INITIATION, PROPAGATION, AND MITIGATION OF ALUMINUM AND CHLORINE INDUCED PITTING CORROSION

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Initiation, Propagation, and Mitigation of Aluminum and Chlorine Induced Pitting Corrosion

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ABSTRACT

Previous research by Rushing et al. (2002) identified key factors contributing to the formation of pinhole leaks in copper plumbing. These factors included high chlorine, pH levels and the presence of aluminum solids. Experiments were conducted to 1) examine the interplay between these constituents, 2) confirm that the water was aggressive enough to eat a hole through a pipe, 3) examine phosphate inhibition, and 4) try to determine the scope of this pitting problem in other distribution systems and on a national level.

The first set of experiments clearly defined the controversial trends from earlier work. At certain pH values, the presence of chlorine and aluminum solids does seem to initiate pitting corrosion of copper. Although the problem is most severe at higher pH, it is likely that long-term exposure at lower values such as pH 8 could lead to pitting. There is a concentration effect of aluminum solids at pH 9.0, in that higher concentrations cause an earlier rise in the potential for copper to corrode if sufficient chlorine is present.

The second phase of experiments are the first to prove that a potable water containing aluminum, high chlorine residual, and relatively high pH can cause pinholes in copper tube. To our knowledge this is the first time the phenomenon of pinhole leaks has been reproduced in the laboratory as it occurs in the field. It therefore proves that “aggressive water” alone can cause the problem of pitting. The role of flow, pipe orientation and hypothesized surface defects was directly examined as part of this evaluation. Pitting increased with greater water usage and for sections of straight pipe exposed to hydraulic conditions near bends. Copper pipe sections polished to a mirror like finish to remove surface defects were also severely attacked.

The role of phosphate in mitigation of copper pitting corrosion was defined in a subsequent experiment using synthesized water. Phosphates did not have an effect at pH 7.7 and were found to reduce electrochemical indications of pitting in the synthetic water at the pH of 8.3. Phosphates had lesser benefits at higher pH even in synthetic water, but overall, even at pHs as high as 10, some benefits from orthophosphate dosing might be anticipated.

Effects of orthophosphate on the inhibition of copper pitting corrosion were then applied to treated water from a utility in Washington D.C., whose consumers have experienced an outbreak of pinhole leaks in household copper plumbing. After comparing electrochemical results from synthetic and actual water from the treatment plant, there was evidence of a natural inhibitor to pitting corrosion in WSSC water that is not present in the synthetic water. The higher chloride concentration in the water after ferric chloride was dosed at the treatment plant may have reduced the pitting propensity of the water. The effects of phosphates seemed to reduce the pitting propensity of real water at pH 8.3 although little benefit was seen at pH 9.1.

These defined characteristics of copper pitting were then applied in a systematic evaluation of a water utility experiencing pitting corrosion in Roanoke, VA. This case study further supported the hypothesis that high levels of aluminum, chlorine, and pH may be combining to catalyze copper pitting in practice. Recommendations to alter the treatment strategies at these utilities were proposed to help mitigate the pitting corrosion problems in these areas. A national survey then confirmed pitting is occurring at a significant frequency at other large utilities across the U.S.
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CHAPTER 1: INTRODUCTION AND BACKGROUND TO COPPER PITTING CORROSION

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INTRODUCTION

While copper is often considered among the most trouble free plumbing materials, recent outbreaks of pitting failures within copper pipes have prompted action to understand and mitigate these problems. Pitting occurs from non-uniform corrosion that forms pits or holes in the pipe surface. Premature failure of pipes may occur in as little as a few months after installation when excessive corrosion occurs at a small area on the pipe surface [1]. Pitting corrosion results in a loss of pipe material, which leads to decreased strength, followed by bursting or leaking of pipes. There are also serious costs and public health concerns associated with water damage and mold growth [2].

The problem of pinhole leaks can be divided into two stages: initiation and propagation. Initiation refers to the circumstances that are necessary to first start non-uniform corrosion in pits. Propagation refers to the subsequent growth of the pit, which in the case of pinholes culminates in complete penetration through the wall of the pipe. At the time this work was undertaken, previous research had developed some understanding of factors thought to allow propagation of pits, but initiating factors were speculative since the entire pitting process had never been reproduced through the pinhole leak stage in the laboratory. This research was aimed at reproducing the entire pitting process in the laboratory based on recent principles of pit initiation established by Rushing et al., [9] and Edwards et al. (2004).

BACKGROUND

Basic Electrochemical Understanding and Measurement of Pitting Corrosion

In order for pitting corrosion to occur, all components of an electrochemical cell are required including an anode, cathode, an external circuit to conduct electrons, and a connecting fluid with ions to maintain electro-neutrality [3]. Pits in a drinking water distribution system typically occur under mounds known as tubercles, which are usually formed by precipitative reaction between released copper ions at the anode and the water (Figure 1.1). The area under the mound is somewhat isolated from solution, and is often of low pH, low dissolved chlorine and oxygen due to continuous release of copper ions. The cathode, in contrast, is typically at higher pH, and the water may be more closely approximated by bulk water chemistry.

In waters that support propagation of pits, these difference tend to support a sustained situation in which electrons at the pit anode are transported to the exposed copper surface at the cathode [4].
All electrons produced in the pit must be consumed at a cathode in order for corrosion to proceed [5].

**Electrochemistry of Pits**

In cases where corrosion is uniform, anodic and cathodic reactions are relatively equally distributed over the surface. In such cases, use of an electrochemical cell, such as that developed by Reiber (1989), can be used to determine corrosion rates. By perturbing the surface through application of a negative or positive electrical potential, the rates of the anodic and cathodic reactions can be increased or decreased. The values for the partial currents must be inferred from the polarization data because it is impossible to completely isolate the respective anodic and cathodic electron exchanges on a homogeneous surface. Use of software and idealized Tafel equations allow the data to be de-convoluted into the component reactions (Figure 1.2). The corrosion current density \( (I') \), the electrode potential \( (E') \), and thus the corrosion rate are defined by the intersection of the partial currents (Figure 1.3). [6]

While these curves give insight into the factors controlling the anodic and cathodic reactions, not all surfaces are homogeneous. In fact, during pitting the anodic and cathodic regions may be treated as two independent homogeneous surfaces. Adequate polarization data for each of the component surfaces could be used to predict the behavior of this more complex heterogeneous system.

A coupled system where the anodic and cathodic processes are isolated to distinct surfaces can be analyzed similar to the homogeneous system. To a first approximation, in most situations where pitting occurs, the anodic reaction is occurring on only a very small part of the surface [6]. Since the cathodic reaction is often the rate limiting step to growth of the pit, the worst situations involve relative large cathodic areas with small anodes [7]. The two sets of polarization data shown in Figure 1.3 represent the data collected for each surface within the complex system. The partial anodic exchange current is given by the base or corroding surface, the surface with the lower electrode potential, while the partial cathodic exchange current is given by the nobel surface, or surface with a higher electrode potential. The relative potentials, of the two surfaces are equal due to the direct electrical connection between them. This value is represented as \( E_g \). [6]

The total anodic or cathodic current, \( I \), at a given potential may be calculated using Equation 1 [8]. During equilibrium, the sum of the anodic exchanges will equal the sum of the cathodic exchanges. This relationship is used to determine the variations in anode and cathode surface area (Equation 2) [6].

\[
I = \sum [i \times \text{Area}] \quad \text{Equation 1}
\]

\[
\sum [i_{\text{corr(anodic)}} \times \text{Area}_{\text{anodic}}] = \sum [i_{\text{corr(cathodic)}} \times \text{Area}_{\text{cathodic}}] \quad \text{Equation 2}
\]

*Where:*
- \( I \) = total current (\( \mu A \))
- \( i \) = density current (\( \mu A/cm^2 \))
- \( i_{\text{corr}} \) = density current at equilibrium (\( \mu A/cm^2 \))

*Note: If the rate limiting step if the cathode reaction, the current is equal to \( \sum [i_{\text{corr(cathodic)}} \times \text{Area}_{\text{cathodic}}] \).
Since the observed polarization of anodic and cathodic sites depends in part on the area over which oxidation or reduction occurs, the anode-cathode area ratio enters as an important factor in the observed corrosion rate [8]. From Equation 2, reducing the area of the anodic region will result in an increase in anodic current intensity. This will increase the rate of the anodic reaction, thereby increasing the degree of corrosive pitting within the anodic region. On the other hand, decreasing the area of the cathode will decrease the rate of the anodic reaction and therefore decrease the extent of corrosive pitting.

Cathodic and Anodic Inhibitors
The concepts of anodic and cathodic reactions are used as a basis for the development of many corrosion inhibitors. The addition of zinc, calcium, or magnesium salts to a water system can in certain circumstances act as cathodic inhibitors [7]. The complexes formed by these salts can coat cathodic regions and interfere with the cathodic reaction by preventing oxygen in the liquid and electrons in the metal from coming close enough to react. These cathodic regions gradually become anodic and the attack is much slower.

Anodic inhibitors are also used in a similar manner to decrease the damaging effects of pitting corrosion. The use of anodic inhibitors has more potential to cause detrimental effects than using cathodic inhibitors. Sodium carbonate, sodium hydroxide, sodium phosphate, sodium silicate, and potassium chromate are often referred to as “dangerous inhibitors,” because, if added in a quantity just insufficient to abolish corrosion completely, it localizes attack and renders it more intense than if no inhibitor had been introduced [7].

This work uses electrochemistry in attempt to track the phenomenon of pitting corrosion. This provides insight to help identify causal factors and mitigate copper pitting corrosion. However, these techniques cannot be used with absolute confidence, since so little is known about pitting.

PREVIOUS RESEARCH AND FUTURE WORK
Pitting may be caused by many factors, some of which are improper pipe installation, bacteria, electrical grounding, pipe manufacturing defects, and water quality. Recent studies completed for the Washington Suburban Sanitary Commission (WSSC) have linked changes in water treatment to crisis levels of copper pitting corrosion [9].

For hundreds of years, government regulations have placed focus on setting, revising, and expanding drinking water standards. Under the 1986 amendments to the Safe Drinking Water Act, the EPA is required to promulgate standards for 25 new contaminants every three years [10]. While these new standards improve the quality of water entering the distribution system, little effort is taken to determine how these changes will affect the distribution system itself. With many utilities now implementing these changes, it is imperative their effects be examined to prevent the degradation of distribution system materials both publicly and privately owned.

After the establishment of the Lead and Copper Rule by the EPA in 1991, utilities began to raise pH to control corrosion by-product release. Other trends in industry practice include cleaning and then lining of iron pipes with cement and the use of enhanced coagulants such as PACl. All of these changes can increase the pH and aluminum content of water reaching consumer’s
homes. In the past, higher pHs were almost always deemed beneficial for copper corrosion, yet recent research at WSSC, whose consumers were experiencing an outbreak of cold water copper pitting, led to circumstantial evidence suggesting that a combination of aluminum deposits, free chlorine, and higher pHs could somehow combine to initiate the pitting of copper in at least some waters [11, 12].

Research completed by Rushing et al. (2003) on copper pitting culminated with several noteworthy discoveries. The most controversial discovery is that chlorine and aluminum solids together could enhance non-uniform corrosion of copper under both stagnant and flow conditions compared to either constituent alone. These effects were most severe at pH 9 compared to lower values. Both chlorine levels and flow seemed to have an important impact on the potential for copper to corrode. This earlier work raised the following questions.

- What are the impacts of various levels of chlorine and aluminum on pitting corrosion at different pHs? (Chapter 2)
- How will the presence or absence of chlorine in combination with aluminum solids affect pitting? (Chapter 2 and 3)
- Could an aggressive water that is reasonably representative of samples collected in practice be synthesized that would cause actual pinholes to form on a copper pipe? (Chapter 3)
- What is the relationship between flow patterns in the pipe and pit initiation?
- Do pre-existing surface defects from the manufacture of copper pipe have an effect on forming lines of pits? (Chapter 3)
- What is the role of pipe orientation in pitting corrosion? (Chapter 3)
- Will the addition of orthophosphate to an aggressive synthetic water help mitigate the initiation of copper pitting corrosion? (Chapter 4)
- What is the influence of increased pH levels on the effectiveness of orthophosphate inhibition? (Chapter 4)
- Will orthophosphate help mitigate the propagation of initiated pits using potable water? (Chapter 5)
- Are there any significant differences between the synthetic water used in laboratory testing and potable water from a drinking water utility whose consumers are experiencing substantial pitting corrosion? (Chapter 5)
- How do the results of previous studies compare to the problems investigated in practice? (Chapter 6)
- What is the significance of this rare copper pitting problem on a national level? (Chapter 6)

The research presented herein was designed to answer these important questions. This thesis is organized into seven chapters. After this introductory chapter, chapters 2 through 6 develop an understanding of questions posed by previous research. These chapters have been prepared in manuscript format for submission to relevant journals. Finally, chapter 7 summarizes the key conclusions of this research.
REFERENCES


Figure 1.1. Developed of Anodic and Cathodic Areas on a Copper Pipe.
Figure 1.2. Polarization Curves for a Hypothetical Homogeneous Surface [6].

Figure 1.3. Polarization Curves for a Hypothetical Mixed-Couple System [6].
ABSTRACT. This research clearly confirms the controversial trends from earlier work. At certain pHs, the presence of chlorine and aluminum solids does seem to initiate pitting corrosion of copper. Although the problem is most severe at higher pH, it is likely that long-term exposure at lower values such as pH 8 could lead to pitting. There is a concentration effect of aluminum solids at pH 9.0, in that higher concentrations cause an earlier initial rise in corrosion potential ($E_{corr}$) if sufficient chlorine is present.

INTRODUCTION

Previous research revealed an important synergistic effect between aluminum solids and chlorine in promoting the pitting corrosion of copper at pH 8.0 (Rushing et. al, 2002). The initial circumstantial evidence for this effect was found from forensic analysis of failed household plumbing at Washington Suburban Sanitary Commission (WSSC), where consumers experienced a high frequency of copper pitting problems. The analysis showed that aluminum deposits were frequently present on failed pipe samples. Later field work demonstrated that possible sources of the aluminum in the deposits included the raw water, carryover of poly-aluminum chloride coagulant (PACl), and dissolution of cement-based distribution system materials that contained aluminum.

Bench scale experiments were then conducted to investigate the influence of aluminum solids and chlorine on copper corrosion, both of which have separately been implicated as causes of hot water copper pitting [1,2]. The experiments conducted at pH 8 under stagnant conditions
revealed increased chlorine decay and non-uniform corrosion tendencies when aluminum solids and chlorine were exposed to copper metal. Other experiments at this pH demonstrated that under alternating periods of flow and stagnation, the presence of aluminum and chlorine led to rising copper pipe corrosion potentials which are often interpreted as a sign of water that supports pitting [3]. In comparison, corrosion potentials were largely unaffected by chlorine and aluminum solids under mostly stagnant conditions, which was surprising given that current hypotheses suggest that pitting is more likely to occur during stagnant conditions [4].

