i>	Pitting Water in a Pipe Loop with an Aged Iron Tee

Electrochemical Measurements

All metal components of a given pipe loop, whether copper, brass, or iron, were physically isolated from each other by vinyl tubing, but electron flow was facilitated via an external copper wire. The exception was one condition with a brass tee that was electrically isolated from the three connected copper pipes, and another scenario had a brass tee connected to only CPVC pipes. By physically separating but externally connecting the individual pipe sections, corrosion currents flowing from one section to another could be measured by temporarily removing the copper wires and inserting an ammeter in line between two sections. A Fluke 189 True RMS Multimeter was used during this experiment to measure the currents flowing between the different pipe sections. Current measurements were taken once a week for each condition and always after the chlorine and pH had been manually adjusted to their respective targets.

In this study, the electrical currents were measured from one isolated pipe section to the rest of the pipes in the apparatus that remained electrically connected. In other words, the copper wire connecting one of the pipe sections to the rest of the system was removed and an ammeter was used to measure the current flowing from that one section of pipe (electrically isolated) to the rest of the electrically connected pipes. Thus, the corrosion currents presented in this work are the net flow of electrons from one metal section to the rest of the system.

For example (refer to figure 2 – 3), if the current of the tee were being measured, the external copper wire electrically connecting the tee to the three other copper pipes would be removed such that the tee would be electrically isolated (not connected to anything else). The remaining three copper pipes would still be connected by external copper wires running from pipe to pipe. An ammeter would then be placed in-line connecting the tee to the rest of the pipes such that the current flowing from the tee to the rest of the pipes passed through the ammeter for measurement. This method for measurement was used for all of the pipe sections in a network.

The sign of the currents is important since it indicates the overall activity of the different copper sections. The sign convention used in this work designates a positive current for electrons flowing from a given section of pipe to the rest of the system, indicating that that section is anodic overall. Negative currents, therefore, identify a primarily cathodic pipe section. Each of

the measured corrosion currents was normalized by the corresponding internal pipe surface area for direct comparison and is presented as current density ($\mu\text{A}/\text{cm}^2$).

Chlorine Demand

Chemical feed pumps were used to deliver a highly concentrated chlorine solution at a slow rate in order to continuously maintain the chlorine concentration of the bulk water at its target level. Chlorine concentrations were measured daily and adjustments were made to both the bulk water and feed solution in order to correct any chlorine concentrations that were off target. Chlorine demand was measured once every week by a method that considered the concentration of the feed solution and its delivery rate to the bulk water, as well as any changes in chlorine concentration of the bulk water over a given time period. Specifics related to this methodology are presented in Chapter 2.

Water Quality Measurements

Water samples were collected before and after each water change in order to track the changes in various chemical species concentrations over the time period between water changes. Samples were primarily measured by Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) following Standard Method 3125-B (APHA, AWWA, and WEF, 1998) using a Thermo Electron X-Series ICP-MS. The bulk waters were manually mixed prior to sample collection. The amount of natural organic matter was assessed via conventional total organic carbon (TOC) analytics. The pH and chlorine were measured as per Standard Methods (APHA, 1998).

RESULTS:

This following experimental work is currently ongoing with the tentative plan to continue until pinhole leaks form for each of the conditions that appear to experience pitting corrosion. With that being the case, the pipe sections could not be removed to fully evaluate pitting propensity within the copper tubes at the time of this writing. Therefore, the bulk of the findings presented herein are representative evaluations of corrosion activity or pitting propensity by indirect methods. Conventional parameters consisting of corrosion currents and chlorine demand, which have been found in prior work to be accurate indicators of corrosion activity and pitting propensity in this type of water, are presented for the first 5 months that this experiment was

conducted. The results are grouped into subsections representative of the key parameters varied. Thereafter, a discussion section will consider the implications of these findings.

Flow Conditions

Three of the twenty-one test conditions examined the effects of fluid velocity and flow configuration on pitting corrosion (Table 3 – 3). The conditions labeled Low Q and No Tee had the same configuration, used the same water chemistry, and only differed in fluid velocity. The conditions labeled No Tee and Control had the same fluid velocity, used the same water chemistry, and only varied in configuration (i.e. the presence or absence of the copper tee). The control had an out of flow copper tee while the other condition, labeled “No Tee”, did not.

Table 3 – 3: List of Flow Conditions

Condition	Water Chemistry	Fluid Velocity (fps)	Surface Area of Copper In Flow (in²)	Surface Area of Copper Out of Flow (in²)
<i>Low Q</i>	<i>Pitting Water</i>	1.6	91.7	0.0
<i>No Tee</i>	<i>Pitting Water</i>	4.5	91.7	0.0
<i>Control</i>	<i>Pitting Water</i>	4.5	91.7	5.1

Higher fluid velocity, as well as the presence of an out of flow section of copper was observed to have an impact on corrosion currents (Figure 3 – 3). A velocity of 4.5 fps increased the corrosion current for each section of pipe by three times compared to the same condition at a velocity of 1.6 fps. The presence of the out of flow copper tee had a significant impact on the adjacent, first section of copper in flow. The tee was observed to be the strongest anode, and due to close proximity to the first section of copper pipe, the heavily anodic tee appeared to force the adjacent, first section of copper pipe to become cathodic relative to the system. In contrast, the first section of copper pipe was definitively anodic when the tee section was absent from the system, which is consistent with previous experimental observations with the same water quality (Lattyak, 2007). However, it appears that the presence of the strongly anodic, out of flow, copper tee influenced the first section of copper to become cathodic when it would have otherwise been anodic.

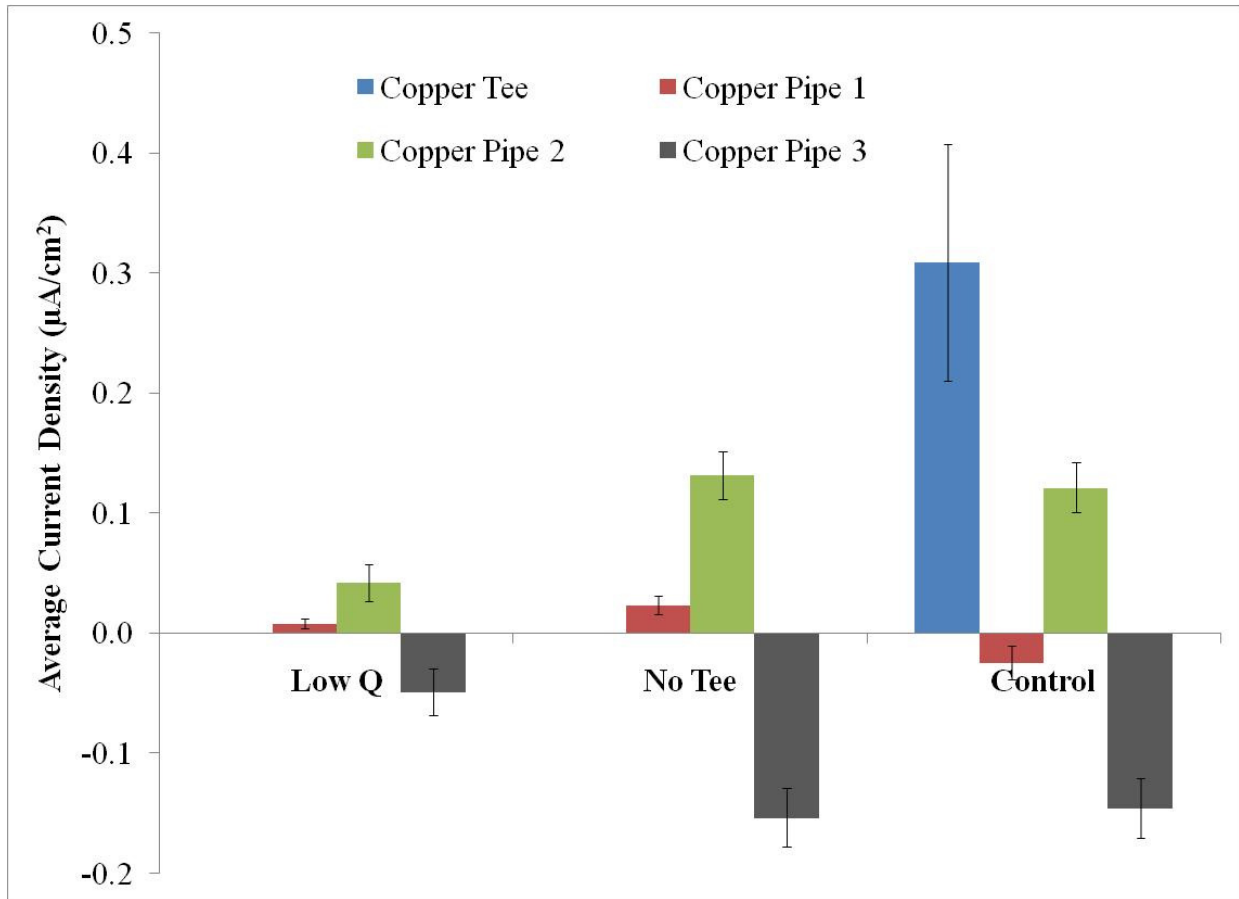


Figure 3 – 3: Current Densities for Copper Sections Under Different Flow Conditions (Week 12 – Week 20).

Error Bars Represent 95% Confidence Assuming a Normal Distribution

The two most anodic sections of copper for the control condition were the copper tee and the second copper pipe. This trend was also observed for all of the other conditions that had this flow configuration. Therefore, the corrosion current data presented in this work is the data for the out of flow tee as well as the second copper pipe since these two sections were consistently observed to be the most anodic.

Water Chemistry

The amount of corrosion activity varied substantially between the nine different water chemistries tested in this study. Each subgroup of conditions is presented below.

Coagulant Solids

The addition of coagulant solids, either aluminum or iron at the same mass concentration (2 mg/L), were observed to have an effect on the corrosion activities of the different pipe sections, especially the tee section (Figure 3-4). Aluminum solids nearly doubled the average corrosion current within the tee compared to the control water, which is not necessarily surprising considering that aluminum solids were a constituent of the original pitting water found by Marshall (2004). Yet, in comparison, iron solids reduced the corrosion currents in both the tee and second copper pipe. The effects of these coagulant solids on the anodic activity of the second copper pipe were minimal and, on average, slightly decreased the activity of this pipe compared to the control.

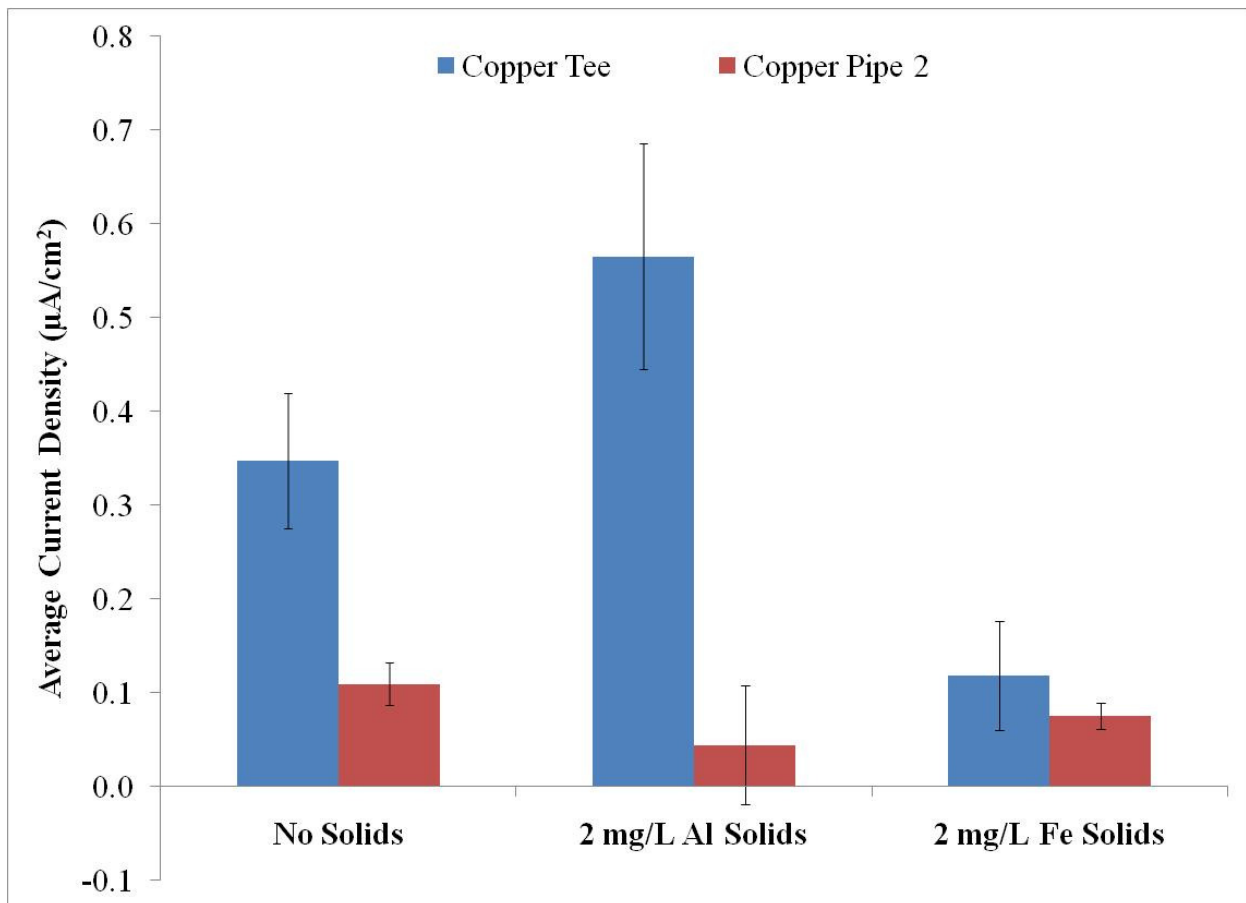


Figure 3 – 4: Corrosion Currents of the Copper Tee and Pipe 2. Error Bars Represent 95% Confidence Assuming a Normal Distribution

Alkalinity

Alkalinity was also observed to play a significant role in corrosion activity. Although the currents flowing from the copper tee to the rest of the system were statistically the same for all alkalinity levels tested, the currents flowing from pipe 2 were observed to increase substantially as alkalinity decreased (Figure 3 – 5). The chlorine demand data also showed this dramatic trend of increased corrosion activity at lower alkalinities.

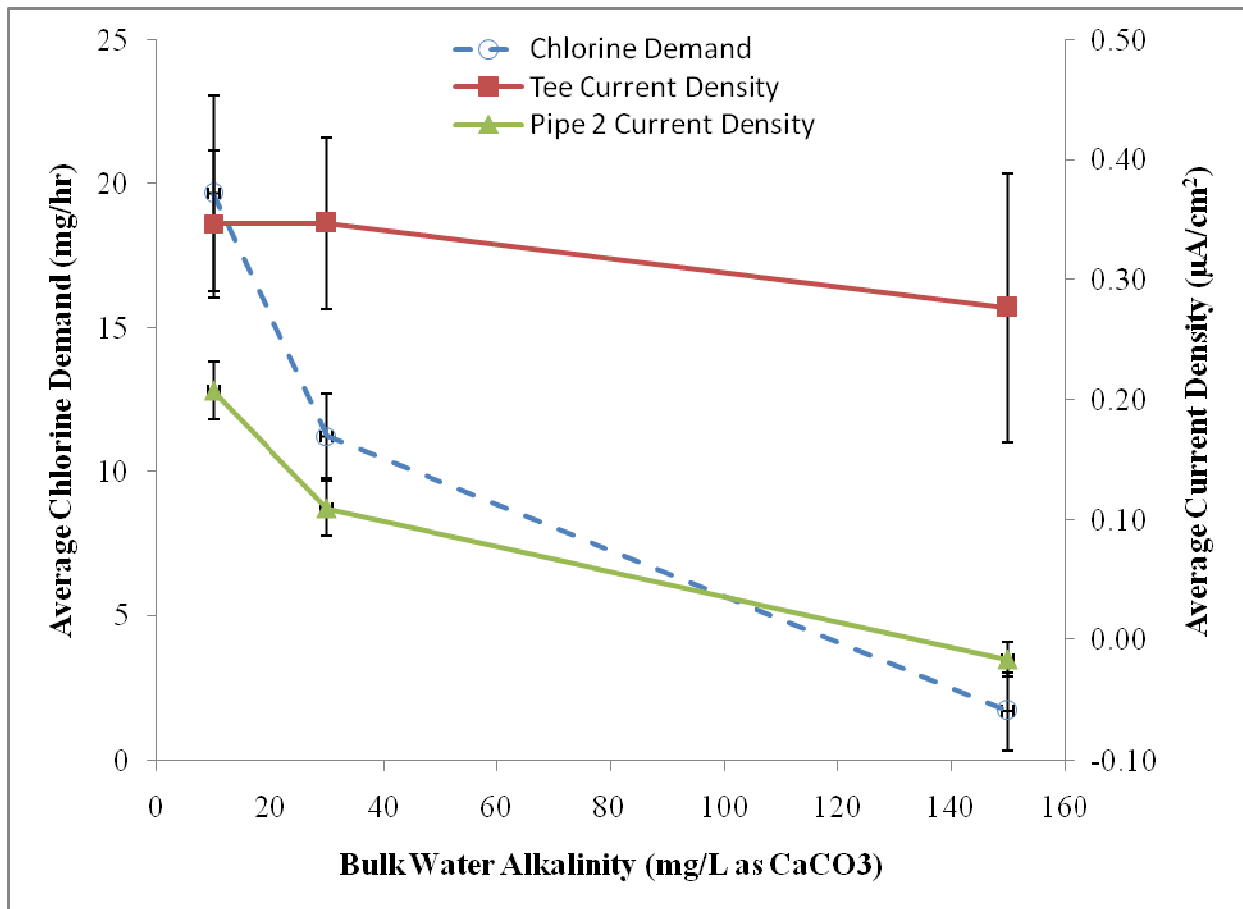


Figure 3 – 5: Chlorine Demand and Current Densities for Different Alkalinities. Error Bars Represent 95% Confidence Assuming a Normal Distribution

Chlorine and pH

Corrosion in this type of water is thought to be driven by high chlorine and high pH. Therefore, when varied, these two parameters are expected to have a significant influence upon the corrosion activity. In this study, lowering the residual chlorine concentration by a factor 10 cut

the corrosion currents by almost the same amount within the tee section (Figure 3 – 6). The apparent reduction in chlorine demand was even greater for this condition (Figure 2 – 8). The concentration of chlorine clearly exerts a dominant control on this type of pitting.

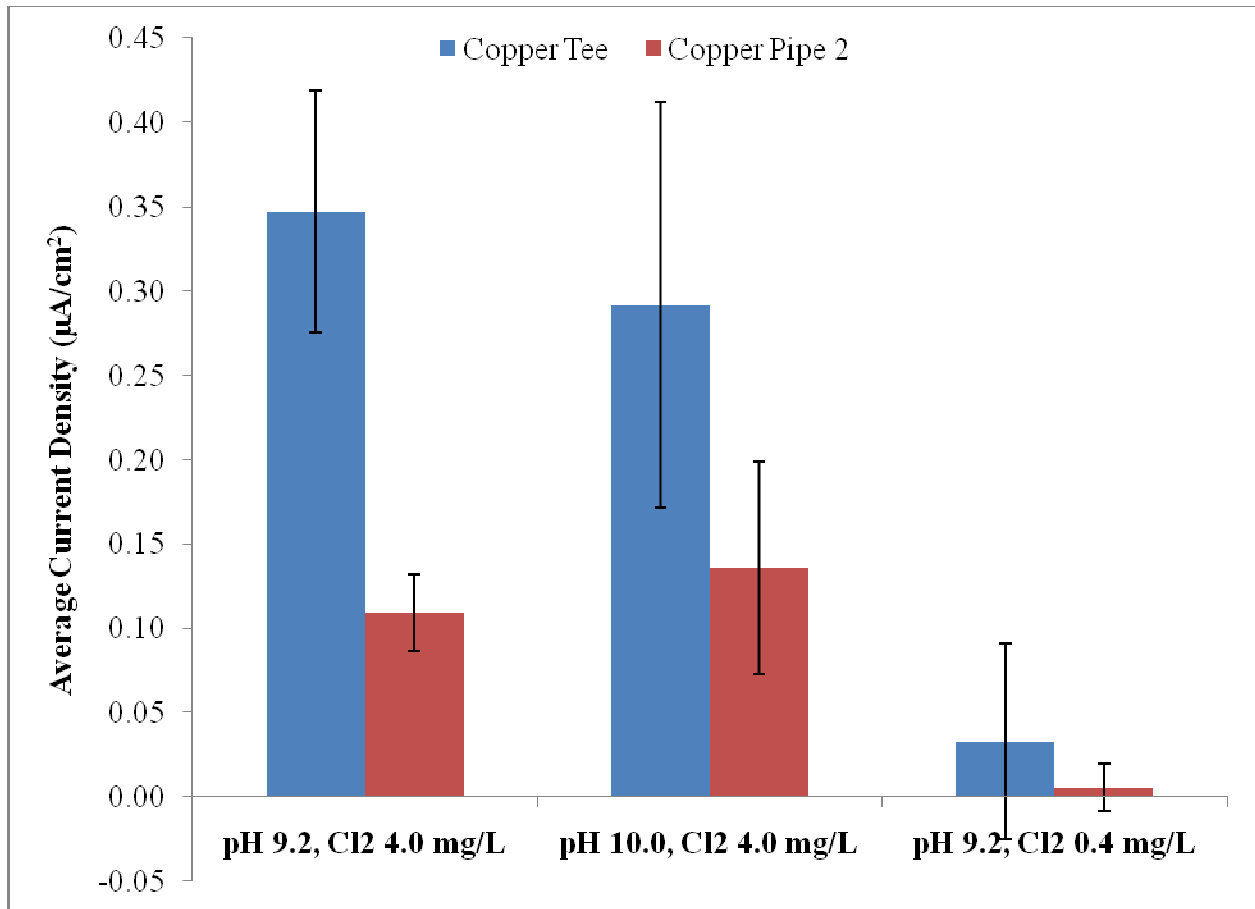


Figure 3 – 6: Corrosion Currents for Different Chlorine and pH Levels. Error Bars Represent 95% Confidence Assuming a Normal Distribution

Visual inspection of the out of flow copper tees confirmed that there had been minimal corrosion in the low chlorine water (0.4 mg/L) compared to the control condition at 4 mg/L (Figure 3 – 7). There was very little scale on the interior copper surface and there were no raised tubercle mounds in the low chlorine water. However, non-uniform corrosion, in the form of tubercles scattered across the interior of the pipe, was prevalent for the control which contained a higher chlorine concentration (Figure 3 – 7).