When the same alternating flow experiment was repeated at pH 7 in the presence of aluminum solids and chlorine, corrosion potentials declined with time, suggesting that the higher pH values are more likely to induce pitting in conjunction with chlorine and aluminum solids. This is also contrary to current theories that predict higher pH will reduce most copper corrosion problems [5], although a noteworthy exception is the problem of blue water corrosion which occurs around pH 9. Ironically, blue water corrosion can usually be stopped with the addition of chlorine [6].

In summary, the hypothesis that higher pH, higher chlorine, higher aluminum and higher flow could somehow combine to initiate copper pitting is controversial to conventional wisdom suggest that each of these factors are beneficial in reducing copper corrosion. Experiments were designed to test this hypothesis by examining the effect of aluminum solids and chlorine on copper corrosion at a range of pH values common in potable water supplies under constant flow conditions.

MATERIALS AND METHODS

5/8” nominal size copper couplings (surface area = 20 cm²) were purchased from a local hardware store, rinsed with pure water, and placed in Reiber flow-through polarization cells (details elsewhere) [7]. Three liters of simulated drinking water was circulated through the cells at a flow rate of 1 gpm. The water initially contained 50 mg/L alkalinity as HCO₃⁻, 50 mg/L SO₄²⁻, 40 mg/L Cl⁻, and 40 mg/L Ca²⁺ added as reagent grade sodium or calcium salts to filter sterilized deionized water. pH was adjusted to target values by adding 1 M HCl or NaOH, and no attempt was made to maintain alkalinity.

In the first set of experiments examining the role of pH, free chlorine was increased incrementally every two days from zero to 4.8 mg/L as Cl₂ using bleach (6% NaOCl). The target level of chlorine was increased as follows: 0, 0.5, 0.8, 1.2, 1.5, 1.8, 2.1, 2.4, 3.6, and 4.8 mg/L as Cl₂. Targeted pH values of 6, 7, 8, and 9 were tested in duplicate (8 cells total), pH values were continuously held to within 0.3 units of the target value, and Cl₂ residuals were replenished twice daily.

In all experiments, free chlorine was measured using the DPD colorimetric test per standard method 4500-Cl G [8]. The water was completely changed on day 12 and tests were ended on day 20 of the experiment. Cumulative copper release to the water was measured at these times using the bicinchoninate method. Corrosion potential (Ecorr) and polarization resistance (RP) measurements were collected hourly using a multiplexer connected to a personal computer, using
a polarization scan rate of 0.5 mV/sec from –5 to +5 mV of the open circuit potential. Platinum counter and Ag-AgCl reference electrodes were checked and maintained regularly to insure accuracy. Instantaneous corrosion rates were estimated using potentiodynamic scans and Tafel analyses.

The combined impacts of Al and Cl₂ were examined by repeating the above tests, but with addition of 2 mg/L as Al of Al(OH)₃ solids. The Al(OH)₃ stock solution was created by raising the pH of 3000 mg/L as Al-AlCl₃ solution to 8.0 using NaOH, allowing the solids to settle, decanting the water, re-suspending the solids in fresh water, until the conductivity of the suspension was less than that of the experimental water. The same chlorine dosing schedule was used, except an additional level of 6.0 mg/L Cl₂ was tested on day 20 for all pH conditions. Copper release was measured and water was changed on day 22, and chlorine was again dosed to 6.0 mg/L. The pH for all conditions was then raised to 9.0, and Ecorr and Rp were measured for another 2 days.

The effects of different levels of aluminum solids in promoting pitting were tested at constant pH and chlorine concentration. The target aluminum levels were 0, 0.05, 0.1, and 0.5 mg/L as Al(OH)₃-Al solids. Targeted pH values of 8 and 9 were tested for each aluminum concentration making 8 tests total, and pH was adjusted and Cl₂ residuals were replenished twice daily. For pH 8, the target chlorine concentration was 3.6 mg/L as Cl₂, while pH 9 had a target chlorine level of 2.4 mg/L as Cl₂. pH values were kept within +/- 0.3 units of the target value. The water was completely changed on days 7, 20, and 28 and tests were ended on day 36 of the experiment. Additional testing was conducted at pH 9.5 and pH 10 as discussed in text.

To account for possible deposition of aluminum solids within the experimental apparatus, aluminum solids were re-dosed once approximately 24 hours after each water change. Thus, the actual level of aluminum in the water could have been as much as 50% higher than the target levels, and lower than the target levels dependent on losses to the apparatus surface or pipe samples. At the end the experiments, samples were cut in half and photographs were taken of the corroded copper surfaces using a digital camera.

RESULTS AND DISCUSSION

Results and discussion are presented in two sections, the first of which examines the role of Al solids and pH, and the second describes effects of variable Al concentrations.

Effects of pH and Al Solids on Aspects of Copper Corrosion

Chlorine Decay Kinetics

During the first set of experiments, chlorine decay rates were calculated by tracking the loss of chlorine after 8 hours and calculating the rate in terms of mg/L of chlorine loss per day. The pH and presence of aluminum solids had a large effect on the rate of chlorine decay in these systems (Figure 2-1). When aluminum solids were absent, the rate of chlorine decay was consistently
faster with decreasing pH values. Furthermore, the rate of chlorine decay when the target chlorine level was 4.8 mg/L was significantly higher compared to lower doses of chlorine at a given pH, consistent with anticipated first order or higher kinetics.

When aluminum solids were present the behavior changed significantly, in that the rate of chlorine decay was almost always faster when aluminum solids were present in the system. Furthermore, the rate of chlorine decay in the systems with the aluminum solids was not as pH dependent. If the percent increase in chlorine decay rate in the systems with aluminum solids is calculated as follows:

$$100 \times \left[ \frac{\text{decay rate w/ Al} - \text{decay rate w/o Al}}{\text{decay rate w/o Al}} \right]$$

a 0% increase indicates that chlorine decay does not increase, whereas a 200% increase indicates that the presence of Al solids doubled the rate of Cl$_2$ decay. It is clear that aluminum caused much higher chlorine decay rates at higher pH (Figure 2-2).

**Corrosion Potential and Polarization Resistance**

Electrochemical data were collected for each pH condition in duplicate, and since these measurements were always very close to one another only one set of data is presented. Corrosion potential ($E_{corr}$) was affected by both pH and chlorine in the system (Figure 2-3). At pH 6 when aluminum solids were absent, the corrosion potential began to decrease when chlorine dosing was initiated on day 2, and stayed fairly constant at around 30 mV until the chlorine level reached 2.1 mg/L, when a slight gradual increase in corrosion potential was observed with increasing chlorine doses. For the pH 7 condition, chlorine slightly depressed the corrosion potential, which then gradually increased from 30 to 60 mV as the level of chlorine was increased. Aluminum solids had no obvious effect on corrosion potential measurements at pH 6 and 7.

At pH 8, chlorine initially caused a slight decline in corrosion potential to 30 mV in the system without aluminum solids, until the chlorine residual reached 1.5 mg/L when potential began to increase. A significant increase in corrosion potential to 60 mV was observed when the water was changed on day 12. This might be attributed to a loss of reactant that causes higher $E_{corr}$ from the original system, or a buildup of a contaminant such at Cl$^-$, which could hinder a rise in $E_{corr}$. $E_{corr}$ continued to increase as the chlorine dose was ramped upwards. The same trends were seen in the system at pH 8 with aluminum solids, but the potential was usually 20-30 mV higher, which is consistent with trends noted in earlier research.

At pH 9, the first addition of chlorine on day 2 raised the potential in the systems with and without aluminum solids from approximately 40 to 80 mV. The potential remained at this level throughout the rest of the experiment in the system without aluminum solids, but started rapidly increasing when the chlorine residual reached 1.8 mg/L in the system with aluminum solids. The potential in this system increased to around 160 mV when the residual was 2.4 mg/L. A relatively rapid rise in $E_{corr}$ is often considered an indicator that copper is activating towards pitting [3]. The highest potentials were recorded after pH and chlorine levels were adjusted to
their target values. The decline in potential between pH and chlorine adjustments in the pH 9 rig is due to slight decreases in pH from 9.3 to 8.7 as well as lower levels of chlorine (typically less than 25% lower than target values).

Polarization resistance (\(R_p\)) data was also collected in all the systems (Figure 2-4). \(R_p\) can be used to assess trends in corrosion rate, with lower values indicating higher rates of corrosion [5]. For the systems without aluminum solids, \(R_p\) was higher at higher pH, confirming the expectation that corrosion rate increases at lower pH values. At pH 8, the presence of aluminum solids slightly depressed \(R_p\) values, suggesting an increase in corrosion rate due to their presence. The \(R_p\) data for the pH 9 condition with aluminum is perhaps the most interesting. Before chlorine was added to the system on day 2, the \(R_p\) values for the systems with and without aluminum solids were almost equal. However, 2 days after the first dose of chlorine in the presence of aluminum solids, the \(R_p\) value declined to a value of 500-1000 ohms, where it stayed for the rest of the experiment. These were among the lowest values for \(R_p\) measured, indicating that aluminum solids and chlorine were somehow causing higher corrosion rates at pH 9 compared to the same system without aluminum. Assuming \(R_p\) is proportional to the corrosion rate, if aluminum is present the copper corrodes as fast at pH 9 as it does at pH 6 without aluminum.

Additional tests were conducted on the samples exposed 20 days (Figure 2-5). On day 20, the chlorine was ramped up to 6.0 mg/L in all the systems. 2 days later, the water was completely changed and chlorine was restored to 6.0 mg/L. After 18 hours, corrosion rates were measured (discussed later) and then the pH in all the systems was increased to 9. After the pH was increased to 9 in the systems that initially were exposed to lower pH, the corrosion potentials temporarily increased. The rapid decrease in potential during the 23rd day observed in the system that was initially at pH 6 can be attributed to a rapidly changing pH in this system due to low buffering. These results suggest that copper corrosion can activate in systems with chlorine and aluminum if pH is raised to 9.0, regardless of initial pH.

**Copper Release**

The amount of copper released to the water was a function of the pH, with increased copper release at lower pH values, consistent with accepted knowledge of copper solubility and metals release in drinking water. The presence of aluminum solids slightly decreased the amount of copper released to water for all pH levels, but was most apparent at pH 6 (Figure 2-6).

**Mass Change**

The amount of mass loss or gain of the copper samples was affected by pH and the presence of aluminum solids (Figure 2-7). The mass loss of copper samples exposed to no Al solids at pH 6, 7 and 8, was equal to or greater than the amount of copper released into the water of these systems, suggesting relatively little copper scale was formed on the walls of the copper samples at these pH values. The copper samples exposed to pH 9 exhibited a small mass gain of 1 mg. Considering the low levels of copper released to the system (approximately 2 mg total), only a small amount of copper scale (~3 mg) formed on the copper walls at this pH value as well. This conclusion was supported by visual observations discussed later.
Aluminum solids significantly altered the change in mass of the copper samples compared to the system without aluminum. At pH 6, mass loss was less in the samples exposed to aluminum solids, but still approximately equal to the amount of copper release to the water. For all other pH conditions, the copper samples gained mass, ranging from 5 to 18 mg, perhaps due to accumulation of significant amounts of copper and aluminum scale.

**Corrosion Rates**

Corrosion rates were measured on day 23 in the experiment with aluminum solids (Figure 2-8). The results indicate that corrosion rate decreased with increasing pH, except for the pH 9 samples. This trend is especially clear if one of the two corrosion rate measurements from the pH 6 conditions would have been ignored. Besides the pH 9 results, the corrosion rates are consistent with the amount of mass change and copper byproduct release to the water, suggesting that the sample at pH 9 is corroding faster and reacting fundamentally differently with the water than the other samples with aluminum solids. The corrosion rate measurements are consistent with expectations based on trends in $R_p$ discussed earlier.

**Visual Observations**

Aluminum and pH had profound impacts on the visual characteristics of copper corrosion (Figure 2-9). The surfaces of the samples exposed to only chlorine (no aluminum solids) were generally orange to red in color with no significant copper oxide or scale layer present. The pH 9 samples had blue streaks on its surfaces. The presence of aluminum caused a dark brown-black scale to develop on the samples for all pH conditions. Because there was a slightly different protocol during the last few days of the experiment for the copper exposed to aluminum solids, it is impossible to attribute the scale unambiguously to aluminum; the increase in pH to 9.0 for all conditions may have attributed to its formation. However, a comparison between the pH 9 samples is possible, because they were exposed to nearly the same amount of chlorine for the same time. The visual differences between the conditions with and without aluminum at this pH are striking. Mounds of copper corrosion byproducts formed on the pH 9 samples exposed to aluminum, a feature that was absent from all other conditions tested (Figure 2-10). The presence of such mounds after just 3 weeks, the high corrosion rate of the samples and corresponding trends in corrosion potential are highly indicative of the onset of serious copper corrosion problems.

Thus, the hypothesis that flow, high pH and aluminum could cause pitting was deemed worthy of additional study.

**Effects of Aluminum Solid Concentration on Corrosion Tendencies**

**Corrosion Potential and Polarization Resistance**

A second phase of experiments was designed to determine if there was a safe level of aluminum solids in terms of preventing copper corrosion problems. The corrosion potential ($E_{corr}$) was influenced by the aluminum solids concentration in the samples, with the clearest distinction observed at pH 9.0 (Figure 2-11). At pH 9.0, the initial climb in corrosion potential began earlier at higher aluminum concentration. Specifically at 0.5 mg/L aluminum the climb started on day
7, at 0.1 and 0.05 mg/L the climb began on day 10, and for the sample without aluminum the climb in potential did not begin until day 16. Ultimately, all conditions tested leveled off around day 25 to an approximate value of 210 mV, regardless of aluminum concentration. For all pH and aluminum levels, the variability in potential between pH and chlorine adjustments is due to slight decreases in pH from as well as lower levels of chlorine (typically, chlorine decayed up to 25% from target values).

The results at pH 8 were consistent with previous experiments. Very little difference in corrosion potential was observed for samples with no or 0.5 mg/L Al after 8 days. As a result, a decision was made to increase pH to 9.5 in this system (Figure 2-11). The corrosion potential measurements obtained at pH 9.5 indicate that both samples, 0 and 0.5 mg/L Al(OH)_3, began climbing immediately after pH was raised. The sample with the aluminum typically had a higher $E_{corr}$ than the sample without aluminum.

A short term test was then conducted using new copper samples at pH 10. The results indicate that, in terms of corrosion potential, the aluminum actually starts to have some possible benefits at this pH range. The potential of the sample containing aluminum remained fairly constant around 200 mV, while the corrosion potential of the sample without aluminum began to climb on day 6 with a maximum value of 446 mV on day 13. Unfortunately, a power outage in the middle of this test led to loss of some data.

The maximum corrosion potential ($E_{corr}$) and minimum polarization resistance ($R_p$) values were examined for each sample. The maximum corrosion potential was affected by both pH and aluminum solids concentration. At pH 8 and 9 the aluminum concentration affected the initial climb in $E_{corr}$, but the ultimate maximum $E_{corr}$ was relatively unaffected. However, there were notable differences in the maximum corrosion potentials at pH 9.5 and 10 due to aluminum. At pH 9.5, the maximum $E_{corr}$ for the sample containing 0.5 mg/L of aluminum was approximately 16 percent higher than the sample without aluminum. In contrast, the maximum corrosion potential obtained at pH 10 was 43 percent lower for the 0.5 mg/L aluminum sample then for the sample without aluminum. This difference is not unexpected, given the profound changes in aluminum chemistry that occur from pH 8.0 to 10, where aluminum is predicted to change from insoluble solids to completely soluble Al(OH)$_4^-$ as pH increases. pH also influenced the maximum $E_{corr}$ of samples. As pH increased, the maximum $E_{corr}$ also increased (Figure 2-12).