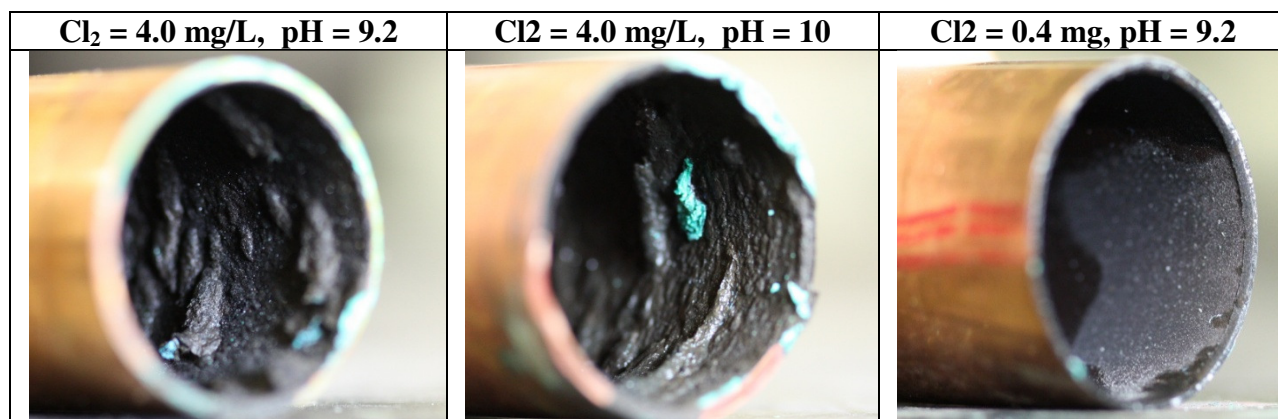


Figure 3 – 7: Scale Formation on Copper Tees for Different Chlorine and pH Levels After Four Months

Increasing the pH from 9.2 to 10 had no statistical effect upon the corrosion activity (Figure 3 – 6). In agreement with the electrochemical data, there were no visible differences in scale formation between the tees exposed to pH 9.2 and pH 10 waters (Figure 3 – 7).

Conductivity and Hardness

Representative waters with different levels of calcium hardness were evaluated, and the presence or absence of calcium hardness was observed to have a strong influence on corrosion currents. The corrosion currents for both the tee and pipe 2 nearly doubled for the condition with no calcium hardness compared to the control which had a hardness level of 42 mg/L as CaCO₃ (Figure 3 – 8). Conductivity, however, did not appear to have any impact on corrosion activity. This water had an alkalinity of 15 mg/L as CaCO₃, and when compared to the low alkalinity water (also 15 mg/L as CaCO₃), there was no statistical difference in corrosion currents between these two conditions in either the tee or the second copper pipe. This indicates that the high corrosion currents for the low conductivity condition are most likely due to low alkalinity rather than low conductivity.

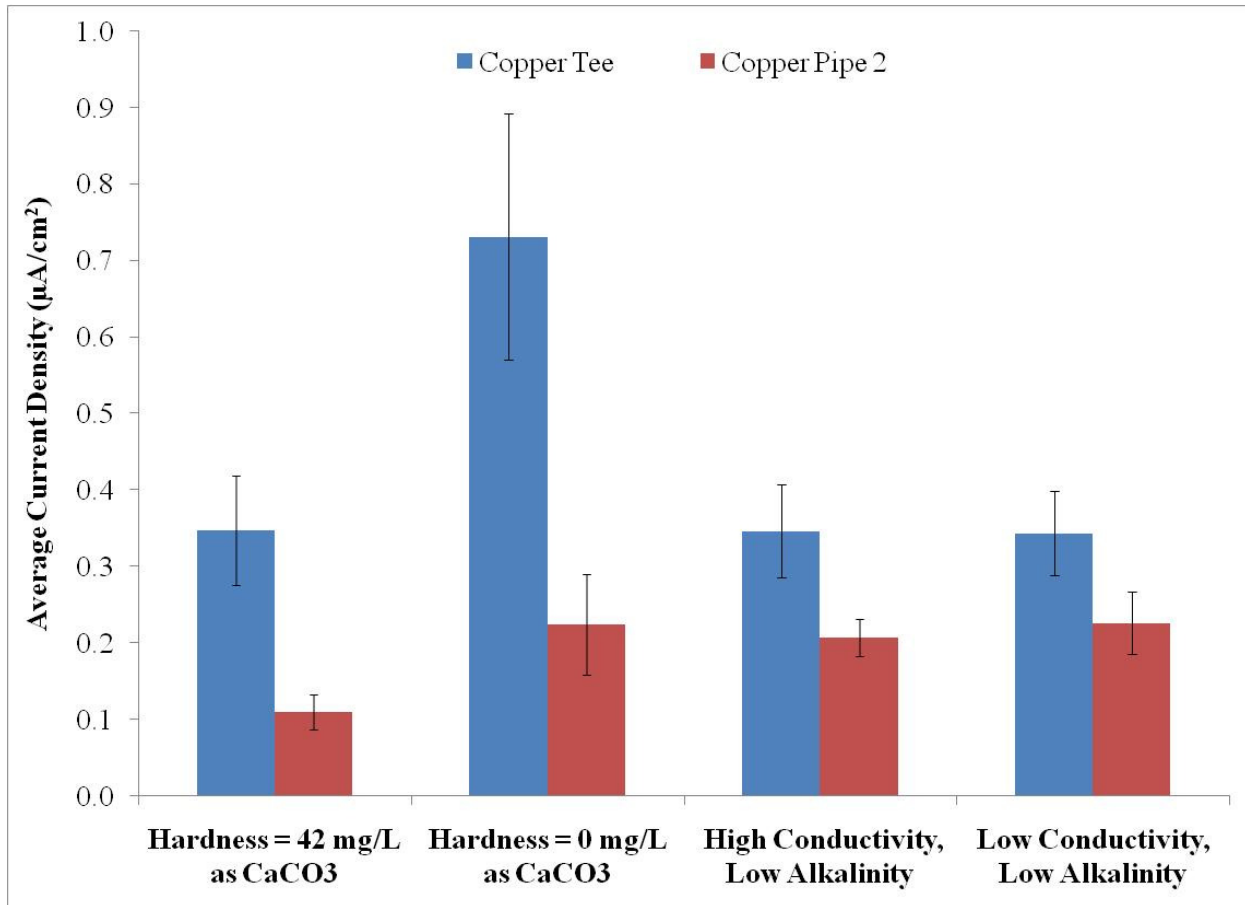


Figure 3 – 8: Electrical Currents for Different Levels of Hardness and Conductivity. Error Bars Represent 95% Confidence Assuming a Normal Distribution

Copper Release

In addition to influencing electrical currents and chlorine demand, water chemistry also influenced the extent of copper subsequently corroded and released to the bulk water (Figure 3 – 9). Copper release was observed to slightly increase for the conditions with coagulant solids compared to the control, and the most dramatic increase in copper release occurred in the two low alkalinity waters (low alkalinity and low conductivity), which had copper levels that were nearly ten times that of the control condition on average. This data further complimented the other trends, where copper leaching was significantly less in the pH 10, high alkalinity, and low chlorinated waters.

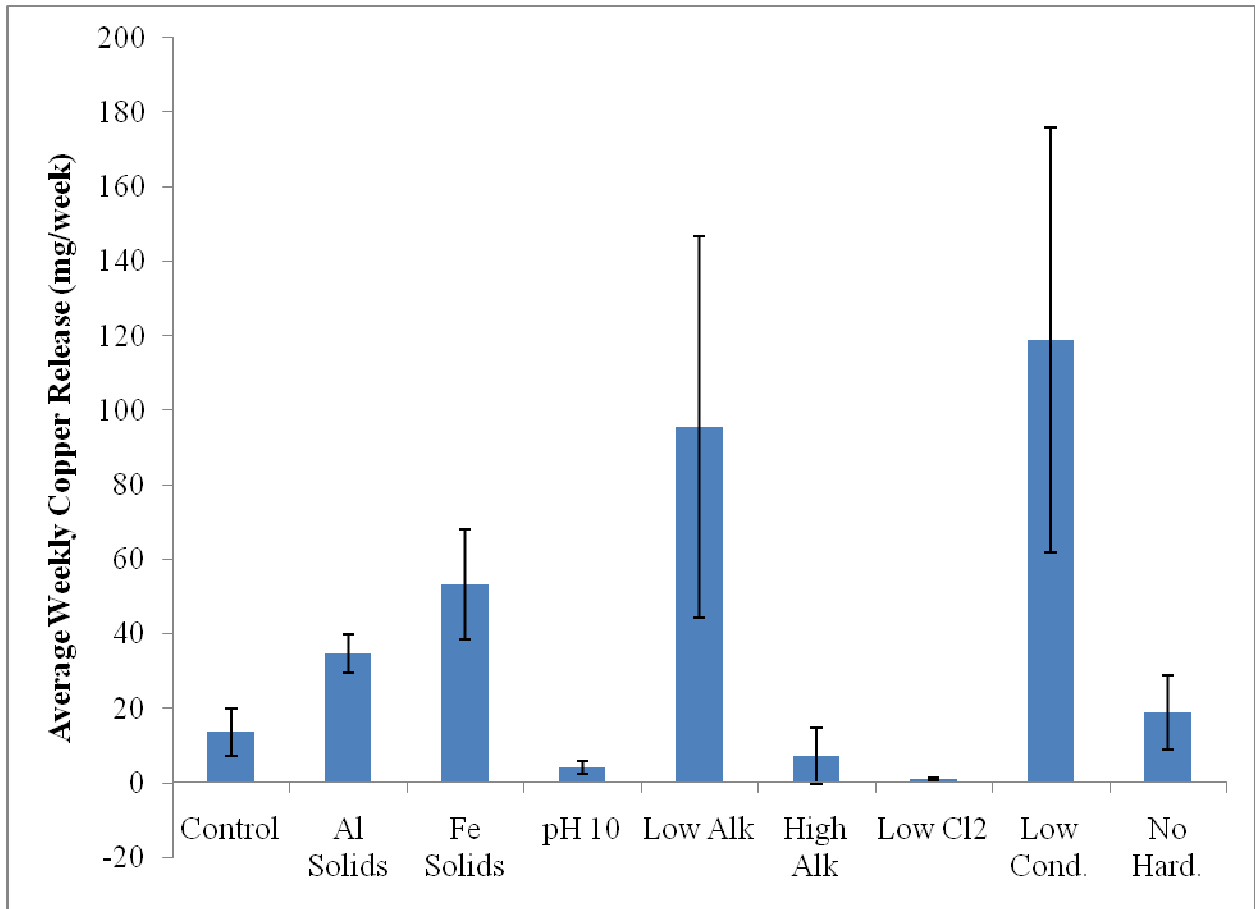


Figure 3 – 9: Copper Release for Different Water Chemistries (Week 2 – Week 8). Error Bars Represent 95% Confidence Assuming a Normal Distribution

Corrosion Inhibitors

Several possible corrosion inhibitors were tested in order to evaluate the effectiveness to mitigate copper pitting including high and low concentrations of silica, orthophosphate, and natural organic matter (NOM). In each case, increasing the concentration of the respective inhibitor appeared to significantly decrease corrosion activity; however, low inhibitor concentrations were somewhat limited in their ability to prevent the copper pipes from aggressively corroding (Figure 3 – 9). Chlorine demand was also strongly dependent on the inhibitor dosage, decreasing at higher inhibitor dosages.

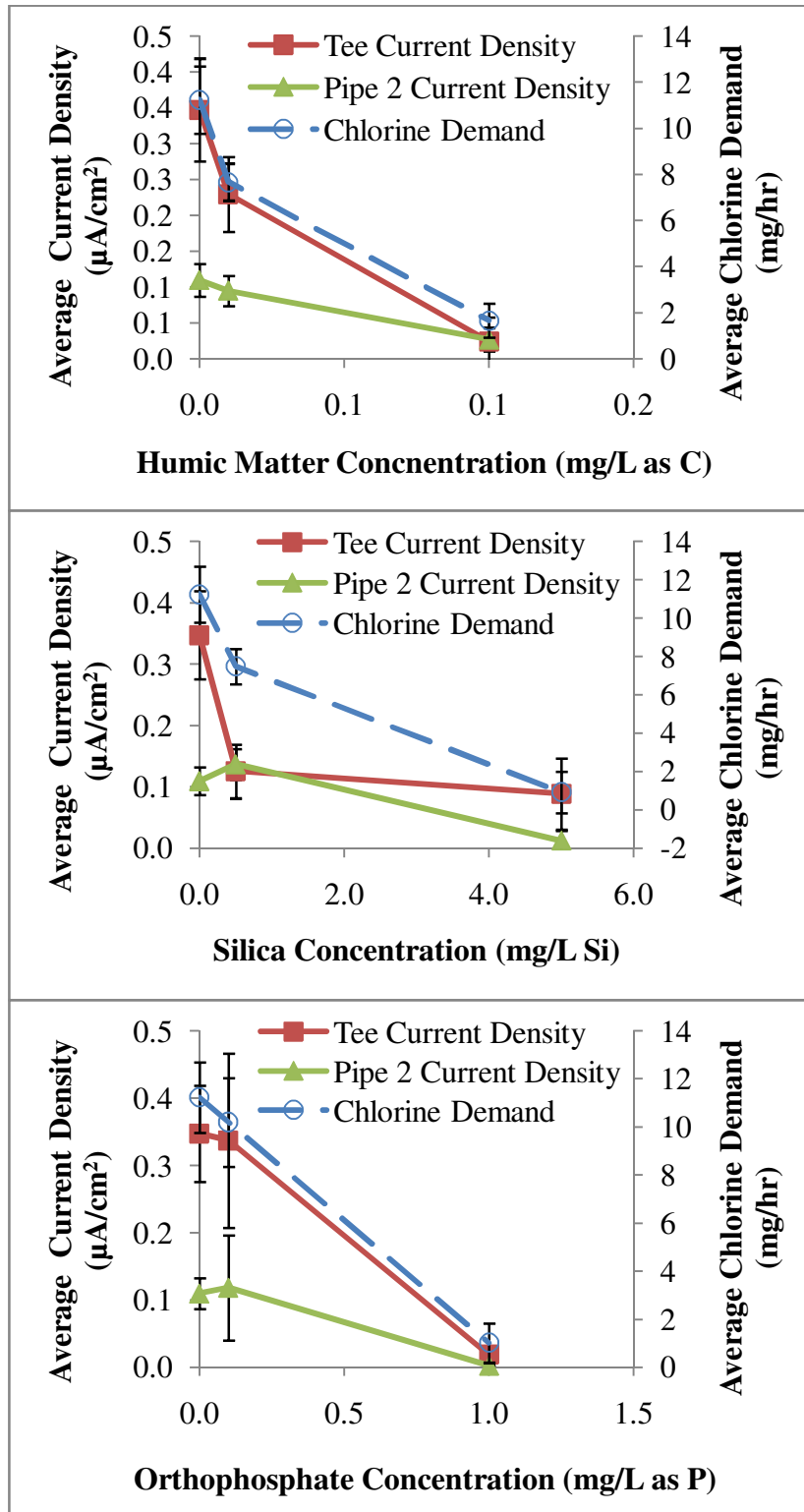


Figure 3 – 10: Effects of Various Inhibitor Concentrations on Electrical Currents and Chlorine Demand: NOM (Top), Silica (Middle), Orthophosphate (Bottom). Error Bars Represent 95% Confidence Assuming a Normal Distribution

Visual inspection of the out of flow copper tees confirmed the apparent benefits of the various inhibitors (Figure 3 – 10). Compared to the control (i.e. Figure 3 – 7, far Left), the extent and even visual appearance of the interior copper scale was fundamentally altered and improved by the addition of the inhibitors. While lower doses of the inhibitors produced minor differences compared to the control, very clear differentiation was easily observed at the higher dosage of each inhibitor. For example, higher dosages of silica and orthophosphate effectively caused the formation of substantially less scale that also was bright blue in color. Additionally, the presence of pitting tubercles were either less or all together absent.

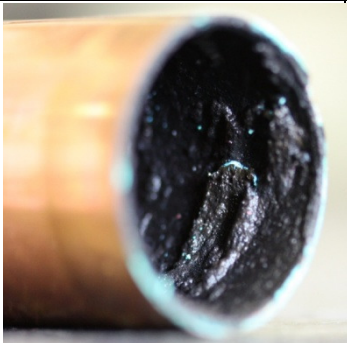


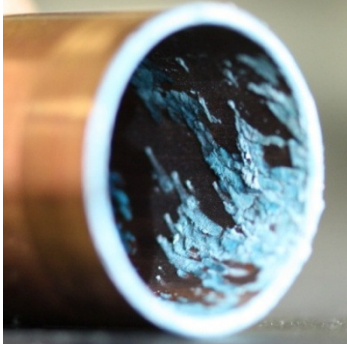


Dose	Silica	Orthophosphate	Natural Organic Matter
<i>Low</i>			
<i>High</i>			

Figure 3 – 11: Scale Formation in Copper Tees for Various Inhibitor Concentrations After Four Months

It appears that the high NOM condition (0.1 mg/L humic matter) was not a high enough concentration to provide the desired protection against aggressive pitting. Although it significantly decreased both chlorine demand and corrosion currents, visual inspection would suggest that higher doses of this inhibitor (greater than 0.1 mg/L humic matter) would be necessary in order to provide more adequate protection of the copper pipes. Nevertheless, each

of the inhibitors tested appear to protect the copper pipes from aggressive pitting corrosion in this type of water when dosed at sufficient concentrations.

Galvanic Connections

At the start of this study, it was theorized that the galvanic connection of copper to a small amount of less noble metal plumbing material (e.g. brass or iron) could protect large lengths of copper from corroding. Anecdotal evidence had suggested that large lengths of copper pipe in electrical connection with an iron service main could protect copper from corroding even in aggressive waters. To test this theory, several experiments were run with copper pipes connected to short lengths of either brass or iron pipe at the out of flow location (tee).

Each of the less noble tees appeared to be highly anodic and actively corroding which is not surprising given that both brass and iron are less noble than copper on the galvanic series (Figure 3 – 11). Although the presence of such a strong anode near the first section of copper was observed to make that first section of copper more cathodic on average, the electrochemical data showed no significant protection of the copper pipes for the condition with electrical connection to iron (Iron Tee) or electrically isolated brass (Brass Tee Disconnected). In fact, pinhole leaks occurred in these two conditions prior to leaks observed in the control condition (i.e. same water quality), albeit leaks were only several weeks apart (Table 3 – 4).

While the brass and iron in these two conditions may have provided some protection, especially to the adjacent pipe section (i.e. copper pipe 1), these less noble metals clearly did not fully protect the entire pipe network, which was not excessively large in this apparatus. The only condition that appeared to possibly be protecting the in-flow copper pipes from corrosion was the condition with electrically connected brass (Brass Tee Connected), as this condition was observed to decrease the corrosion currents of the second and third copper pipe, by a factor of 2 on average (Figure 3 – 11).