**Polarization Resistance Data**

Polarization resistance ($R_p$) data is typically inversely proportional to the corrosion rate [5]. Therefore, the lower the $R_p$, the higher the corrosion rate. At pH 8, the presence of aluminum solids had little effect on the minimum $R_p$ values (Figure 2-13). The $R_p$ data for the pH 9, 9.5, and 10 conditions are perhaps the most interesting. At each pH level, the $R_p$ values were consistently lower in the presence of aluminum, although at pH 9 the decrease in $R_p$ did not
seem linearly related to the amount of aluminum added. The decreased $R_P$ measurements suggest that the presence of aluminum solids leads to higher corrosion rates at pH 9, 9.5, and 10, and most certainly, fundamentally alters the mechanism of corrosion.

**Tafel Analysis**

Analysis of the Tafel plots at pH 8 and 9 in the presence and absence of aluminum is revealing. At pH 8.0 at the time of the measurement, the corrosion rate of the sample with aluminum was actually lower than that observed in the absence of aluminum (Figure 2.14). While aluminum slightly catalyzed the cathodic reduction reaction, the anodic reaction was inhibited, leading to the overall decrease observed. On this basis, it is highly probable that the presence of aluminum significantly decreased the oxygen reduction reaction at the copper surface, since the rate of free chlorine decay was increased as determined by direct measurement. At pH 9.0 it is very clear that the presence of aluminum caused a marked increase in the cathodic reaction and the anodic reaction was unchanged (Figure 2.15). This independently confirms that the aluminum solids catalyzed the rate of Cl$_2$ reduction on the copper surface.

**Visual Observations**

Aluminum and pH had a profound impact on the visual characteristics of copper corrosion. The samples exposed to pH 8.0 for this short experiment (8 days) showed few signs of pitting or scale development at all aluminum concentrations. However, at pH 9, 9.5, and 10, the presence of aluminum increased the amount of scale deposited on the samples (Figure 2-16). The most striking difference between samples with and without aluminum occurred at pH 9 and 9.5. While the samples at pH 10 with aluminum had only two small deposits about 1.5 mm in diameter, numerous mounds of dark brown and blue-green copper corrosion byproducts formed on the samples exposed to aluminum at pH 9 and 9.5. The surfaces of the samples exposed to only chlorine (no aluminum solids) were generally dark orange to red in color, and the sample at pH 9 was the only one to show significant depth of scaling. The surfaces of the samples exposed to pH 10 were also striking because, aside from two very small deposits on the 0.5 mg/L aluminum, they had virtually no scale or residue on them and the surface looked shiny and new. Even though the experiments were relatively short duration, a profile picture of some samples clearly suggest development of a pit with tubercles (Figure 2-17).

**CONCLUSIONS**

The short-term experiments described here clearly confirm the controversial trends from earlier work. At certain pHs, the presence of chlorine and aluminum solids does seem to initiate pitting corrosion of copper.

- Although the problem was most severe at higher pH, it is likely that long-term exposure at lower values such as pH 8 could lead to pitting. $E_{corr}$ rose sharply at pH 8.0 above 1.8 mg/L free chlorine. A major rise in $E_{corr}$ occurred at 0.5 mg/L Cl$_2$ at pH 9.0.

- There is a concentration effect of aluminum solids at pH 9.0, in that higher concentrations cause a rising $E_{corr}$ sooner if sufficient chlorine is present. We interpret this result to indicate that aluminum is increasing susceptibility to pitting. However, if Cl$_2$ remains at very high levels for a long time, it appears likely that pitting would occur without
aluminum at pH 9.0 or higher. Thus, there does not seem to be a “safe” level of aluminum above pH 9.0, in that higher aluminum is leading to a higher tendency for pitting.

- It does not appear that the adverse effects of aluminum extend to pH 10, since the presence of aluminum tended to decrease the $E_{corr}$ rise at this pH. It seems possible that the synergistic impacts of aluminum and chlorine on copper pitting are confined to pH between 8.0 to somewhere below 10.0.

- Utility practice in terms of coagulant selection, aluminum carryover, concrete lining, pH control and disinfectant dose need to be reconsidered in light of these startling results.

ACKNOWLEDGEMENTS

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REFERENCES


Figure 2-1. Average chlorine decay rates based on duplicates for various target chlorine doses. Chlorine decay measured over an 8-hour period, and rate is presented in mg/L Cl₂ lost per day.

Figure 2-2. Percent increase in chlorine decay rate for given target dose with 2 mg/L aluminum solids present compared to same system without aluminum.
**Figure 2-3.** E$_{corr}$ results. Open and closed circles denote with and without aluminum solids, respectively. Complete Water change on Day 12.
Figure 2-4. Polarization resistance data in Ohms. Open and Closed circles denote with and without aluminum solids, respectively. Complete Water change on Day 12.
Figure 2-5.  $E_{corr}$ results from experiments with aluminum solids after day 20.  Chlorine = 6.0 mg/L as Cl$_2$.

Figure 2-6.  Average Copper Release based on duplicates measured before water change on Day 12 and end of experiment.  Error bars represent the low and high measurements of the duplicate samples.
Figure 2-7. Average mass loss from copper samples based on duplicates. Negative values indicate a mass gain. Error bars represent the low and high measurements of the duplicate samples.

Figure 2-8. Average corrosion rate during day 23 with aluminum solids present. Water changed 18 hours before data was collected. Cl$_2$ = 6.0 mg/L. Error bars represent the low and high measurements of the duplicate samples.
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**Figure 2-9.** Copper samples cut in half after end of experiment.

**Figure 2-10.** Close up of corrosion byproducts formed on pH 9 sample exposed to aluminum solids and chlorine.
Figure 2-11. $E_{corr}$ data results. Chlorine concentration was not precisely controlled over the indicated time interval late in the experiment.
Figure 2-12. Maximum $E_{corr}$ during test at each condition.

Figure 2-13. Minimum $R_p$ during test at each condition.
Figure 2-14. Tafel analysis plot of pH 8 samples with and without aluminum.

Figure 2-15. Tafel analysis plot of pH 9 samples with and without aluminum.
Figure 2-16. Visual observations of copper samples after experiments.

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<th>pH 9</th>
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Figure 2-17. Profile view of a sample exposed to aluminum plus Cl\(_2\) at pH 8.0 for 8 days, then exposed to pH 9.5 water with aluminum plus Cl\(_2\) for 28 days.
CHAPTER 3: COPPER PINHOLE LEAK DEVELOPMENT
IN THE PRESENCE OF Al(OH)₃ AND CHLORINE

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ABSTRACT. This work is the first to prove that a potable water containing aluminum, high chlorine residual and relatively high pH can cause pinholes in copper tube. To our knowledge this is the first time the phenomenon of pinhole leaks have been reproduced in the laboratory as it occurs in the field. It therefore proves that “aggressive water” alone can cause the problem of pitting. The role of flow, pipe orientation and hypothesized surface defects were directly examined as part of this evaluation. Pitting increased for pipe sections with high flow and for sections of straight pipe exposed to hydraulic conditions near bends. Copper pipe sections polished to a mirror like finish to remove surface defects were also severely attacked.

INTRODUCTION AND BACKGROUND:

Copper pitting is a form of localized corrosion that can lead to formation of small holes in pipe walls. In some instances, premature failure of the pipes may occur after just a few months service, although a minimum of a few years is more common. Post mortem investigation of recent copper failures from pinhole leaks led to identification of significant aluminosilicate deposits on the pipe surface (Edwards et al., 2004). The term “aluminosilicate” is a generic name for solids forming in water that contain both aluminum and silica, in addition to other components. Clay is a common aluminosilicate. Prior to the mid to late 1990’s, aluminum was only detected in a very small percentage of pits. However, from 1998 onwards, aluminum was detected in well over 40% of hot and cold water pits each year (Kireta, 2003).

Recent literature is not clear regarding the role of aluminum deposits in copper corrosion, much less cold water pitting corrosion in particular. Tunteri (1968) cited Al deposits as a cause of hot water copper pitting, and mentioned that if the treated water contained above 0.1 mg/L Al a higher frequency of pinhole leaks occurred in one system. At first glance the 0.1 mg/L threshold level of Al should not be overly restrictive to water utilities, since 0.05-0.2 mg/L is the secondary drinking water regulation in the United States and 0.1-0.2 mg/L is the operational guidance value in Canada (Kvech et al., 2003). In contrast Lauer et al. (1992) speculated that the aluminosilicate deposits on copper were beneficial in preventing corrosion in Denver. However, in a direct short-term test of the Lauer et al hypotheses, Kvech and Edwards (2001) discovered that the aluminosilicate particles actually worsened aspects of copper leaching and made corrosion less uniform. A recent literature review also speculated that a complete coating of these solids would have beneficial impacts under at least some circumstances [1], a hypothesis not inconsistent with the experimental results or interpretation of Kvech et al. (2001) obtained for partial coatings.
However, more recent research has developed convincing evidence that aluminum deposits can initiate cold water copper pitting corrosion (Rushing et al, 2002, 2003; Marshall et al, 2003). One of the most startling findings was that if Cl₂ and aluminum were present, the tendency of copper to pit actually became worse at higher pH. That earlier work raised specific questions deserving of follow-up study.

A key question is whether an actual pinhole leak could form in a period of months when exposed to aggressive water that is reasonably representative of samples collected in practice. All previous research on copper pitting, at least as conducted under scientifically reproducible laboratory conditions with known water chemistry, has stopped well short of forming actual pinholes. Although the literature is replete with studies of micropits, especially those formed when copper corrosion is driven by an applied electrochemical potential, it is uncertain if those pits would ever propagate through a pipe wall or if they would form at all in the absence of an artificial potential. This is also of critical importance to future scientific advances on the subject, since if pitting cannot be initiated in the lab, all possible causes are merely hypotheses. Even today, many suspect that lightning and carbon films (or other manufacturing defects) are the primary causes of pit initiation on tube, and still others believe that flux or poor installation practices are responsible [3]. Indeed, if most pitting is “an act of god” as many homeowners are routinely told, what assistance can they seek in trying to stop the problem? Finally, without assurance that we can initiate pitting as it occurs in practice, it is not possible to confidently test remediation strategies that can stop the problem by modifying water chemistry.

In terms of the relationship between flow and pit initiation, many have speculated that pitting is more likely to occur during stagnant conditions [4] as opposed to continuous flow. In contrast, still other experiments demonstrate that under alternating periods of flow and stagnation, the presence of aluminum and chlorine led to rising copper pipe corrosion potentials, which has been interpreted as a sign of water that supports pitting [5]. In our most recent work (Marshall, 2004), we discovered that constant flow actually led to more pitting than did nearly constant stagnation. It is important to examine this hypothesis directly, not only to understand causes of pitting, but to explain why one home has a severe pitting problem, whereas a home next door built using the same copper installed by the same plumber and drawing the exact same water does not. Water usage patterns within each home might be a primary factor determining likelihood of pitting.

Forensic analysis of failed tubes often demonstrates that pits occur in “rows” down the pipe. This is invariably interpreted as a manufacturing defect, since the investigators suspect that the pits are developing on lines of carbon films or other unspecified defects arising from tube drawing operations. However, one interesting aspect of the earlier work is that “lines” of corrosion deposits formed only in the presence of aluminum [13]. This raised the possibility that particles were somehow depositing on the pipe in patterns that caused formation of the lines, as opposed to lines of scale forming on pre-existing surface defects. It would be instructive to examine this hypothesis directly by polishing the surface of some tubes to a mirror like finish, thereby completely removing all such deposits.

Experiments also examined the role of pipe orientation, and the role of chlorine, in promoting pitting. It is often noted that pits occur near bends, in predominantly horizontal sections, and it
was desirable to closely track such trends in the laboratory. Others have suspected that any type of deposit might cause pitting (During, 1988), even if a strong oxidant such as chlorine or chloramine as absent, so tests were conducted to examine that hypothesis.

MATERIALS AND METHODS:

The basic pipe exposure rig consisted of a large reservoir containing water with the desired salt content, pH, Cl\textsubscript{2} level, and aluminum solids concentration (Figure 3-1). ¾ inch, grade M copper piping was obtained from a local plumbing supply company and cut into 12 inch sections. There were 5 flow loops inside each reservoir, and each loop contained three 12 inch long copper pipe samples. The top horizontal copper pipe sample was cut in half, polished to a mirror like finish to eliminate any surface defects introduced during manufacturing, and equipped with a clear plastic viewport to allow visual observations of scale development during the experiment. During normal operation the viewport was covered to prevent possible photochemical reactions. Another section was directly underneath, and a third 1 foot sample was oriented vertically in the flow loop. Each of the five loops was equipped with its own submersible epoxy coated pump operated on a precise schedule via an automatic timer (Table 3-1). It is believed that these flow regimes reasonably represent some of the variations that might occur in consumer plumbing. When the pump was “on” flow was approximately 1.3 gallons per minute. The flow within the pipes was characterized by calculating a Reynolds number of approximately 5,755. This value is greater than the threshold of 2,000 for turbulent flow.

The water used in the test was designed to simulate the gross ionic constituents found at a utility whose consumers were experiencing a serious pitting problem (Table 3-2). In this type of water [14], prior research led to a hypothesis that pitting was caused by the combination of high Cl\textsubscript{2} and pH in the presence of aluminum solids. The water was synthesized by adding 4.46 g CaCl\textsubscript{2}*2H\textsubscript{2}O, 2.7 g of CaSO\textsubscript{4}*2H\textsubscript{2}O and 6.14 g of NaHCO\textsubscript{3} to 108 L of distilled and deionized water. Targeted levels of chlorine were maintained as desired and consistently held within 1.5 mg/L of the target level. Chlorine residuals were replenished daily using bleach (6% NaOCl. Free chlorine was measured using the DPD colorimetric test per standard method 4500-Cl G. The pH levels of both tanks were maintained at 9.2 using an automated pH pump and consistently held within 0.1 units of the target value. These meters were calibrated once a week to assure accuracy in readings. pH was adjusted using a 0.2 M NaOH solution.

The water in each rig was completely changed once a week. 108 liters of synthetic water was prepared. Both tanks were emptied and refilled with 54 liters of synthetic water followed by the addition of 2 mg/L of fresh Al(OH)\textsubscript{3} solids, the stock solution for which was created by raising the pH of a 3000 mg/L AlCl\textsubscript{3} solution to pH 8.0 using NaOH, followed by repeated washing with reagent grade water (followed by solids settling) until the conductivity of the solution was equal to the experimental water. After adding 4 mg/L of free chlorine to one of the tanks, the pH of both tanks was adjusted to 9.2 using 2 M NaOH. All Ag-AgCl reference electrodes were checked and maintained regularly to ensure accuracy.
The corrosion potential, or $E_{\text{corr}}$, measurements were obtained using a multimeter and a Ag-AgCl reference electrode. These values were measured in millivolts (mV). Measurements were taken once a day for the first 4 months of the experiment and then 2 to 3 times a week thereafter. Both stagnation and flow corrosion potential measurements were taken for each pipe series.