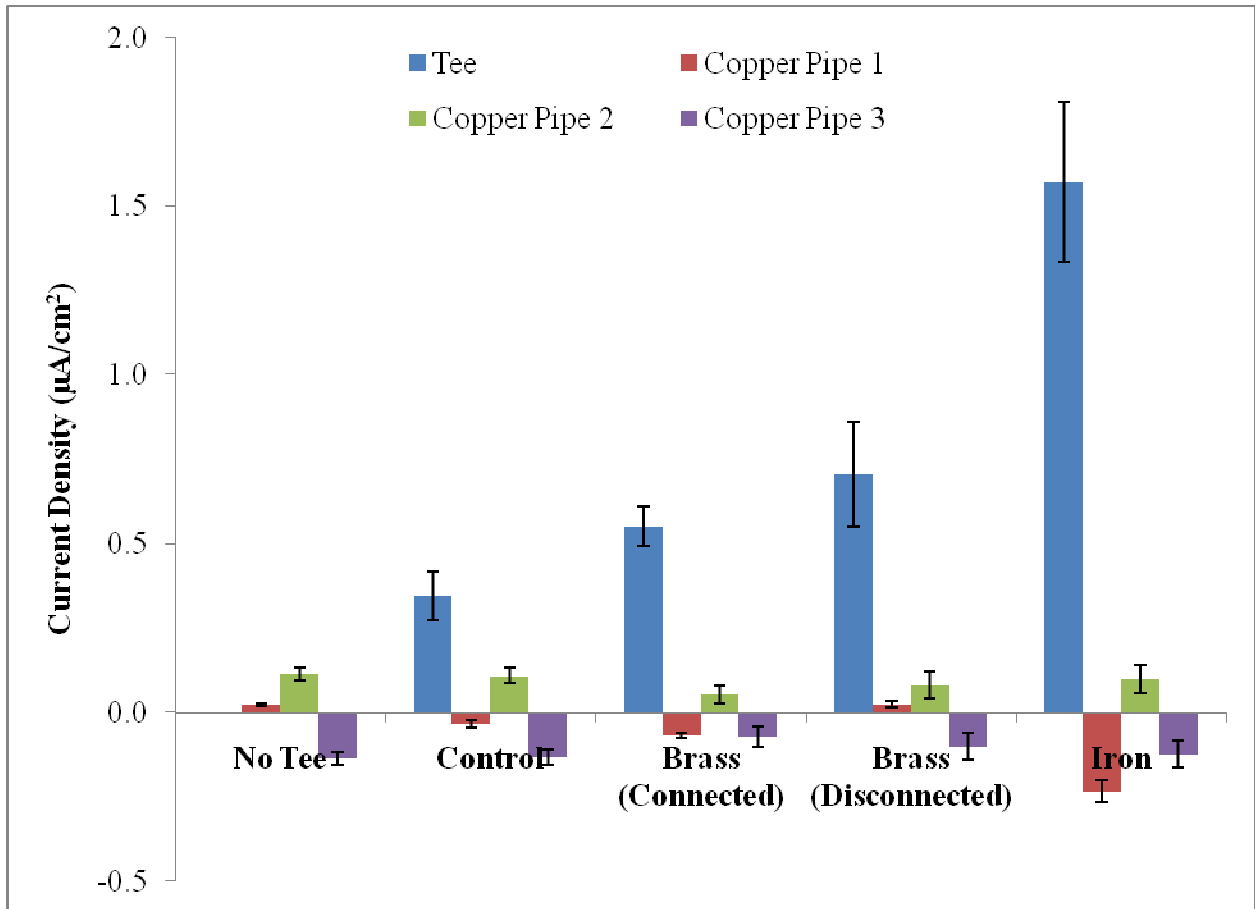


Figure 3 – 12: Effects of Galvanic Connections on Corrosion Currents. Error Bars Represent 95% Confidence Assuming a Normal Distribution

DISCUSSION:

A large number of experimental conditions were considered in this copper pitting study. The four parameters that were observed to have the strongest effect on pitting in this type of water were natural organic matter, silica, orthophosphate, and alkalinity. These four parameters at high enough concentrations were observed to dramatically reduce corrosion activity (Figure 3 – 5, Figure 3 – 9). Furthermore, the condition with a low alkalinity (15 mg/L as CaCO₃) was found to significantly increase the aggressiveness of this water (Figure 3 – 5).

A factor driving this particular type of pitting is clearly the amount of available chlorine, since corrosion activity was substantially reduced at lower levels of free chlorine (Figures 3 – 6 and 3 – 7). Therefore, it appears that this pitting water is cathodically limited, and when more free chlorine is available, the cathodic half reaction and the overall extent of corrosion are increased

accordingly. Given the strong relationship between chlorine reactions and pitting corrosion observed in this and prior work (Murray-Ramos, 2006), chlorine demand is believed to be a good indicator of the extent of corrosion activity in premise plumbing systems with this type of water. While chlorine demand definitely would not be a good surrogate for all water systems and other types of pitting, this simple measurement was a useful tool for quantifying corrosion activity in this study.

Another factor observed to influence corrosion activity in this study was the presence of aluminum solids. The pipes were visually inspected after four months of testing and dramatic differences were observed between the pitting water with and without aluminum solids. The condition with aluminum solids had a very thick scale as well as large, pronounced tubercles throughout the pipe that greatly reduced the cross section for fluid flow. In contrast, the condition without aluminum solids had significantly less scale and much smaller tubercles across the surface of the pipes suggesting that this pitting water is more aggressive with aluminum solids than without. Previous research had identified aluminum solids as being a vital constituent for pit propagation in this water at lower pH levels (Rushing 2002, Marshall 2004), but the mechanism by which aluminum solids enhance pitting in this water is still unknown. The observations from this study indicate that, although aluminum solids are not vital for pit propagation as observed for lower pHs, they do enhance pitting propensity in this water at a high pH of 9.2.

Differential Water Chemistry Theory

When the original experimental design was conceived, the tee section with stagnant water was thought to possibly experience a greater degree of pitting. In addition to being exposed to the same aggressive pitting water, the concentration of certain water quality parameters was thought to further increase the existing pitting propensity compared to the pipes subjected to continuous flow and “fresh” water. As corrosion occurred within this tee, the corresponding abundance of positive copper cations would be expected to draw counterbalancing anions (chloride, sulfate, etc.) into the tee. The imbalance of chlorine and chloride concentrations between the “fresh” flowing water and stagnant water within the tee, along with potentially much lower pH's in the tee (due to reactions between hydroxide and corresponding copper ions) may increase pitting via

concentration cells (Coyne, 2009). Furthermore, the orientation of this stagnant section allowed for an increasingly more dense solution to be better retained within the tee section.

The stagnant water in the tee section was exclusively analyzed periodically during this study. This sampling confirmed the theory of the development of a differential water chemistry between the flowing and stagnant sections for most of the conditions tested. For example, most conditions had a pH that was 0.4 log units less than that of the bulk water, a chloride mass concentration that was about 15% greater than the bulk water on average, and a chlorine concentration that was about four times less than that of the bulk water.

The copper concentration in the stagnant water was about one thousand times the copper concentration in the bulk water for most conditions. This abundance of copper cations in the stagnant water attracted counterbalancing anions such as chloride and sulfate in the flowing water (Figure 3 – 11). The levels of sulfate buildup were observed to increase for conditions with higher levels of copper in the stagnant water. Thus, it appears that more actively corroding systems developed higher copper concentrations in the stagnant section, which in turn attracted more counterbalancing anions such as sulfate.

In congruence with the initial hypothesis and other analytical water quality measurements, the electrochemical data indicated that the tees consistently had the highest corrosion current density ($\mu\text{A}/\text{cm}^2$) and more anodic activity than the other pipes in continuous flow. Consequently, the copper tees were expected to be the first to fail with pinhole leaks.

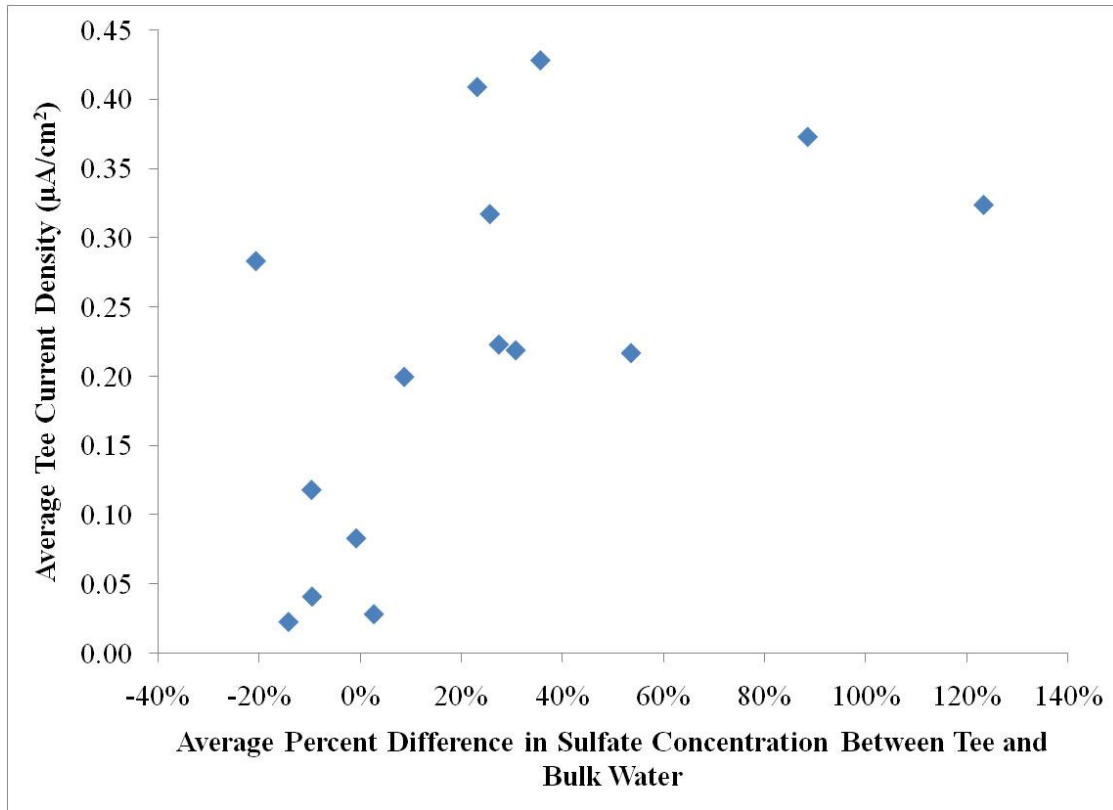


Figure 3 – 13: Effects of Copper Concentration on Sulfate Migration to the Stagnant Tee Water

Pinhole Leaks

At the time that this work was written, nine of the test conditions had formed fully penetrating pinhole leaks (Table 3 – 4). However, for all of the conditions with pinhole leaks, none of the leaks developed on the out of flow copper tee. Also, the condition without the copper tee (No tee) was observed to form its first pinhole leak very near the time when the control formed its first leak (Table 3 – 4). This may indicate that the effects of the differential water chemistry that developed between the out of flow and in-flow sections does not accelerate this type of corrosion when subject to such an aggressive pitting water. However, conclusions could not be reached at the time of this writing since the pipes could not be physically examined for pitting severity.

Table 3 – 4: List of Pinhole Leaks at Seven Months

Condition	Description	Time To First Pinhole Leak (weeks)	Number of Pinholes			
			Tee	Pipe 1	Pipe 2	Pipe 3
<i>Iron Tee</i>	Pitting Water in a Pipe Loop with an Aged Iron Tee	21.5	-	-	2	-
<i>No Hardness</i>	Pitting Water with No Calcium	21.5	-	-	1	-
<i>Low Alkalinity</i>	Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃	24.5	-	1	1	1
<i>Brass Tee (Disconnected)</i>	Pitting Water in a Pipe Loop with a Brass Tee Electrically Disconnected from the Copper Pipes	26.5	-	2	2	2
<i>Low NOM</i>	Pitting Water with 0.01 mg/L Humic Matter	27.5	-	-	1	-
<i>Al Solids</i>	Pitting Water with 2 mg/L Al Solids	28.5	-	1	1	-
<i>High pH</i>	Pitting Water at pH 10	29.5	-	-	-	1
<i>Control</i>	Pitting Water	29.5	-	-	-	1
<i>No Tee</i>	Pitting Water in a Pipe Loop without a Copper Tee	30	-	1	-	-

It is interesting to note that the pipe that formed the most pinhole leaks for the conditions tested was the second copper pipe. This pipe was observed to be the strongest anode in the flow configuration other than the out of flow tee. The currents do indicate that a significant amount of corrosion occurred on the copper tees and, although it appears that much of the corrosion activity at this out of flow location was not due to pitting, the extent of corrosion has yet to be determined by wall thinning and weight loss measurements. While it is clear that there are some

limitations to the conventional corrosion current measurements in predicting pitting corrosion, the data can be used to provide valuable insight into the differences in corrosion activity for different water chemistries and other system conditions.

Since this study is still ongoing, the aggressiveness of each condition was summarized using all experimental data (Table 3 – 5). Other implications of this work are discussed below.

Corrosion Measurements

While the definitive method for quantifying pitting propensity is measuring the extent of pitting (pits/cm² and pit depth) on exposed copper tubes, there is a need for indirect methods since the test durations necessary to form sufficient pits are both lengthy and expensive. Although the independent methods for measuring corrosion activity (corrosion currents, chlorine demand, copper release) did not necessarily agree all of the time, there was a strong positive correlation between the three parameters. On average, systems with high corrosion currents also had high chlorine demand (Figure 3 – 13), which is not surprising since this pitting system was driven by the cathodic corrosion reaction. Chlorine consumption or demand conceivably would have certain limitations as a surrogate especially for other types of corrosion such as microbial induced pitting, where higher chlorine levels should help mitigate corrosion.

Designing a corrosion study in which pipe sections are physically separated, but still electrically connected externally provides another method of quantifying corrosion activity via corrosion current measurements. These measurements indicate only the overall average activity for a given pipe section. For example, while pipe three in this apparatus was consistently cathodic on average, pinhole leaks were still observed to form on these pipes. In other words, even though pipe three is the strongest cathode on average, there are still anodic areas (pits) on the pipe that can develop into pinhole leaks.

While corrosion currents do provide some useful information, their limitations were observed in this work. The strongest anode, as assessed via corrosion currents, was consistently the copper tee, but no pinhole leaks occurred on this section at the time of this writing. Therefore, corrosion currents as collected in this study provide some insight into the activity of the system, but do not truly reflect localized activity of a given pit.

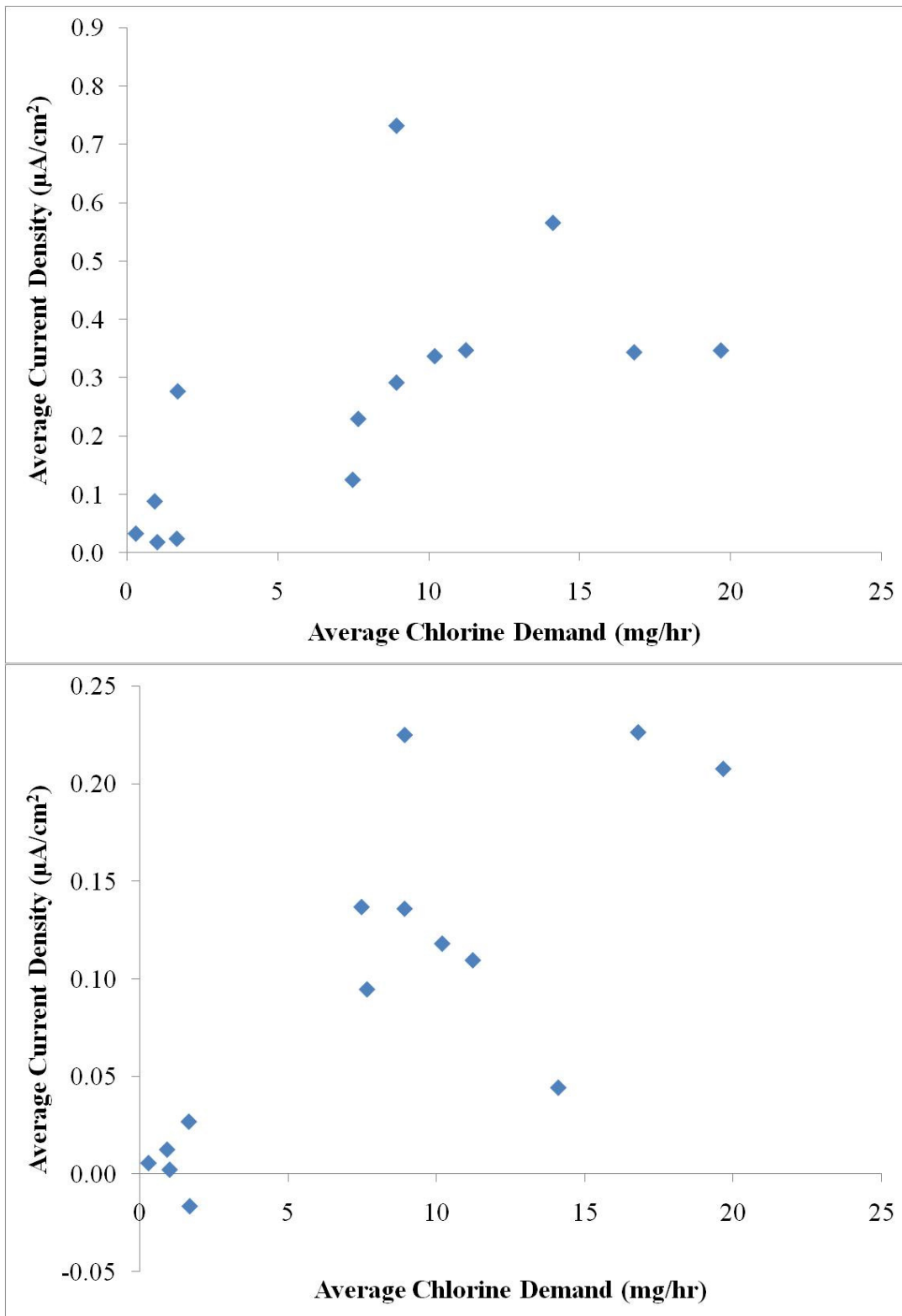


Figure 3 – 14: Correlation Between Electrical Current and Chlorine Demand Data: Tee (Top) and Pipe 2 (Bottom)

Lastly, copper leaching was only moderately successful for indicating pitting (Figure 3 – 14). This finding is quite common since pitting is very localized and does not necessarily correspond to a sufficient surface area or volume of actual copper destruction (corrosion). Furthermore, bulk copper levels would be heavily dependent on how much scale remained attached to the interior pipe wall, since sloughing of uniform scales would tend to elevate copper levels but not be reflective of pitting propensity.

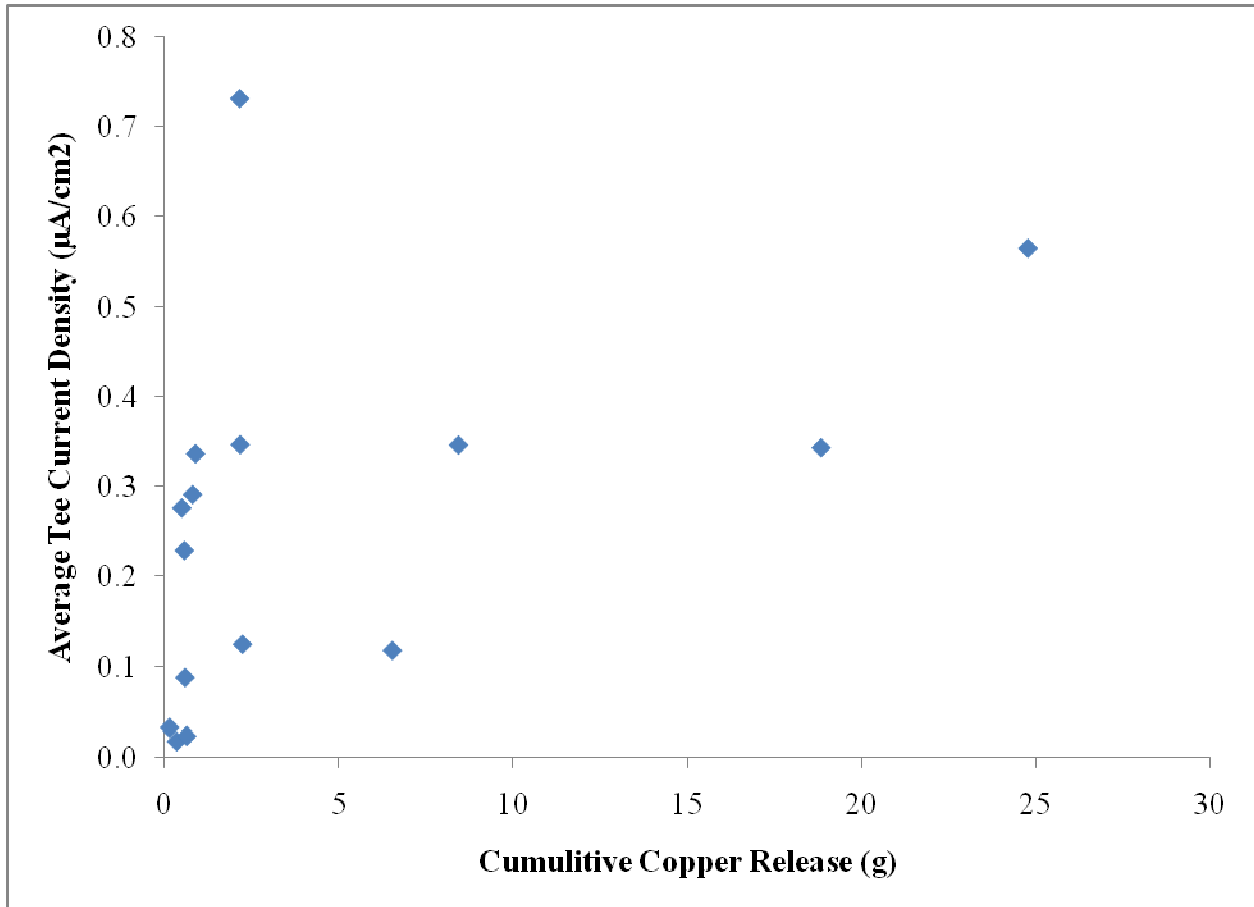


Figure 3 – 15: Correlation Between Tee Currents and Copper Release

In summary, direct measurements of real pits still remains to be the preferred measurement. Under some situations, indirect corrosion surrogates can provide additional insight into the nature of the corrosion activity and could even be useful for comparing activity for identical system setups. However, there are limitations associated with comparing indirect measurements between dissimilar systems or experiments.