In each of the two rigs there are 5 loops x 3 pipe samples per loop or 15 samples total. Samples in the first rig were exposed to the water with addition of 4 mg/L free chlorine and 2 mg/L aluminum solids (as Al). The second rig had the exact same conditions initially, but without the free chlorine. After sufficient data was gathered to demonstrate that pitting was not initiating in the second rig, water quality was changed as specified in the text to attempt and find conditions that would initiate pitting.

Upon the completion of the experiment, all pipes were dried in an oven at 85 °C. All large tubercles were physically removed and stored for analysis. Additional deposits on the pipe wall were then removed using a felt-tipped Dremel tool, taking care not to remove metallic copper on the pipe. All pipes were then dried until a constant mass was obtained, and later cut lengthwise into four, three inch sections. Each three inch section was then cut in half to expose the inside of the pipe for both visual and physical analysis (Figure 3-2). The physical analysis was completed using a 0-25 mm caliper with an accuracy of 0.01 mm.

RESULTS AND DISCUSSION

The effects of chlorine are described initially, followed by effects of flow patterns and pipe orientation on pit formation. After discussing the unforeseen fact that corrosion was occurring differently at pipe entrances and exits, the role of purported surface defects is examined.

**Effect of Chlorine**

**Corrosion Potential, $E_{\text{corr}}$**

Examination of all the data indicate obvious electrochemical and visual differences between pipes with and without free chlorine (Figure 3-3). While the corrosion potential ($E_{\text{corr}}$) during flow remained below 100 mV and fairly constant in all the samples without chlorine, the samples exposed to free chlorine showed a rapid increase in $E_{\text{corr}}$. $E_{\text{corr}}$ of samples exposed to chlorine leveled off at high values 100 to 750 mV larger then the corrosion potentials in samples without chlorine. $E_{\text{corr}}$ in samples containing free chlorine was highly erratic during the experiments. While the samples without chlorine generally stayed varied within 50 mV of a given value, the samples with chlorine varied in a range of 200 to 500 mV. Interestingly, the greatest shifts in $E_{\text{corr}}$ were noted in the sample with continuous flow, which had the most consistent chemical environment within the tube since it did not have periods of stagnation.

The effects of free chlorine on $E_{\text{corr}}$ were less dramatic during stagnant conditions. While the corrosion potential during stagnation remained higher for the system containing free chlorine, there was less of a distinction between the samples with and without chlorine (Figure 3-4).
After running the experiment for 45 days, there were absolutely no signs of pitting or accelerated corrosion in the samples without chlorine, while obvious visual non-uniformities were developing in the samples with chlorine. Since previous pitting research had suggested that the presence of high levels of silica and zinc may accelerate copper corrosion and formation of blue water pitting [5, 6], 15 ppm of silica and 2 ppm of zinc were added to the system without chlorine to determine their effects on corrosion (Figure 3-5). The corrosion potential increased slightly, about 20 to 25 mV, but leveled off quickly and remained relatively constant. After a total experimental run time of 8 ½ months, these pipes were changed, and new pipes were tested without chlorine. The same synthetic water was used but with 2 ppm aluminum, 15 ppm silica, 0.2 ppm zinc, and 5 ppm of particulate humic natural organic matter (NOM) added to the system (Figure 3-6). As before, though corrosion potentials were somewhat lower in the presence of NOM when compared to the same conditions without NOM, no significantly higher potentials were obtained without the presence of free chlorine. A final test was made with the addition of NO$_3$ to the system, however, no effect was observed. In summary, nothing noteworthy was observed in the absence of free chlorine and in the presence of aluminum, despite numerous attempts to create an aggressive condition.

**Mass Reduction**

Mass loss is a direct indicator of corrosion rate. The corrosion rate was determined using percent mass loss rate of each pipe over the time of exposure, calculated as follows:

\[
\text{% Pipe Mass Loss Rate} = \frac{\text{Total Pipe % Mass Lost}}{\text{Total Time Length of Experiment}}
\]

As was the case with $E_{corr}$, there was a very large difference between samples with and without free chlorine. The samples exposed to water containing chlorine lost pipe mass at a much higher rate than the same water without chlorine (Figure 3-7). This relationship was most evident in the results during continuous flow. The horizontal and vertical sections exposed to free chlorine decreased in mass at a rate of 2.3% and 2.4% per year, respectively, while the mass of samples without chlorine remained constant (Table 3-3). These results, though single measurements, indicate that the amount of flow, in combination with free chlorine, influence the corrosion rate of a pipe system. It is also interesting to note that in the vertical pipes, mass loss in the presence of chlorine was roughly linear with total flow, having an $R^2$ value of 0.99 for the linear regression. In contrast, in horizontal pipes, mass loss was highly non-linear. Instead, mass loss increased rapidly with very low flow rates, and then leveled off markedly at flows above out 100 min/day.

**Visual Analysis**

Perhaps the most striking difference between the samples with and without chlorine was the deposit patterns formed on the pipe walls. The surfaces of the pipes without chlorine were coated with a very thin layer of brownish-black deposit, exposing the copper surface in some areas. In the absence of chlorine but with aluminum, there did not seem to be any patterns within the deposition of the solids on the pipe walls. In contrast, the pipes containing chlorine and aluminum had lines of distinct black and blue deposits on the walls of the pipe. The most noticeable difference was observed in the samples under higher flow conditions. While there
were no large deposits on the pipe without chlorine, the samples exposed to chlorine had large mounds of copper corrosion byproducts scattered along the pipe walls (Figure 3-8). These results indicate that in the absence of free chlorine, flow rates do not have an effect on either the corrosion potentials or scale patterns of copper pipes.

**Pinhole leaks**
The most dramatic corrosion effects were manifested in the pipes containing free chlorine under continuous flow conditions. Corrosion of the 3 pipes in series was non-uniform. A total of 12 breakthrough pits were formed within the vertical and horizontal pipe sections under continuous flow in the one year experiment, 8 of which were in the horizontal section (Figure 3-9). The leaks self sealed with corrosion byproducts during these tests conducted at nearly 0 atmosphere gauge pressure, which allowed the holes to be undetected until the very end of the test. Since an analysis of water chemistry at homes where pitting actually occurred led us to this water quality condition, this result is deemed highly representative of pitting as it occurs in at least some instances in drinking water treatment practice. There were also large deposits and depressions, or premature pits, in the 240 min/day vertical pipe. The deepest pit for this condition had already eaten through over 80% of the pipe wall depth. It is believed that these pits would have broken through at this flow condition had the experiment been run for a longer time period. All pits created in the experiment were formed under large mounds of copper corrosion byproducts (Figure 3-10).

**Analysis of Tubercles**
There were approximately 75 to 85 large black surface tubercles, or mounds of corrosion byproducts, on both the vertical and horizontal 12 inch sections of copper piping exposed to chlorine under continuous flow conditions.

The mounds were then physically removed, revealing an underlying blue-green deposit (Figure 3-11). The outer black surface and inner blue-green deposits were analyzed using a scanning electron microscope (SEM) to characterize their composition (Table 3-4 and Figure 3-12). This SEM could not detect elements of atomic number less than carbon.

A minimum of eight composition measurements were taken for each deposit in order to get an overall average of the species present within the deposits. These results indicate that the outer black layer was primarily composed of an aluminum, calcium, and copper oxide, whereas the inner blue deposit was predominantly composed of a sulfur, chloride, and copper species (Table 3-4 and Figure 3-12).

**Effects of Flow Patterns on Pit Formation:**
In all four alternating flow and stagnation patterns, the corrosion potential was almost always higher during flow than during stagnation (Figure 3-13). Free chlorine serves as an oxidant during the corrosion reaction. Therefore, the replenishment of free chlorine during flow may have been responsible for the higher potentials. When the water is stagnant within the pipe, the
free chlorine breaks down into chloride during corrosion; therefore the lower the free chlorine level, the lower the level of oxidants for corrosion to occur. Alternately, free chlorine at the pipe wall is replenished with the onset of flow.

To illustrate this relationship, $E_{\text{corr}}$ measurements were taken during a typical flow cycle (Figure 3-14). Time zero represents the onset of flow after a cyclic stagnation period. In all cases except for the 5 second flow condition, the programmed cycle was to allow flow for 5 minutes, so in the test flow was for 5 minutes even for the condition at 5 seconds. For all flow patterns, the $E_{\text{corr}}$ rises quickly, and then steadily increases until it reaches a peak when flow stopped. When flow is stopped, the $E_{\text{corr}}$ immediately begins to drop off. This pattern may illustrate the rapid replenishment of free chlorine with the onset of flow, as well as the slower process of free chlorine breakdown into chloride during the stagnation period. If free chlorine is responsible for this dramatic increase in corrosion potential, it is not surprising that the continuous flow system had higher $E_{\text{corr}}$ measurements (Figure 3-15). This system was continually replenished with fresh free chlorine.

Considering the maximum corrosion potential reached by the systems exposed to free chlorine, the continuous flow system averaged twice that of the other systems (Figure 3-16). Likewise, as the flow increased, the maximum corrosion potential also increased. These results suggest that in the presence of free chlorine, pitting corrosion is more likely to occur at higher flow.

A physical comparison of the chlorine samples and corrosion byproduct distribution helped illustrate the significance of flow on copper pitting corrosion (refer back to Figure 3-2). Many patterns were observed between the pipes which related to both their orientation and flow patterns. An illustration of the original pipe surface is provided for comparison (Figure 3-17). For both the horizontal and vertical pipe sections, as the flow decreased, the corrosion and deposits on the pipes became more uniform. While the sample at lower flows showed distinct lines of blue-green deposits, the deposition of corrosion byproducts on the pipes exposed to higher amounts of flow was random and sporadic (Figure 3-18).

In the samples with lower flows of 0.67, 5, and 40 minutes per day, well-defined blue stripes developed within the black deposits in the direction of flow. As the flow frequency increased, however, these lines were less pronounced, and mounds of copper corrosion by products began forming on the pipes with higher flows of 40, 240, and 1440 min/day. The deposits on these higher flow samples were variable and randomly scattered on pipe walls. Settling of particles under turbulent conditions is much less likely than under laminar or stagnant conditions. Perhaps it is not surprising that the preferential deposition of particles on pipe walls was lessened at higher flows.

A comparison of the maximum decrease in pipe wall thickness for each segment was completed (Figure 3-19). As the frequency of flow increased, the maximum loss in pipe wall thickness increased. This data also showed a distinction between pipe orientations, as well as the entrance and exit portions of the pipe
Effect of Pipe Orientation on Scale Deposition:

To evaluate the affect of pipe orientation on scale deposition, a visual analysis was performed on the pipe samples. Also, one month prior to the completion of the experiment, corrosion potential measurements were recorded for each pipe within the continuous flow system containing free chlorine to determine the electrochemical relationships of the three pipes if they had been electrically connected.

Two possible explanations for the patterns discovered on the pipe surfaces will be discussed. The characteristic lines may have been the result of imperfections in metal manufacturing. Another possible and more likely explanation is that particles heavier than water had a preferential deposition due to gravity or centripetal forces, or that particles were depositing preferentially on anodic/cathodic regions of the pipe that were determined based on flow.

Horizontal pipe orientation
The bottom portion of the 3rd horizontal pipes demonstrated the most distinct deposition of blue-green lines on the pipe walls (Figure 3-18). This deposition is most likely due to the settling of particles. The top portions of these pipes illustrated a more random deposition of corrosion byproducts. These line patterns decreased as the amount of flow within the pipes increased. The top entrance section of the horizontal samples seems to be the most prone to pitting corrosion. Five of the eight breakthrough pits in the horizontal section were formed within the first 3 inches of the pipe entrance, and four of those formed on the top segment.

Vertical pipe orientation
The results for the 1st vertical sections are very similar. The portion of the pipe on the outside of the bend seemed to have a more distinct line pattern. The deposition of particles in this manner can be explained in two ways. One explanation for the patterns developed on the vertical pipes is the centripetal force causing particles to preferentially deposit on the outer walls of the pipe. As with the horizontal sections, the most dramatic corrosion in the vertical sections took place in the entrance to the continuous flow sample. The exit showed very little signs of pitting corrosion. Additionally, the portion of pipe on the outer bend to the vertical pipes demonstrated a higher amount of pitting corrosion.

As a general tendency, based on a visual analysis of copper pipe loss in the horizontal pipe sections, the bottom sections tended to be cathodic relative to the top section. For example, most signs of the anodic corrosion reaction, or pitting, were on the top portion of the pipe wall. The 2nd sample with the viewfinder had the top portion of the pipe removed. Using this general rule, this section would have been cathodic relative to the 1st vertical and 3rd horizontal sections, in which the entire circumference of the pipe was intact. Corrosion potential measurements taken between samples during the experiment confirmed that the 2nd viewfinder sample was, in fact, relatively cathodic compared to the other pipe sections (Table 3-5). This is consistent with the notion that aluminum particles settling and sticking to the bottom of the pipe would catalyze the cathodic reaction (Rushing et al., 2002-2003), but it could also be due to the fact the pipe was polished or was exposed to 2 times the flow velocity (since the top half of the pipe was removed). On average, the horizontal section was only about 10 mV higher than the vertical
section. These results agree with the visual analysis of samples, as the horizontal segment revealed a higher level of corrosive pitting than the vertical segment.

**Differences between corrosive properties of pipe entrance and exit:**

To quantify the extent of pitting in each pipe section, ten of the thinnest points in the pipe wall measurements for each section were averaged. There was also a surprising difference between these average depths of the entrance and exit portions of the continuous flow samples. While the horizontal and vertical exit sections revealed a decrease in average thickness of 4% and 13%, the entrance segments yielded a much higher 45% and 41% reduction, correspondingly (Table 3-6). This is again consistent with the observation that the samples near the turbulent entrance experience a greater tendency toward corrosion.

A visual analysis of the 2nd horizontal viewfinder samples throughout the experiment helped determine a sequence of deposit formation on the pipe walls. Initially, the deposits formed in the entrance segment of the pipe (Figure 3-20). This indicates that there is a fundamental difference between the entrance and exit portions of the pipe. There are two apparent explanations for these variations. First, the stream of flow entering the pipes was more turbulent than the stream of flow exiting the pipe. As shown in our experimental setup, there were 90° and 180° bends in flow directly before each pipe segment (Figure 3-1). The flow was then streamlined along the length of the pipe. This change in flow may have impacted the deposition of particles on the pipe surface.

This preferential corrosion might also be attributed to a higher chlorine concentration at the pipe entrance in addition to a more turbulent flow after the transition between pipe sections. As the water travels through a pipe, the free chlorine, an oxidant, is converted to chloride, which in previous experiments has been shown to decrease the rate of copper corrosion. Although it is hard to believe it would be significant, this reaction does possibly create two distinct chemical environments for the pipe wall at the entrance and exit, since chlorine concentrations may decrease in the laminar flow region near the pipe wall. Since free chlorine promotes the corrosion process, it is understandable that most of the corrosion would take place where its concentration is the highest, at the pipe’s entrance.