CONCLUSIONS:

This study was still ongoing at the time of this writing and, as such, only preliminary results are presented. However, significant differences in corrosion activity between the different conditions tested were observed. An assessment summary for all of the different conditions tested is given in Table 3 – 5 below:

Table 3 – 5: Assessment of All Test Conditions

FLOW CONDITIONS					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>Low Velocity, No Tee</i>	Pitting Water at a Lower Fluid Velocity of 1.6 fps in a Pipe Loop without a Copper Tee	Low, ($P_2 = 0.02 \mu\text{A}/\text{cm}^2$)	Low (2.6 mg/hr)	Low, (29 mg/week)	Aggressive Water Chemistry
<i>High Velocity, No Tee</i>	Pitting Water at a Fluid Velocity of 4.5 fps in a Pipe Loop without a Copper Tee	High, ($P_2 = 0.12 \mu\text{A}/\text{cm}^2$)	Moderate (8.2 mg/hr)	Low, (69 mg/week)	Aggressive Water Chemistry, Significantly More Aggressive at Higher Velocities
<i>High Velocity, With a Tee</i>	Pitting Water at a Fluid Velocity of 4.5 fps in a Pipe Loop with a Copper Tee	High, (Tee = $0.35 \mu\text{A}/\text{cm}^2$, $P_2 = 0.11 \mu\text{A}/\text{cm}^2$)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive with Out of Flow Tee

Table 3 – 5 (Continued): Assessment of All Test Conditions

<i>COAGULANT SOLIDS</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>No Solids</i>	Pitting Water	High, (Tee = 0.35 $\mu\text{A}/\text{cm}^2$, $P_2 =$ 0.11 $\mu\text{A}/\text{cm}^2$)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive with Out of Flow Tee
<i>Al Solids</i>	Pitting Water with 2 mg/L Al Solids	High, (Tee = 0.57 $\mu\text{A}/\text{cm}^2$, $P_2 =$ 0.04 $\mu\text{A}/\text{cm}^2$)	High (14.1 mg/hr)	Extremely High, (1,450 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive with Al Solids Compared to No Solids
<i>Fe Solids</i>	Pitting Water with 2 mg/L Fe Solids	Moderate, (Tee = 0.12 $\mu\text{A}/\text{cm}^2$, $P_2 =$ 0.08 $\mu\text{A}/\text{cm}^2$)	Extremely High (44.8 mg/hr)	High, (544 mg/week)	Aggressive Water Chemistry, Slightly Less Aggressive with Fe Solids Compared to Al Solids
<i>CHLORINE and pH</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>Cl₂ = 4.0 mg/L, pH = 9.2</i>	Pitting Water	High, (Tee = 0.35 $\mu\text{A}/\text{cm}^2$, $P_2 =$ 0.11 $\mu\text{A}/\text{cm}^2$)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive with Out of Flow Tee
<i>Cl₂ = 4.0 mg/L, pH = 10</i>	Pitting Water at pH 10	High, (Tee = 0.29 $\mu\text{A}/\text{cm}^2$, $P_2 =$ 0.14 $\mu\text{A}/\text{cm}^2$)	Moderate (8.9 mg/hr)	Low, (53 mg/week)	Aggressive Water Chemistry, Slightly Less Aggressive at pH 10 compared to pH 9.2
<i>Cl₂ = 0.4 mg/L, pH = 9.2</i>	Pitting Water with a Total Chlorine Concentration of 0.4 mg/L	Extremely Low, (Tee = 0.03 $\mu\text{A}/\text{cm}^2$, $P_2 =$ 0.01 $\mu\text{A}/\text{cm}^2$)	Extremely Low (0.3 mg/hr)	Extremely Low, (11 mg/week)	Non-Aggressive Water Chemistry, Significantly Less Aggressive at Lower Chlorine Concentrations

Table 3 – 5 (Continued): Assessment of All Test Conditions

<i>ALKALINITY</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>Low Alkalinity</i>	Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃	High, (Tee = 0.35 μ A/cm ² , P ₂ = 0.21 μ A/cm ²)	High (19.7 mg/hr)	High, (562 mg/week)	Aggressive Water Chemistry, Significantly More Aggressive at Lower Alkalinities
<i>Moderate Alkalinity</i>	Pitting Water with an Alkalinity of 30 mg/L as CaCO ₃	High, (Tee = 0.35 μ A/cm ² , P ₂ = 0.11 μ A/cm ²)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive with Out of Flow Tee
<i>High Alkalinity</i>	Pitting Water with an Alkalinity of 150 mg/L as CaCO ₃	Moderate, (Tee = 0.28 μ A/cm ² , P ₂ = -0.02 μ A/cm ²)	Low (1.7 mg/hr)	Low, (38 mg/week)	Non-Aggressive Water Chemistry, Significantly Less Aggressive at Higher Alkalinities
<i>CONDUCTIVITY</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>High Conductivity, Low Alkalinity</i>	Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃	High, (Tee = 0.35 μ A/cm ² , P ₂ = 0.21 μ A/cm ²)	High (19.7 mg/hr)	High, (562 mg/week)	Aggressive Water Chemistry, Significantly More Aggressive at Lower Alkalinities
<i>Low Conductivity, Low Alkalinity</i>	1:10 Dilution of Pitting Water with an Alkalinity of 15 mg/L as CaCO ₃	High, (Tee = 0.34 μ A/cm ² , P ₂ = 0.23 μ A/cm ²)	High (16.8 mg/hr)	Extremely High, (1,255 mg/week)	Aggressive Water Chemistry, No More Aggressive at Lower Conductivities
<i>HARDNESS</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>Moderate Hardness</i>	Pitting Water with a Calcium Hardness of 42 mg/L as CaCO ₃	High, (Tee = 0.35 μ A/cm ² , P ₂ = 0.11 μ A/cm ²)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry
<i>No Hardness</i>	Pitting Water with a Calcium Hardness of 0 mg/L as CaCO ₃	Extremely High, (Tee = 0.73 μ A/cm ² , P ₂ = 0.23 μ A/cm ²)	Moderate (8.9 mg/hr)	Moderate, (154 mg/week)	Aggressive Water Chemistry, May Be More Aggressive at Lower Hardness Levels

Table 3 – 5 (Continued): Assessment of All Test Conditions

<i>CORROSION INHIBITORS</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>No Inhibitor</i>	Pitting Water	High, ($T_{ee} = 0.35 \mu A/cm^2$, $P_2 = 0.11 \mu A/cm^2$)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry
<i>Low Silica</i>	Pitting Water with 0.5 mg/L Silica	Low, ($T_{ee} = 0.13 \mu A/cm^2$, $P_2 = 0.14 \mu A/cm^2$)	Moderate (7.5 mg/hr)	Moderate, (149 mg/week)	Aggressive Water Chemistry, Considerably Less Aggressive with Low Amount of Silica Compared to No Silica
<i>High Silica</i>	Pitting Water with 5 mg/L Silica	Low, ($T_{ee} = 0.09 \mu A/cm^2$, $P_2 = 0.01 \mu A/cm^2$)	Extremely Low (0.9 mg/hr)	Low, (42 mg/week)	Non-Aggressive Water Chemistry, Significantly Less Aggressive with High Amount of Silica Compared to Low Silica
<i>Low Phosphate</i>	Pitting Water with 0.1 mg/L Phosphate	Low, ($T_{ee} = 0.02 \mu A/cm^2$, $P_2 = 0.12 \mu A/cm^2$)	High (10.2 mg/hr)	Low, (63 mg/week)	Aggressive Water Chemistry, Considerably Less Aggressive with Low Amount of Phosphate Compared to No Phosphate
<i>High Phosphate</i>	Pitting Water with 1 mg/L Phosphate	Extremely Low, ($T_{ee} = 0.02 \mu A/cm^2$, $P_2 = 0.00 \mu A/cm^2$)	Extremely Low (1.0 mg/hr)	Extremely Low, (25 mg/week)	Non-Aggressive Water Chemistry, Significantly Less Aggressive with High Amount of Phosphate Compared to Low Phosphate
<i>Low NOM</i>	Pitting Water with 0.01 mg/L Humic Matter	High, ($T_{ee} = 0.23 \mu A/cm^2$, $P_2 = 0.10 \mu A/cm^2$)	Moderate (7.7 mg/hr)	Low, (40 mg/week)	Aggressive Water Chemistry, Slightly Less Aggressive with Low Amount of Humic Matter
<i>High NOM</i>	Pitting Water with 0.1 mg/L Humic Matter	Extremely Low, ($T_{ee} = 0.02 \mu A/cm^2$, $P_2 = 0.03 \mu A/cm^2$)	Low (1.7 mg/hr)	Low, (49 mg/week)	Moderately Aggressive Water Chemistry, Considerably Less Aggressive with Higher Amounts of Humic Matter

Table 3 – 5 (Continued): Assessment of All Test Conditions

<i>Galvanic Connections</i>					
Condition	Description	Electrical Current	Chlorine Demand	Copper Release	Comments
<i>No Dissimilar Metals</i>	Pitting Water	High, (Tee = 0.35 $\mu\text{A}/\text{cm}^2$, $P_2 =$ $0.11 \mu\text{A}/\text{cm}^2$)	High (11.1 mg/hr)	Moderate, (144 mg/week)	Aggressive Water Chemistry
<i>Brass Tee (Connected)</i>	Pitting Water in a Pipe Loop with a Brass Tee	High, (Tee = 0.55 $\mu\text{A}/\text{cm}^2$, $P_2 =$ $0.06 \mu\text{A}/\text{cm}^2$)	Moderate (6.0 mg/hr)	Low, (89 mg/week)	Aggressive Water Chemistry, Slightly Less Aggressive with Electrical Connection to Brass Tee
<i>Brass Tee (Disconnected)</i>	Pitting Water in a Pipe Loop with a Brass Tee Electrically Disconnected from the Copper Pipes	High, (Tee = 0.71 $\mu\text{A}/\text{cm}^2$, $P_2 =$ $0.08 \mu\text{A}/\text{cm}^2$)	Moderate (7.9 mg/hr)	Low, (40 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive when Brass is not Electrically Connected to the Copper
<i>Brass Tee (CPVC)</i>	Pitting Water in a Pipe Loop with a Brass Tee and CPVC Pipes	-	Low (0.7 mg/hr)	-	Aggressive Water Chemistry, Low Chlorine Demand in Plastic Plumbing Configuration
<i>Iron Tee</i>	Pitting Water in a Pipe Loop with an Aged Iron Tee	High, (Tee = 1.57 $\mu\text{A}/\text{cm}^2$, $P_2 =$ $0.10 \mu\text{A}/\text{cm}^2$)	High (12.8 mg/hr)	Moderate, (281 mg/week)	Aggressive Water Chemistry, Slightly More Aggressive with Electrical Connection to Iron than either Brass or Copper

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APPENDIX A: SUPPLEMENTAL FIGURES