**Impacts of polishing on patterns of scale formation on pipe surfaces:**

The effects of polishing the pipe surfaces to remove any imperfections and films were examined by comparing the polished 2nd horizontal viewfinder sample to both the unpolished 1st vertical and 3rd horizontal pipes in the each flow series. There were distinctions between the and unpolished pipe samples as noted earlier, but at present we believe these differences are due to velocities, or the fact that the viewfinder sample lacked up an upper half. Interestingly, even the viewfinder samples, which were polished to a mirror-like finish, showed “lines” of pipe deposits forming under certain conditions. The conditions with the clearest deposit lines were those with lower, intermittent flow patterns. The polished pipes under higher flow conditions, specifically the 240 min/day and the continuous flow samples, did not exhibit lines of scale. This finding is
consistent with the idea that such lines are caused by settling of fine particles from the water in patterns. However, the vertical pipe segments also showed lines of deposits at lower flow frequencies (Figure 3-21). These deposition patterns may indicate the lines may also be caused by the manufacturing of the pipe, although it is also possible the lines were caused by deposition of particles in patterns under centripetal force at the bends. In summary, this work provides some strong evidence that “lines” of pits do not imply that surface imperfections are a cause of pitting.

IV. CONCLUSIONS

The presence of free chlorine leads to higher and more erratic corrosion potentials. Severe pitting was observed in the presence of free chlorine and aluminum at pH 9.2, whereas no pitting was observed in the absence of aluminum.

All pits formed under mounds of copper corrosion byproducts, or tubercles. Two distinct forms of deposits developed on the pipe surfaces, a blue-green and a black deposit. While the blue-green deposits were composed of sulfur, chloride, copper oxide, the black deposits were mainly composed of aluminum, calcium, copper oxide.

Higher corrosion potentials were obtained during flow than during stagnation. The rise in $E_{\text{corr}}$ after a stagnation period may be due to the replenishment of free chlorine with the onset of flow. In the presence of free chlorine, pitting corrosion is more likely to occur at higher flow frequencies.

The location of bends and pipe orientation had more complicated impacts on corrosion tendencies than initially anticipated. At lower flow frequencies, characteristic lines developed on both the horizontal and vertical samples. This deposition is likely caused by the preferential deposition of particles due to gravity or centripetal forces. The top horizontal and outermost vertical entrance sections seem to be the most prone to pitting corrosion. Away from the entrance the short pipes showed little signs of non-uniform corrosion or pitting.

Consistent with the notion that particles settling and sticking to the pipe bottom can catalyze the cathodic reaction, both visual and electrochemical analyses indicate that the bottom horizontal sections tended to be more cathodic.

Surface imperfections from manufacturer are not a likely cause of pitting corrosion in waters of this type, nor are do lines of pits indicate that surface imperfections are involved. It remains possible that surface imperfections could be an indirect contributor to pitting, but that remains to be proven.
ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Copper Development Association (CDA) and the National Science Foundation under grant DMI-0329474. Opinions and findings expressed herein are those of the authors and do not necessarily reflect the views of the National Science Foundaiton or the Copper Development Association.

REFERENCES


Figure 3-1. Experimental setup, flow patterns, and pipe nomenclature. There was a sharp $90^\circ$ bend in flow entering the 1st vertical pipe, followed by a gradual bend between the perpendicular 1st and 2nd pipes, and finally a $180^\circ$ bend in flow between the 2nd and 3rd horizontal pipes.

Table 3-1. Flow Cycles.

<table>
<thead>
<tr>
<th>Program Number</th>
<th>Flow Pattern</th>
<th>Time Flow On (minutes)</th>
<th>Time Flow Off (minutes)</th>
<th>Total Flow Time per day (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Continuous</td>
<td>1440</td>
<td>0</td>
<td>1440</td>
</tr>
<tr>
<td>2</td>
<td>5 minutes, once a day</td>
<td>5</td>
<td>1435</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>5 minutes, 8 times a day</td>
<td>5</td>
<td>175</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>5 minutes, 48 times a day</td>
<td>5</td>
<td>25</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>5 seconds, 8 times a day</td>
<td>0.083</td>
<td>179.92</td>
<td>0.67</td>
</tr>
</tbody>
</table>
Table 3-2. Final Concentration.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity as CaCO₃</td>
<td>34</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>20</td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>17</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>14</td>
</tr>
</tbody>
</table>

Figure 3-2. Cutting of pipes into 8 open sections.
Figure 3-3. Ecorr measurements taken during flow for systems with and without free chlorine.

Figure 3-4. Ecorr measurements taken during stagnation for systems with (closed shapes) and without (open shapes) free chlorine.
Figure 3-5. Ecorr measurements taken before and after the addition of silica and zinc to the system under flow conditions. (Note: silica and zinc not added to Al + Cl₂ experiment).

Figure 3-6. Ecorr measurements of three experimental setups under flow conditions (Three experiments: Al + Cl₂, Al + Si + Zn, and Al + Si, + Zn + NOM).
Figure 3-7. Decrease in pipe mass per year. Dotted line is linear regression.
Table 3-3. Summary of mass decrease in samples exposed to synthetic water containing 4 mg/L of free chlorine.

<table>
<thead>
<tr>
<th>Flow Time (min)</th>
<th>Position</th>
<th>% Decrease per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67</td>
<td>1st and vertical</td>
<td>0.15%</td>
</tr>
<tr>
<td>5</td>
<td>1st and vertical</td>
<td>0.15%</td>
</tr>
<tr>
<td>40</td>
<td>1st and vertical</td>
<td>0.35%</td>
</tr>
<tr>
<td>240</td>
<td>1st and vertical</td>
<td>0.37%</td>
</tr>
<tr>
<td>1440</td>
<td>1st and vertical</td>
<td>2.44%</td>
</tr>
<tr>
<td>0.67</td>
<td>3rd and horizontal</td>
<td>0.47%</td>
</tr>
<tr>
<td>5</td>
<td>3rd and horizontal</td>
<td>1.23%</td>
</tr>
<tr>
<td>40</td>
<td>3rd and horizontal</td>
<td>1.27%</td>
</tr>
<tr>
<td>240</td>
<td>3rd and horizontal</td>
<td>1.67%</td>
</tr>
<tr>
<td>1440</td>
<td>3rd and horizontal</td>
<td>2.31%</td>
</tr>
</tbody>
</table>

Figure 3-8. Continuous flow samples without, A, and with, B, free chlorine.
**Figure 3-9.** Pitting and corrosion byproduct deposition of continuous flow pipe exposed to free chlorine.

**Figure 3-10.** Development of Anodic and Cathodic Regions within a Copper Pipe.
Figure 3-11. Uncovered blue-green deposits on continuous flow copper pipe sample exposed to synthetic drinking water containing 4 mg/L of free chlorine.

Table 3-4. Overall % average composition of deposits on continuous flow pipes exposed to water containing free chlorine.

<table>
<thead>
<tr>
<th></th>
<th>Black</th>
<th></th>
<th>Blue</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic %</td>
<td>Conc. (% wt)</td>
<td>Atomic %</td>
<td>Conc. (% wt)</td>
</tr>
<tr>
<td>[O]</td>
<td>75.1</td>
<td>46.4</td>
<td>69.2</td>
<td>38.9</td>
</tr>
<tr>
<td>[Al]</td>
<td>2.8</td>
<td>2.9</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>[Ca]</td>
<td>1.9</td>
<td>4.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[Cu]</td>
<td>19.8</td>
<td>47.3</td>
<td>24.9</td>
<td>54.3</td>
</tr>
<tr>
<td>[S]</td>
<td>0.3</td>
<td>0.3</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>[Cl]</td>
<td>0.1</td>
<td>0.1</td>
<td>4.4</td>
<td>5.3</td>
</tr>
<tr>
<td>total %</td>
<td>100</td>
<td>102</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 3-12. Overall % atomic composition of inner blue-green and outer black surface deposits.
Figure 3-13. Comparison of Ecorr measurements during stagnation and flow for four alternating flow patterns of 0.67, 5, 40, and 240 min/day.
Figure 3-14. Typical rise in Ecorr with the onset of flow after a stagnation period.
Figure 3-15. Corrosion potential, $E_{corr}$, measurements during flow and stagnation periods for water containing both aluminum and free chlorine.
**Figure 3-16.** Maximum corrosion potentials, $E_{corr}$, for each flow pattern during the course of the experiment.

**Figure 3-17.** Original pipe interior wall.
<table>
<thead>
<tr>
<th>FLOW TIME (min/day)</th>
<th>HORIZONTAL (top over bottom)</th>
<th>VERTICAL (inside over outside)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67</td>
<td>![Image 1]</td>
<td>![Image 2]</td>
</tr>
<tr>
<td>5</td>
<td>![Image 3]</td>
<td>![Image 4]</td>
</tr>
<tr>
<td>40</td>
<td>![Image 5]</td>
<td>![Image 6]</td>
</tr>
<tr>
<td>240</td>
<td>![Image 7]</td>
<td>![Image 8]</td>
</tr>
<tr>
<td>1440 (continuous)</td>
<td>![Image 9]</td>
<td>![Image 10]</td>
</tr>
</tbody>
</table>

**Figure 3-18.** Cut open interior walls of pipe sections exposed to aluminum and free chlorine.
Figure 3-19. Percent decrease in pipe thickness at different flow patterns for the horizontal and vertical segments.
Table 3-5. Measurements for 1\textsuperscript{st} and vertical, 2\textsuperscript{nd} and viewport, and 3\textsuperscript{rd} and horizontal pipe segments of continuous flow program exposed to free chlorite.

<table>
<thead>
<tr>
<th>Date</th>
<th>Ecorr of Viewport (mV)</th>
<th>Differential Current (µA)</th>
<th>Ecorr (mV)</th>
<th>Differential Current (µA)</th>
<th>Ecorr (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/21/2003</td>
<td>254</td>
<td>0.025</td>
<td>192</td>
<td>0.034</td>
<td>244</td>
</tr>
<tr>
<td>7/22/2003</td>
<td>686</td>
<td>0.015</td>
<td>564</td>
<td>0.03</td>
<td>492</td>
</tr>
<tr>
<td>7/23/2003</td>
<td>594</td>
<td>6</td>
<td>429</td>
<td>7.6</td>
<td>404</td>
</tr>
<tr>
<td>7/24/2003</td>
<td>637</td>
<td>6.9</td>
<td>469</td>
<td>8.8</td>
<td>414</td>
</tr>
<tr>
<td>7/25/2003</td>
<td>330</td>
<td>5.6</td>
<td>198</td>
<td>8</td>
<td>150</td>
</tr>
<tr>
<td>AVERAGE:</td>
<td>500</td>
<td>3.7</td>
<td>370</td>
<td>4.9</td>
<td>341</td>
</tr>
</tbody>
</table>

Figure 3-20. Initial formation of deposits on pipes.
Table 3-6. Decrease in thickness of copper pipe exposed to chlorine under continuous flow conditions. The original depth was 0.75 mm.

<table>
<thead>
<tr>
<th>Pipe Segment</th>
<th>Average Depth (mm)</th>
<th>Percent Decrease (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Entrance</td>
<td>Exit</td>
</tr>
<tr>
<td>Horizontal</td>
<td>0.41</td>
<td>0.72</td>
</tr>
<tr>
<td>Vertical</td>
<td>0.44</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Flow (min/day) | Polished | Unpolished
--- | --- | ---
0.67 | ![Polished](image1) | ![Unpolished](image2)
5 | ![Polished](image3) | ![Unpolished](image4)
40 | ![Polished](image5) | ![Unpolished](image6)
240 | ![Polished](image7) | ![Unpolished](image8)
1440 | ![Polished](image9) | ![Unpolished](image10)

Figure 3-21. Comparison of corrosion and scale formation on polished and unpolished horizontal pipes.
CHAPTER 4: PHOSPHATE INHIBITION OF COPPER PITTING CORROSION

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ABSTRACT. This study defines the role of phosphate in mitigation of copper pitting corrosion in synthesized water. Phosphates did not have an effect at pH 7.7 and were found to reduce electrochemical indications of pitting in the synthetic water at the pH of 8.3. Phosphates had lesser benefits at higher pH, but overall, even at pHs as high as 10, some benefits from orthophosphate dosing might be anticipated.

INTRODUCTION

Contrary to conventional belief, recent studies have verified that flowing water containing higher pH and chlorine in the presence of aluminum solids initiates copper pitting (Rushing et al., 2004, Marshall et al. Chapter 3, 2004). In the past, higher pHs were almost always deemed beneficial for copper corrosion, but in these studies pitting corrosion tendencies worsened as pH increased to 9.0. The Rushing hypothesis was unambiguously verified in laboratory experiments by Marshall et al. 2004, as 8 leaks were formed in a 1 foot section of type M copper tube in just over 11 months (Figure 4-1).

Potential mitigation of this type of corrosion was investigated. Since the problem seems to worsen as the pH increases to 9.5, and reducing pH might cause lead or copper leaching, dosing of an inhibitor is desirable. Orthophosphate is among the most promising proposed, as it has controlled copper pitting outbreaks in some circumstances (Edwards, 2002). Given that the activity of orthophosphate may depend on pH, a special focus of this investigation is to determine whether orthophosphate would be effective in a range of pH values as high as pH 9.0, which commonly occurs for distributed water that has contacted concrete.

MATERIALS AND METHODS

Potential Use of Orthophosphate to Stop Pitting

This experiment examined the use of orthophosphate to mitigate copper pitting using water synthesized in the laboratory. 5/8” nominal size copper couplings (surface area = 20 cm$^2$) were purchased from a local hardware store, rinsed with pure water, and placed in Reiber flow-through polarization cells (Reiber et al., 1989). Additionally, two 12 inch long, 5/8” nominal copper pipes were attached to each recirculating system, one of which was cut in half horizontally and sealed with clear plexiglass to visually observe the progression of scale development (Figure 4-2). Sixteen liters of synthesized drinking water was circulated through the copper coupons and Reiber flow cells at a flow rate of 1 gpm. The water was synthesized by adding 0.66 g CaCl$_2$*2H$_2$O, 0.40 g of CaSO$_4$*2H$_2$O and 0.91 g of NaHCO$_3$ to 16 L of distilled and deionized water. The water initially contained 34 mg/L alkalinity as CaCO$_3$, 14 mg/L SO$_4^{2-}$,
20 mg/L Cl\textsuperscript{−}, and 17 mg/L Ca\textsuperscript{2+} added as reagent grade sodium or calcium salts to filter sterilized distilled-deionized water. pH was adjusted to target values by adding 1 M HCl or NaOH, and no attempt was made to maintain alkalinity.

Two concentrations of inhibitor (0 and 1 mg/L as P) were examined at pH 7.7 and 8.3 (4 waters total). The target chlorine and aluminum levels were both 5 mg/L. The Al(OH)\textsubscript{3} stock solution was created by raising the pH of a Al-AlCl\textsubscript{3} solution to 8.0 using NaOH, allowing the solids to settle, decanting the water, re-suspending the solids in fresh water, until the conductivity of the suspension was less than that of the experimental water. To account for possible deposition of aluminum solids within the experimental apparatus, aluminum solids were re-dosed 4 days after each weekly water change. Thus, the actual aluminum concentration could have been as much as double the target levels, and they could have been lower dependent on the loss to the apparatus surface or pipe samples. Photographs were taken of the samples before and after the pH change using a digital camera for a visual analysis.

The pH was adjusted and Cl\textsubscript{2} residuals were replenished daily using bleach (6\% NaOCl). In all experiments, free chlorine was measured using the DPD colorimetric test per standard method 4500-Cl G \cite{8}. pH values were held to \pm 0.2 units of the target value. The water was completely changed weekly and the test was ended on day 34 of the experiment. On day 22, the pH of four samples was increased to 9.0 or 10.0 as specified in later discussion to examine the effects of higher pH on phosphate effectiveness.

Corrosion potential (E\textsubscript{corr}) and polarization resistance (R\textsubscript{p}) measurements were collected hourly using a multiplexer connected to a personal computer, using a polarization scan rate of 0.5 mV/sec from −5 to +5 mV of the open circuit potential. As discussed in previous work by Marshall et al. (2004), it is generally believed that in a typical pipe, E\textsubscript{corr} decreases slowly with time as the surface passivates. However, if E\textsubscript{corr} is increasing with time, the surface is believed to be activating towards pitting. Platinum counter and Ag-AgCl reference electrodes were checked and maintained regularly to insure accuracy.

**RESULTS AND DISCUSSION**

**Effects of Orthophosphate and pH on Copper Corrosion in Synthetic Water**

**Chlorine Decay Kinetics.** Chlorine can react with (corrode) copper surfaces according to the following balanced general equation:

\[
\text{OCl}^- + \text{Cu (metal)} \rightarrow \text{CuO} + \text{Cl}^- \quad \text{Equation 1}
\]

As a result of this reaction, free chlorine is converted to chloride, and the copper metal is oxidized or corroded. While copper can also be corroded by oxygen reduction, and chlorine can decay spontaneously by other pathways such as volatilization, the rate of chlorine decay may be related to the copper corrosion rates.
Chlorine decay rates were calculated by tracking the loss of chlorine after 24 hours and calculating the rate in terms of mass Cl\textsubscript{2} lost per unit pipe surface area, (\(\mu g \text{ Cl}_2\) lost/cm\textsuperscript{2}). The percent decrease in chlorine decay rate due to orthophosphate was calculated as follows:

\[
\%\text{decrease} = \frac{(R - R_p)}{R} \times 100
\]

Equation 2

Where:  
\(R\) = decay rate without phosphate, \(\mu g/cm^2\) \n\(R_p\) = decay rate with phosphate, \(\mu g/cm^2\)

A 0\% decrease indicates that chlorine decay does not change, whereas a 50\% decrease indicates that the presence of orthophosphate cut the rate of chlorine decay in half. The presence of orthophosphate generally led to a 34-53\% reduction in chlorine decay rates in the systems tested (Table 4-1). This suggests that throughout the experiment the phosphate was interfering with the cathodic reaction between copper metal and free chlorine, resulting in higher chlorine residuals in the system containing phosphate. These higher chlorine residuals can be expected to make the water more aggressive in the context of this particular copper pitting mechanism (Figure 4-3 and 4-4). Somewhat surprisingly, the rate of chlorine decay was not a strong function of pH.

**Corrosion Potential**

In addition to chlorine decay, electrochemical data were collected for each pH condition in duplicate (Figure 4-5 and 4-6). On day 23, 550 hours into the experiment, the pH of one of the duplicate samples at both pH 7.7 and 8.3 was increased to examine the effects of higher pH values on the effectiveness of orthophosphate. Samples at pH 7.7 were raised to pH 9.0 and the samples at pH 8.3 samples were raised to pH 10.0. Corrosion potential (\(E_{corr}\)) was affected by both pH and the presence of phosphate in the system. In the systems not exposed to the pH increase and maintained at pH 7.7, there was small difference in \(E_{corr}\) values of samples with and without phosphate (Figure 4-5). This is probably due to the fact that even in the presence of aluminum, pitting is not observed at this pH in the first place (Edwards, 2002). At pH 8.3, the samples containing phosphate consistently yielded lower \(E_{corr}\) values (Figure 4-6). In the cases where pH is raised above 9.0, \(E_{corr}\) spiked upwards 100’s of mV even if phosphate was present. We interpret this to indicate that, while orthophosphate greatly reduces the pitting type activity at higher pH, it does not completely inhibit spikes in \(E_{corr}\). On the basis of existing understanding and the very limited data collected in this short term test, the suggestion is that phosphates would be ineffective at pH 7.7, greatly reduce pitting frequency at pH 8.3, be less effective at pH 9.0, and would be quite effective at pH 10 relative to the synthesized water at the same pH without phosphate.

Another distinction was observed in the typical response to daily pH and chlorine adjustments using sodium hydroxide (NaOH) to increase pH and redosing free chlorine to target values (Figure 4-7). \(E_{corr}\) decreased in samples containing phosphate, whereas samples without phosphate showed a rapid spike upwards in \(E_{corr}\). This further demonstrates that orthophosphate is fundamentally changing the reaction between the copper metal and the chlorine, as was already established previously in Table 4.1. This is also interpreted to indicate that orthophosphate ameliorates the potentially harmful effects of chlorine on copper corrosion.
In general, at pH 8.3, the samples without phosphate had a larger daily fluctuation in $E_{\text{corr}}$. Specifically, $E_{\text{corr}}$ typically varied by 40 mV in the system without phosphate, versus 13 mV with phosphate. This may be due to the greater variation of the free chlorine concentration within the water, since chlorine was decaying at a higher rate in the system without phosphate. It is not understood whether this is good or bad in the context of pitting, although variations in $E_{\text{corr}}$ (i.e., electrochemical noise) are often believed to be an indicator (albeit a poor indicator) of pitting.

The maximum corrosion potentials ($E_{\text{corr}}$) were determined for samples before and after the increase in pH (Figure 4-8). The selection of the maximum $E_{\text{corr}}$ excluded data that was known to be faulty as determined using electrode QA/QC. To summarize the results, the $E_{\text{corr}}$ was affected by pH, as well as the presence of orthophosphate within the system. In all cases, higher pH increased the maximum $E_{\text{corr}}$ attained. At pH 7.7, the sample with phosphate had a lower maximum $E_{\text{corr}}$. In contrast, when the pH was increased to 9.0, the sample with phosphate had a higher maximum $E_{\text{corr}}$ than the sample without phosphate. At pH 8.3, the samples containing phosphate seemed to have a distinct advantage with lower maximum $E_{\text{corr}}$ values. For instance, at pH 8.3, the maximum measured $E_{\text{corr}}$ for the sample without phosphate was 156 mV compared to only 71 mV for the sample with phosphate at the same pH. When the pH was raised from 8.3 to 10.0, a large increase in $E_{\text{corr}}$ was observed for samples with and without phosphate. Even though the phosphate appeared to have lost some of its useful effects at this much higher pH, the maximum $E_{\text{corr}}$ was still much less when phosphate was not present.

The highest potential obtained at pH 10 is noteworthy. The maximum voltage for copper at pH 10 is +829 mV, above which water begins to break down into hydrogen and oxygen (Snoeyink and Jenkins, 1980),

$$2\text{H}_2\text{O} \leftrightarrow \text{O}_2(g) + 4\text{H}^+ + 4\text{e}^- \quad \text{Equation 3}$$

which is very close to the observed value of +824 mV. In other words, it is highly possible that the following reaction is occurring at the copper surface.

$$2\text{Cl}_2 + 2\text{H}_2\text{O} \leftrightarrow 4\text{Cl}^- + \text{O}_2(g) + 4\text{H}^+ \quad \text{Equation 4}$$

By comparing the samples at pH 7.7 and 8.3 without phosphate, the effects of pH are obtained. The maximum $E_{\text{corr}}$ readings for both samples were comparable, however, at pH 8.3 the $E_{\text{corr}}$ values were consistently in the range of 250 mV, while the $E_{\text{corr}}$ values at pH 7.7 were much more sporadic, ranging anywhere from 50 to 220 mV (Figure 4-5 and 4-6). The increase in pH had a much more profound effect on the sample previously exposed to pH 8.3 water. For the sample initially at pH 7.7, the maximum $E_{\text{corr}}$ increased about 66 mV when raised to pH 9.0, whereas the sample initially at pH 8.3 sample increased about 669 mV when raised to pH 10.0. It is clear that final pH is an important controlling factor in these synthesized waters. At present, we do not know whether the pH of initial exposure plays a role, although it could.

**Visual Analysis**
Orthophosphate and pH had profound impacts on the visual characteristics of copper corrosion and scale formation (Figure 4-9). Prior to increasing the pH at 7.7 or 8.3, the samples with phosphate developed a blue-green scale, while the equivalent samples exposed to the same water without phosphate had a brown-black scale buildup. When the pH was increased, the appearance of the samples without phosphate remained unchanged; however, the samples with phosphate began to turn brownish-black (Figure 4-9). This change in color occurred at the same time $E_{corr}$ increased, although we cannot be certain the two effects are correlated. When the sample containing phosphate was raised to pH 10, it began to turn color almost immediately, whereas the sample with phosphate raised to pH 9.0 took several days before a complete change in appearance was observed. From these results, it is obvious that phosphate dramatically alters the scale that is present. It is also clear that at pH 9.0, phosphate has dramatically different effects than in the same water at pH 8.3.

CONCLUSIONS

The following conclusions are drawn from experimental results.

- In the synthetic water at pH 7.7, there was not much evidence of pitting as was expected based on previous results. Phosphates did not have much effect on $E_{corr}$ in such systems.
- Phosphates reduced electrochemical indications of pitting in the synthetic water at the pH of 8.3 compared to synthetic water without phosphate. This is deemed very important, since many waters in which aluminum, Cl$_2$, and higher pH are thought to cause pitting are in the range of pH 8.3.
- Phosphates had lesser benefits at higher pH even in synthetic water, but they were clearly having impacts on scale formation. Overall, even at pHs as high as 10, some benefits from orthophosphate dosing are anticipated based on measurements of $E_{corr}$.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Copper Development Association (CDA) and the National Science Foundation under grant DMI-0329474. Opinions and findings expressed herein are those of the authors and do not necessarily reflect the views of the National Science Foundation or the Copper Development Association.
REFERENCES


**Figure 4-1.** Photo illustrating two of seven fully penetrating pits formed in a 12 inch section of type M copper pipe. These breakthrough pits were formed in less than 11 months.

**Figure 4-2.** Experimental setup and flow pattern in recirculating system.

**Table 4-1.** Chlorine Consumption in Synthetic Water.

<table>
<thead>
<tr>
<th>pH</th>
<th>Chlorine Consumption (ug/cm³)</th>
<th>% Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With P</td>
<td>Without P</td>
</tr>
<tr>
<td>7.7</td>
<td>48.1</td>
<td>82.2</td>
</tr>
<tr>
<td>8.3</td>
<td>54.3</td>
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<td>91.5</td>
</tr>
<tr>
<td>10</td>
<td>43.4</td>
<td>91.5</td>
</tr>
</tbody>
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**Figure 4-3.** Daily Chlorine Residual at pH 7.7.

**Figure 4-4.** Daily Chlorine Residual at pH 8.3.
Figure 4-5.  \( E_{\text{corr}} \) for copper exposed to synthetic water initially at pH 7.7, but then raised to 9.0 in a few cases.

Figure 4-6.  \( E_{\text{corr}} \) in synthetic water initially at pH 8.3, but then raised to pH 10.0 in a few samples.
Figure 4-7. Typical $E_{\text{corr}}$ Response to Daily pH and Cl$_2$ Adjustment.

Figure 4-8. Maximum $E_{\text{corr}}$ Readings Before and After pH Increase.
**Figure 4-9.** Visual comparison of samples before (top row) and after pH increase (bottom row) at end of experiment.
CHAPTER 5: ORTHOPHOSPHATE INHIBITION OF COPPER PITTING CORROSION IN POTABLE WATER

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ABSTRACT. This study investigates the effect of orthophosphate on the inhibition of copper pitting corrosion in treated water from a utility in Washington D.C. (WSSC), whose consumers have experienced an outbreak of pinhole leaks in household copper plumbing. After comparing electrochemical results from synthetic and actual water from the treatment plant, there was evidence of a natural inhibitor to pitting corrosion in WSSC water that is not present in the synthetic water. The higher chloride concentration in the water after ferric chloride was dosed at the treatment plant may have reduced the pitting propensity of the water. The effects of phosphates seemed to reduce the pitting propensity of real water at pH 8.3 and little benefit was seen at pH 9.1.

INTRODUCTION

Recent research has indicated that certain water treatment and distribution system conditions can increase the pitting propensity of potable water towards copper tube used in domestic plumbing (Rushing 2002a, Marshall et al., 2004). However, under some seemingly similar circumstances where all key ingredients that make water aggressive to copper tube are present, pitting does not occur. This clearly points to secondary factors in drinking water that can ameliorate or completely inhibit pitting attack. Natural organic materials are believed to be among the best known natural inhibitors of pitting, but other factors such as chloride, pH and sulfate can also play a decisive role (Campbell, 1954a, 1954b and 1979; Edwards et al., 1994a and 1994b; Rehring et al., 1996; McNeill et al., 2003). NOM, chloride, sulfate and pH are all influenced by coagulation processes at treatment plants, with the most pronounced impacts associated with higher coagulant doses used during enhanced coagulation (Rehring et al., 1996; McNeill et al., 2003).

Since pinhole leaks were only recently reproduced in the laboratory as they occur in practice (Marshall et al., Chapter 3, 2004), all previous work on inhibition by natural compounds or chemical additives must be viewed with caution, as the interpretation of electrochemical or other short-term data is no more accurate than existing theory. Certain types of extrapolations based on short term experimental data have previously been proven to be inconsistent with actual experiences with copper tube failure in practice, dependent on exposure duration, overpotential that is applied, and failure to adequately reproduce natural water chemistries (Edwards et al., 1994a).

High $E_{corr}$ has been related to actual formation of pinhole leaks during previous research which proved that water containing aluminum and free chlorine at high pH could form pinhole leaks in copper pipe under scientifically reproducible conditions (Rushing et al., 2002a; Marshall et al., 2004).
2004). Consequently, there is relatively high certainty that for attack of this type, water quality factors that decrease $E_{corr}$ will reduce the severity of pitting attack as it occurs in practice.

The water synthesized in the laboratory that caused pitting used bulk salt concentrations closely representative of those present at many utilities whose customers had observed high rates of pitting attack. However, the waters lacked natural organic matter and silicates which are considered by some to inhibit certain aspects of copper corrosion (Campbell, 1954a, 1954b and 1979; Edwards et al., 1994a and 1994b; Rehring et al., 1996; McNeill et al., 2003). Most of the previous research to advance the understanding of copper corrosion (Edwards, Rushing, Marshall et al., 2000-2004) has been conducted under scientifically reproducible conditions using synthetic water. Thus, the goal of this case study is to examine the role of both natural and dosed inhibitors, such as orthophosphate, as a means of preventing pinhole leaks in real treated water.