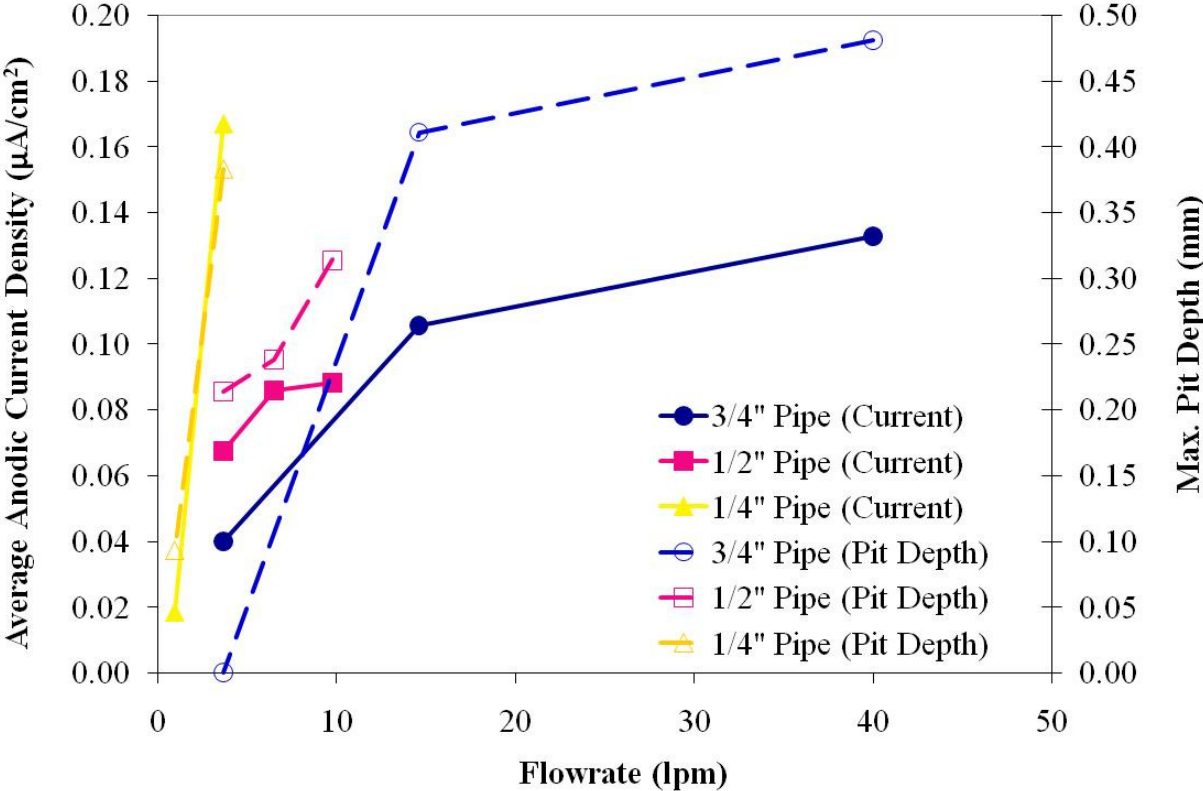


Figure A – 1: Average Anodic Current and Maximum Pit Depth as a Function of Flowrate

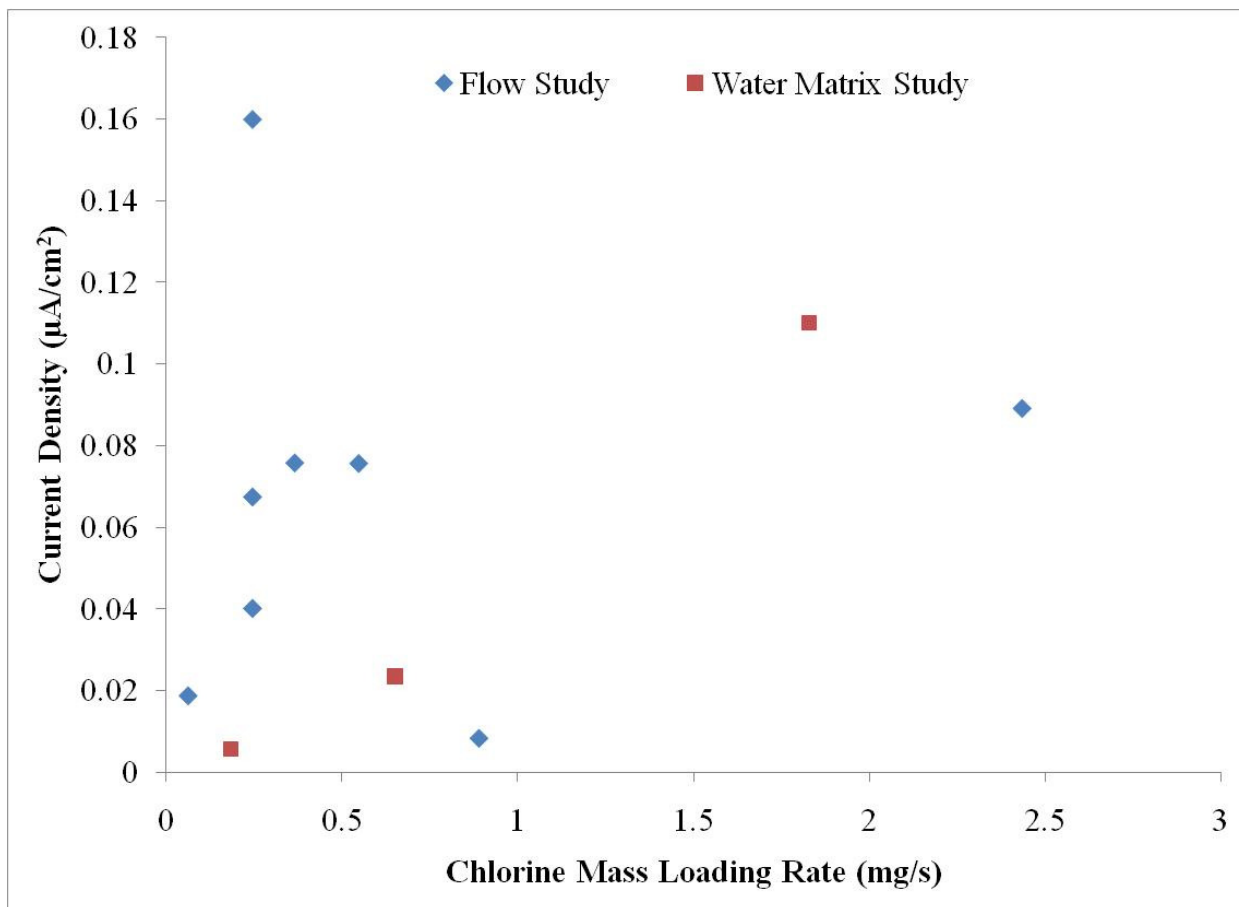


Figure A – 2: Current Density as a Function of Chlorine Mass Loading Rate

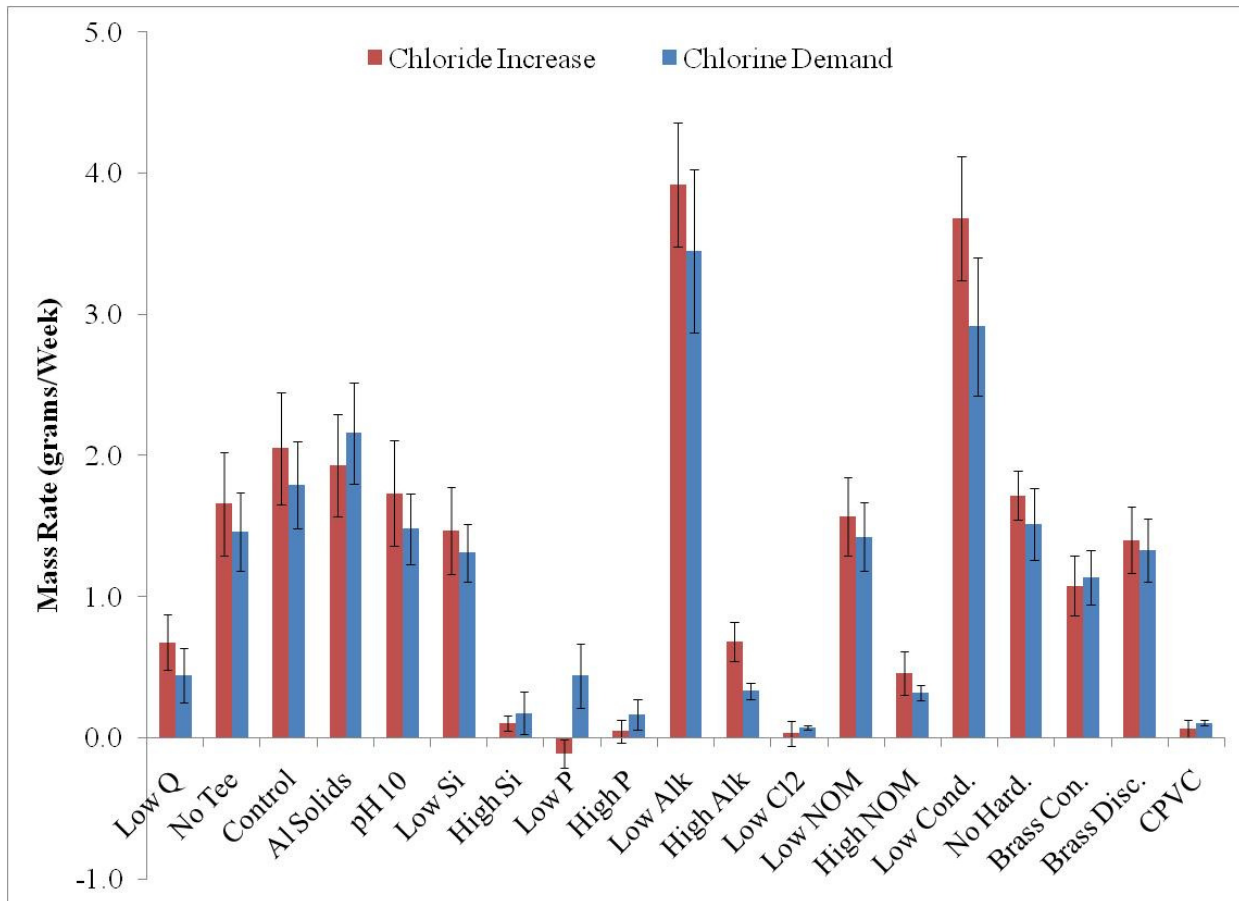


Figure A – 3: Chloride Increase vs. Chlorine Demand For Determining the Accuracy of the Chlorine Demand Formula (Chapter 2, Equation 3). Error Bars Represent 95% Confidence Assuming a Normal Distribution



Figure A – 4: Corrosion Scale in Tees After 4 Months