**MATERIALS AND METHODS**

**Potential Use of Orthophosphate to Stop Pitting**

This experiment utilized synthesized water in an initial phase to commence pitting, followed by use of real treated water from the Washington Suburban Sanitary Commission (WSSC), whose consumers were experiencing an outbreak in copper pitting. WSSC water was shipped to the Virginia Tech research laboratory to examine the effects of orthophosphate in reducing pitting in real WSSC water at constant pH, aluminum, and chlorine concentrations. The pits were initiated on 24 copper coupons by circulating synthetic water containing 5 mg/L chlorine through the pipes in the presence of 5 mg/L aluminum at pH 9.2. On day 36, a conditioning process was started where real WSSC water, without the addition of chlorine or aluminum solids, was circulated through the pipes at pH 9.2. Eight of the copper couplings were then placed in Reiber flow-through polarization cells, with two of the remaining copper couplings attached to each recirculating system.

Six of the eight samples examined contained 1 mg/L of phosphate and were tested in duplicate at pH 8.3, 8.7, and 9.1. The remaining two samples were used as controls without phosphate at pH 8.3 and 9.1. During this phase of the exposure, all samples had a target chlorine concentration of 4 mg/L but no aluminum was added to WSSC water. The pH was adjusted and Cl$_2$ residuals were replenished daily using bleach (6% NaOCl). In all experiments, free chlorine was measured using the DPD colorimetric test per standard method 4500-Cl G [8]. pH values were held to ±0.2 units of the target value. The water was completely changed weekly.

Corrosion potential ($E_{corr}$) and polarization resistance ($R_p$) measurements were collected hourly using a multiplexer connected to a personal computer, using a polarization scan rate of 0.5 mV/sec from −5 to +5 mV of the open circuit potential. Platinum counter and Ag-AgCl reference electrodes were checked and maintained regularly to insure accuracy. On day 73 the effects of surface deposits on the inhibition of corrosion were examined by physically removing scale from one coupon at pH 8.3 and performing an electrochemical tafel analysis. The tests were ended on day 74 of the experiment. At the end of the experiment, photographs were taken of the corroded copper surfaces using a digital camera.
An additional short term jar test experiment was then competed to investigate the effects of different chloride levels on the corrosion of copper metal both with and without aluminum solids. A total of 8 different chloride levels were tested both with and without aluminum, making 16 samples total. A synthetic water, designed to simulate the salt content found at WSSC, was used in these experiments and initially contained 34 mg/L alkalinity as HCO$_3^-$, 14 mg/L $\text{SO}_4^{2-}$, and 6 mg/L Ca$^{2+}$ added as reagent grade sodium or calcium salts to filtered distilled-deionized water. Target chloride levels, 0, 20, 30, 50, 100, 200, 500, and 3200 mg/L, were then obtained by adding NaCl. All samples were adjusted to pH 9.2 by adding 1 M NaOH and contained 5 mg/L of both Cl$_2$ and Al(OH)$_3$ solids as Al. pH was adjusted and Cl$_2$ residuals were replenished every 8 hours and no attempt was made to maintain alkalinity. Corrosion potential and chlorine decay kinetics were examined for a minimum of 24 hours.

RESULTS AND DISCUSSION

Effects of Orthophosphate and pH on Aspects of Copper Pitting in Real WSSC Water
This experiment revealed several key differences between the synthetic and real water. In this test, the copper pipe samples were pre-exposed to the synthetic water containing high levels of chlorine, aluminum, and at a pH of 9.2. The goal was to initiate serious pitting of the surface using the principles defined and proven in earlier tests. Thereafter, real WSSC water was circulated through the samples to investigate the effects of orthophosphate on corrosion in this media.

Chlorine Decay Kinetics.
To compare chlorine decay results of experiments with different setups, the rates were normalized as follows:

$$\left(\text{Cl decay rate}\right) \times \frac{\text{Volume of water}}{\text{surface area}} = \text{normalized decay rate}$$

or

$$\frac{\mu g}{L \times d} \times \frac{1}{cm^2} \times L = \frac{\mu g}{cm^2 \times d}$$

Equation 1

Contrary to what was previously observed in laboratory tests with synthetic water (Marshall and Edwards, 2004), there was only a slight difference in chlorine decay rates in WSSC water with phosphate compared to the same water without phosphate (Table 5-1). For instance, while previous experiments with synthetic water revealed a 28 $\mu g/cm^2$ per day higher decay rate in the samples without phosphate, the chlorine decay rate was only 5 $\mu g/cm^2$ per day faster in the sample without phosphate in WSSC water at pH 8.3. This was the first indication that there was something in the real WSSC water that greatly reduced the rate of reaction between free chlorine and the copper. While the comparison is not perfect due to small differences in the experimental setup in the synthetic water versus real water tests, between 17-55% lower chlorine decay rates were observed in real WSSC water compared to the synthetic water test at the same pH (Table 5-1). This is even more surprising given that WSSC water likely contains organic matter and other substances that would have a chlorine demand compared to the synthetic water.
Unbeknownst to the research team at Virginia Tech, the real water used in testing had been treated with alum prior to January 21, 2003, but treated with ferric chloride after that time. In water samples shipped to Virginia Tech which had been treated with alum, the chlorine residual varied over a wider range than in the water treated with ferric chloride (Figure 5-1), even though we used the exact same chlorine dosing scheme. It is also noteworthy that pH no longer seemed to have an effect on the chlorine decay rate because all samples seemed to follow the same trend (Figure 5-1).

What might be causing these differences between WSSC water treated with alum and ferric chloride? One possible explanation is the difference in chloride levels, with the water treated with ferric chloride having a higher chloride concentration of 36-41 mg/L, compared to 20-25 mg/L chloride in the water treated with alum. To test this idea, chlorine decay data were collected to support the notion that the effect of aluminum on higher chloride levels in the water treated with ferric chloride lead to more stable chlorine residual concentrations as compared to that of the water treated with alum. To show this relationship, the range of chlorine residuals shown in Figure 5-2 were calculated as follows:

\[(\text{Maximum Chlorine Decay Rate}) - (\text{Minimum Chlorine Decay Rate}) = (\text{Decay Rate Range})\]

Therefore, the smaller the range in chlorine decay rate, the more stable the chlorine concentration within samples throughout the experiment.

Chlorine decay rates generally increased with chloride concentration (Figure 5-3). The presence of Al(OH)$_3$ solids also seemed to have an effect on chlorine decay rates at lower chloride levels. For instance, the chlorine levels in samples containing aluminum at lower chloride levels of 0, 20, and 30 mg/L decayed faster than the samples without aluminum (Figure 5-3). This effect seemed to lessen in samples containing aluminum at higher chloride levels of 50, 100, 200, 500, and 3200 mg/L.

**Corrosion Potential.**

All copper samples were previously exposed to the same pit initiation step using synthetic water with aluminum and 5 mg/L chlorine at pH 9.2. Thereafter, they were switched to WSSC water at a given target pH and level of phosphate. In terms of $E_{corr}$, immediately after the switch was made to WSSC water, $E_{corr}$ dropped by approximately 200 mV before we could take our first measurement after a few minutes (Figure 5-4). This could be due to many factors including; aluminum was no longer dosed to the WSSC water whereas it was dosed to the synthetic water, the target free chlorine level was also lowered from 5 down to 4 mg/L, or certain substances in the WSSC water were responsible for reducing the $E_{corr}$ directly. For reasons that are discussed later, the latter prospect is deemed most likely.

A given sample from WSSC was recirculated throughout the samples for a given period of time (a week or two), before it was replaced with a fresh WSSC water sample. “Spikes” in $E_{corr}$ for a given condition occurred whenever the water was changed and “new” WSSC water was recirculated through the copper samples (Figure 5-5). These temporary spikes in $E_{corr}$ did not occur as regularly after about 1000 hours. Upon reflection, we suspect that this could be due to the change in coagulant used for the WSSC water, and the higher amount of Cl$^-$ in the water. Another possible contributing factor to the absence of large $E_{corr}$ spikes when the water was treated with ferric chloride is that water treated with alum may have contained more residual...
aluminum. This was not determined during the test, since we did not know in advance that the coagulant would be changed. If aluminum was higher in alum treated water, this could also be a factor, since WSSC water with added aluminum has previously exhibited greater pitting tendencies in the presence of chlorine when compared to the same water without extra aluminum (Edwards, 2002). We do not have any data as to effects of ferric iron on rates of chlorine decay in the presence of WSSC water or in synthetic water. Finally, the relative merits of ferric chloride versus alum have been manifested for copper corrosion by-product release in previous work (Rerhing et al., 1996), although this was attributed to the difference in chloride versus sulfate in the final water.

Due to the relatively narrow range in $E_{\text{corr}}$ values and the complexity of the results, the data was examined more closely in an attempt to extract additional useful information and trends related to phosphate inhibition. If the percent difference between the $E_{\text{corr}}$ values of the samples with and without phosphate is calculated as follows:

$$\Delta E_{\text{corr}} = (E_{\text{corr}} \text{ with phosphate}) - (E_{\text{corr}} \text{ without phosphate})$$  \hspace{1cm} \text{Equation 2}

Assuming that a higher $E_{\text{corr}}$ is an indication of higher pitting tendencies, if the above difference in $E_{\text{corr}}$ is negative, the effect of phosphate is beneficial (Figures 5-6 and 5-7). For both pH 8.3 and 9.1, the presence of phosphate seemed have an initial detrimental effect on the corrosion potential (i.e., increased pitting tendencies). Between 300 and 1200 hours, the samples dosed with phosphate had a relative positive effect, or decreased pitting tendencies when compared to the samples without phosphate. The benefit was more obvious at pH 8.3 than at 9.0, as might be expected based on results of previous experiments using synthetic water (Marshall and Edwards, 2004). These tests indicated that phosphate may lose some of its inhibition abilities at higher pH levels above pH 9.

After about 1200 hours, there was no evident advantage to using phosphate in WSSC water in the context of $E_{\text{corr}}$ at pH 8.3, although some benefits were noted in one of the two samples at pH 9.1. These results may be due to a change in water composition. After 1200 hours, we started using the water shipped from WSSC that had been treated with ferric chloride instead of alum as a coagulant. Implications of this are discussed in more detail in the following section.

**Tafel Analysis**

Tafel analysis was conducted on copper samples before and after the scale was removed (Figure 5-8). In a normal situation, scaling is protective to the metallic pipe, since it provides mass transfer and reactive barriers to reduction reactions at the cathode and allows buildup of copper ions at the anode. In this unusual case, however, the scale is accelerating the rate of both the anodic and the cathodic reaction. Removal of the scale layer decreased the overall rate of corrosion from 0.06 uA/cm$^2$ TO 0.18 uA/cm$^2$.

**Overall Comparison of Synthetic and Real WSSC Water**

Synthesis of data from the two phases of this experiment, pit initiation with synthetic water and propagation using WSSC water, illustrates two dramatic trends. First, in relation to factors
controlling pitting tendencies, the WSSC water had remarkably lower pitting propensity than the synthesized water. Because of this, impacts of phosphate were more difficult to distinguish in these short-term tests in real WSSC water. It was also suspected that a change in the pitting propensity of WSSC water occurred in the middle of the study. After the study was completed, it was determined the coagulant had been changed, and this was one possible explanation.

It is useful to compare the composition of the synthetic water to that typical for WSSC water treated by alum and WSSC water treated by ferric chloride (Table 5-2). Alkalinity, Ca\(^{2+}\), sulfate levels are very similar in these waters as was desired based on the design of the experiment. However, organic matter, silica, and nitrate were not added to the synthesized water. It is possible that the absence of these trace constituents is mostly responsible for the major difference in corrosivity, especially since it is believed that NOM inhibits copper pitting tendencies (Edwards et al., 1994a).

It is also interesting to note that chloride was 1.7 times higher after the water was treated by ferric chloride. This could also have benefits to pitting, since higher chloride is noted to decrease \(E_{corr}\) of copper samples, and also reduce pitting tendencies (Edwards et al., 1994b). This is also a potential explanation for decreases in \(E_{corr}\) with time during synthetic water and real water experiments. That is, due to reaction 3, \(Cl^-\) concentration was building up in samples with time as free chlorine was replaced. Based on our measurements, increases in chloride concentration up to 1.5 times were occurring in the synthetic water tests, and not much else was changing in the water with time. Thus, the data support the idea that higher \(Cl^-\) in the water after ferric chloride dosing was having effects on \(E_{corr}\).

Additional jar tests confirmed higher chloride levels may affect the likelihood for copper to corrode. Initially, the samples containing higher levels of chloride showed a significantly lower potential to corrode. This is illustrated by representative samples in Figure 5-10. Although the \(E_{corr}\) of samples containing 500 and 3200 mg/L of chloride increased, they leveled off and remained lower than the samples at lower chloride concentrations of 0 and 20 mg/L.

Regardless of the exact causes, higher chloride levels may explain the reduced benefits from phosphate dosing to real WSSC water. While phosphate was nearly always beneficial, it did require time before effects were observed, and the data had to be examined very closely to find significant trends.

The relative pitting propensity of WSSC versus the synthesized water is also obvious based on simple visual observations of the samples. In the synthesized water, tens of protuberances (possible tubercles) were present in an inch long section of copper coupling (Figure 5-11). We believe that all these tubercles were formed in the synthetic water, and not in the WSSC water exposure, and this is the reason there is not an obvious visual difference between the condition with and without phosphate. In forensic analysis of failures from homes of WSSC customers, even one tubercle per inch of pipe would be deemed extraordinarily high. In summary, while it is believed that the trends noted in synthesized water are directly relevant to the problem at WSSC, trace constituents such as NOM are probably playing as important a role in controlling pitting as does the added orthophosphate. In some ways, dosing of orthophosphate is probably only replacing a portion of this “natural” inhibiting capability, and maybe only for waters at pH 8.3. Indeed, it is quite possible that use of ferric chloride coagulant instead of alum or PACl might have more benefits to pitting frequency than dosing of orthophosphate in this water, but
this must be considered speculative at this time. Under the circumstances, any benefits from orthophosphate would be highly desirable, and its dosing is therefore recommended.

CONCLUSIONS

The following conclusions are drawn from experimental results.

- There is a natural inhibitor to pitting corrosion in WSSC water that is not present in the synthetic water. Silica and NOM seem to be the most likely candidates.
- When we put fresh WSSC water into the rig, \( E_{corr} \) spiked up, before slowly coming down as the test progressed. We interpret this to indicate that in our tests with WSSC water, either something was building up during the test that tended to decrease pitting intensity (as measured by \( E_{corr} \)), or something that was promoting pitting was being removed from the water. It is known that chloride was building up during the test. It is unknown what was happening to aluminum levels in the water during the test. These seem to be two likely possible explanations for the phenomena.
- The higher chloride concentration in the water after ferric chloride was dosed at the treatment plant may have reduced the pitting propensity of the water. This could be due to higher chloride in the water, or reduced aluminum, or both.
- In real WSSC pipes where pitting is a serious problem, about one pit is observed every 3 inches or so. In the synthetic water experiments (i.e., Table 5), tens of possible tubercles were formed per inch in a period of one month. It follows that the relatively low pitting density in WSSC water makes benefits of phosphate dosing harder to detect, even though the rate of pitting is unacceptably high to WSSC customers.
- In WSSC water, phosphates were helping to reduce the pitting propensity of the real water at pH 8.3 after a period of days exposure. However, even though the result must be deemed of low confidence, if the water had high chloride from ferric chloride treatment, benefits of phosphate might be less significant due to higher chloride or less aluminum in the water.
- At pH 9.1 benefits of phosphate dosing are very hard to see. However, the trend is toward slight benefits with time.
- As shown in the data, water treated by alum and ferric chloride exhibit major differences in non-uniform copper corrosion behavior.

ACKNOWLEDGEMENTS

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REFERENCES


Table 5-1. Chlorine Consumption of Synthetic vs. WSSC Water.

<table>
<thead>
<tr>
<th>Consumption (μg/cm² per day)</th>
<th>Synthetic Water</th>
<th>WSSC Water</th>
<th>% Reduction</th>
</tr>
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<tbody>
<tr>
<td>pH 8.3 with P</td>
<td>54.3</td>
<td>37.2</td>
<td>31%</td>
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<tr>
<td>pH 8.3</td>
<td>82.2</td>
<td>41.9</td>
<td>49%</td>
</tr>
<tr>
<td>pH 9.1 with P</td>
<td>48.1</td>
<td>39.7</td>
<td>17%</td>
</tr>
<tr>
<td>pH 9.1</td>
<td>91.5</td>
<td>41.4</td>
<td>55%</td>
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</tbody>
</table>

Figure 5-1. Chlorine Residuals Measured Daily.
Figure 5-2. Range in chlorine decay for different chloride concentrations with and without aluminum solids. Value calculated by subtracting the minimum rate from the maximum chlorine decay rate from each sample.

Figure 5-3. Average chlorine decay rates for waters with different chloride levels. Values averaged for the first 24 hours of each experiment.
Figure 5-4. Average Ecorr readings for initiation Stage with synthetic water and propagation stage with WSSC water.

Figure 5-5. Average $E_{corr}$ for samples in WSSC water. Arrows indicate water changes.
Figure 5-6. Delta $E_{\text{corr}}$ Between Samples with and without Phosphate for pH 8.3.

Figure 5-7. Delta $E_{\text{corr}}$ Between Samples with and without Phosphate for pH 9.1.
Figure 5-8. Tafel analysis for sample at pH 8.3 before and after scale removal.

Figure 5-9. Tafel analysis for samples at pH 8.3 with and without orthophosphate (1 mg/L PO$_4$-P).
Table 5-2. Chemical Composition Comparison of Synthetic and WSSC Water.

<table>
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<tr>
<th></th>
<th>units</th>
<th>Synthetic Water</th>
<th>WSSC water (Alum)</th>
<th>WSSC water (Ferric Chloride)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity as CaCO₃</td>
<td>mg/L</td>
<td>34</td>
<td>33-38</td>
<td>30-36</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>mg/L</td>
<td>20</td>
<td>20-25</td>
<td>36-41</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>mg/L</td>
<td>17</td>
<td>17-18</td>
<td>17-20</td>
</tr>
<tr>
<td>NO₃ as N</td>
<td>mg/L</td>
<td>0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Silicon</td>
<td>mg/L</td>
<td>0</td>
<td>2.9-3.2</td>
<td>3-3.6</td>
</tr>
<tr>
<td>Sulfate</td>
<td>mg/L</td>
<td>14</td>
<td>7.7-13</td>
<td>13.4</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>0</td>
<td>1.7-2</td>
<td>1.6-2.2</td>
</tr>
</tbody>
</table>

Figure 5-10. Corrosion potential as a function of time for representative samples with different chloride levels.
Figure 5-11. Visual Comparison of Tubercle Formation.
CHAPTER 6: ASSESSING COPPER PINHOLE LEAK PROBLEMS LOCALLY AND NATIONALLY

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ABSTRACT. Previous research identified several key factors in copper pitting corrosion. A case study at a water utility in Roanoke, VA attempts to apply these procedures to systematic evaluation of the problem. That case study further supported the hypothesis that high levels of aluminum, chlorine, and pH may be combining to catalyze copper pitting in practice. Recommendations to alter the treatment strategies at these utilities were proposed to help mitigate pitting corrosion problems in these areas. A national survey then confirmed pitting is occurring at a significant rate in large utilities across the U.S.

INTRODUCTION

The rates of copper pinhole leaks have reached crisis levels in some localities and there is evidence that new regulations may be contributing. Specifically, more stringent water quality standards have forced water utilities to make unprecedented changes to their treatment processes. These changes include the removal of natural organic matter (NOM), to reduce the concentration of disinfection by-products using enhanced coagulation processes. To meet EPA regulations on lead and copper corrosion by-product release to water, pH values are increasing. Many utilities are also aggressively lining larger water mains with cement, which can dissolve and leach into the water, thereby raising pH and aluminum concentrations. As noted by Rushing et al. (2002a; 2002b), in combination these trends can alter the chemistry of water contacting pipes in consumers’ homes and increasing the pitting propensity of distributed water as noted by Edwards et al., (1994a).

To help assess this developing problem in actual water treatment facilities, a case study was completed for the Roanoke water system and was based on experiments at the Washington Suburban Sanitary Commission (WSSC), a utility experiencing significant copper pitting. In addition, a substantial telephone survey of large utilities in the United States was undertaken to assess the national significance of this corrosive pitting problem.

ROANOKE CASE STUDY

A case where changes in treatment processes might have impacted pinhole leak frequency was reported by WSSC, whose consumers were experiencing an outbreak of cold water copper pitting in homes. In previous work at this utility described in Rushing (2002a; 2002b) and Edwards (2002), circumstantial evidence was gathered suggesting that the problem was partly caused by aluminum deposits on the pipe. Research projects on WSSC water have determined specific conditions under which aluminosilicate deposits seemed to initiate copper pitting
corrosion (Rushing et al, 2004). While the specific sources of these aluminum deposits are unknown, possible sources include raw water, carryover from poly-aluminum chloride coagulant (PACl), and dissolution of cement-based distribution system materials that contained aluminum. One of the most startling findings was that if Cl\textsubscript{2} and aluminum were present, the tendency of copper to pit actually became worse at higher pH. In the past, higher pH values were almost always deemed beneficial for copper corrosion, but in this case pitting corrosion tendencies were worsened as pH increased to 9.0 (Rushing, Marshall et al, 2003; Marshall et al, 2004). The latest study completed (Marshall and Edwards, 2004) also indicated that pitting was most likely to occur near bends and pipe entrances.

As was the case at WSSC, a post mortem investigation of a recent copper failure from pinhole leaks in the Roanoke water distribution system in Virginia led to identification of significant aluminum deposits on the pipe surface. Efforts were made to determine the possible sources and concentrations of aluminum within the Roanoke water treatment and distribution systems, as well as to recommend possible corrosion control strategies.

To fully understand the history and possible sources of the copper corrosion and pitting problems in the Roanoke water distribution system, a survey of local plumbers and a historical investigation of both the treatment and distribution of water throughout the system was conducted. These two methods helped characterize the frequency of current corrosion problems, as well as determine historical trends of corrosive pitting.

The Roanoke County and Roanoke City water utilities both supply water from many different sources. However the two main sources are Spring Hollow Reservoir and Carvin’s Cove. Other less significant sources include Crystal Springs, Vinton, water purchased through contract from the City of Salem, and a series of drilled wells.

Water quality reports for each of these sources were analyzed from 1999-2002 to understand the characteristics of the different waters entering the system (Appendix A). The average levels of chloride and free chlorine within the waters are noteworthy. Chloride and free chlorine have different effects on corrosion. Higher chloride levels have been found to have a beneficial effect by reducing the severity of copper pitting. However, higher levels of free chlorine have been shown to increase the propensity of copper pitting corrosion. Both Spring Hollow and Carvin’s Cove water sources had low chloride levels (approximately 9 ppm), which decreases the beneficial effects of chloride against pitting. High free chlorine levels (2.3 ppm) were also reported in the Carvin’s Cove system, thereby increasing potential for corrosive pitting within the system. Spring Hollow had a lower average free chlorine level of 1.1 ppm.

In January 2003, treatment plant personnel noted an increase in the number of reported pinhole leaks in copper piping. Most of these reports were from the North East Botetourt area. This area was originally fed by mostly well water until 2001, but thereafter it was supplied by Carvin’s Cove water. A survey of local plumbers also helped establish the degree of the pitting problem and to track the source of the problem (Figure 6-1). Four plumbers were surveyed who worked on copper pitting in the Roanoke area. A range of pitting work from 2 pits a year to 25 pits per week was reported by the plumbers. The results from this survey indicated the pits were mainly forming near joints, in hot water lines and the age of the plumbing was anywhere from 1 to 30 years old (Table 6.1).
The survey also established two areas of concern including the North East Botetourt and South West Roanoke areas. These regions will be referred to as area A and area B, respectively. Using a distribution system map provided by Roanoke County, it was determined that the North East Botetourt area was mainly supplied by Carvin’s Cove and the South West Roanoke was supplied by both Spring Hollow and Carvin’s Cove, depending on the exact location. It is therefore possible that Carvin’s Cove water is the key contributor to the problem.

MATERIALS AND METHODS

Water samples were taken throughout the treatment facilities and the distribution system. pH, temperature, and free chlorine measurements were taken on sight using a calibrated pH meter and a DPD colorimetric Hach test kit via standard method 4500-Cl G. Measurements were taken until a consistent value was obtained. A total volume of 200 mL was collected for laboratory testing, 100 mL of each sample was then filtered using a 0.45 um Nylon filter. All samples were acidified to obtain a nitric acid concentration of 2%. These samples were then analyzed in the lab for Al, PO$_4$-P, Ca and K using ICP-ES, Induced Coupled Plasmal-Emission Spectroscopy per Standard Method 3120 B[7].

SAMPLING RESULTS AND DISCUSSION

Samples were taken throughout the different treatment processes of the two water utilities, Spring Hollow and Carvin’s Cove. These two treatment facilities use very different treatment strategies (Figure 6-2). Therefore, certain compounds, such as potassium, were used as tracers to confirm which water was supplying the areas tested in the field. Samples from three homes within the Roanoke distribution system were also sampled 3 times throughout one day to track the changes in water chemistry during different levels of water use. First draw samples were taken in the morning, a second sample was taken mid-day, and the third last draw sample was taken at the end of the day.

When the two main treatment facilities were sampled, the one time sampling results indicated that the waters entering the distribution system from these two sources were very different (Figure 6-3 and Table 6-3). There were two main areas of concern. Both the pH and aluminum concentrations of the Carvin’s Cove treatment facility were high. An average pH of 8.68 was measured. This level has been shown in previous research to increase the tendency of copper pitting corrosion (Rushing et al, 2003). Also, the aluminum levels in the effluent of Carvin’s Cove were above the EPA Secondary Maximum Contaminant Level (SMCL) of 0.05 ppm, measuring an average concentration of 0.12 ppm, and with a maximum concentration of 0.145 ppm. Spring Hollow, on the other hand, had a lower pH of 7.61 and an undetectable concentration of Al.

Aluminum levels in the Roanoke distribution system were high compared to aluminum levels found while investigating the massive pitting outbreak at WSSC (Figure 6-4 through 6-5). The total aluminum concentration measured at WSSC was approximately 0.125 mg/L, whereas the Roanoke sampling revealed startling levels up to 0.285 mg/L total aluminum in samples taken from households experiencing pitting problems.
High levels of aluminum from the Carvin’s Cove treatment facility may be due to the lack of efficient coagulation conditions necessary to minimize the amount of soluble aluminum released into the distribution system. Previous results of jar testing using flocculated WSSC water indicated that soluble aluminum is strongly controlled by the temperature and pH of the water (Figure 6-7). As a general rule, lower pH decreased soluble aluminum, consistent with the fact that the dominant soluble species in this pH range is Al(OH)_4^-, and its formation is favored at higher pH and temperature as predicted by the computer program Mineql+ (Figure 6-7). These trends in aluminum solubility with temperature and treated water pH provide a good explanation for why plants sometimes see spikes in effluent aluminum during the summer when temperatures and algal blooms raise pH.

Several homes which had previously experienced a copper pitting problem were sampled throughout the course of one day to establish any trends in concentrations affected by water usage. These homes were all in the two areas of interest. Both house #1 and house #2 were located in the North East Botetourt region (area A), while house #3 was located in South West Roanoke (area B). Fire hydrants near the sampled areas were tested to obtain pH, temperature, and free chlorine measurements. The fire hydrant near house #1 and #2 will be referred to as “hydrant A” and the fire hydrant near house #3 will be referred to as “hydrant B”. Three samples within the households were taken by residents throughout the day. Samples were obtained the following morning, filtered, acidified, and prepared for testing.

Based on the results from the on-site sampling of the fire hydrants, both hydrant A and B had relatively high pH levels of 7.84 and 8.1, respectively. The free chlorine concentrations were 0.53 and 0.42 for hydrant A and B.

The most consistent trend between the different areas of the distribution system was the increase in aluminum concentration throughout the day (Figure 6-4). Also, significant levels of aluminum were measured in most of these samples. While house #3 in area B revealed a maximum aluminum concentration of 0.037 ppm, houses #1 and #2 in area A measured higher aluminum levels of 0.285 and 0.058 ppm, respectively. Both of these measurements are above the EPA SMCL of 0.05 ppm.

While it is possible that the areas of concern may be receiving water from a variety of sources, the data suggests that these areas are receiving water mainly from the Carvin’s Cove treatment facility (Figure 6-8). The key to this conclusion is the significant concentration of aluminum and phosphate in the water from these homes. The Spring Hollow treatment facility and drilled wells tested had negligible levels of both of these compounds, while treated water from the Carvin’s Cove facility had high levels of both aluminum and phosphate. As previously discussed, free chlorine and high pH levels in the presence of aluminum have been proven to cause pitting corrosion in copper pipes.
RECOMMENDATIONS

The Carvin’s Cove water treatment facility needs to modify their treatment process to decrease the levels of aluminum entering the distribution system. There are two recommended ways to decrease Al concentration. Coagulation conditions can be adjusted by testing the pH and temperature conditions necessary to minimize the amount of alum necessary during the coagulation process. Another option is to switch to ferric chloride. This will remove aluminum from the water, thereby removing a catalyst of the corrosion reaction. Other benefits of this recommendation are the increased level of chloride and decrease in sulfate concentration. This condition has been proven to decrease the tendency of corrosive pitting (Edwards et al.). Iron is also less soluble than aluminum and residual metal is less of a concern.

It is highly recommended that utilities lead efforts in responding to pinhole leak problems, since it is very costly to consumers, and regardless of cause(s) the only way to provide a low cost solution to all consumers is by identifying modifications to water quality that will prevent future pinhole leaks.

CONCLUSIONS FROM ROANOKE CASE STUDY

High aluminum levels may be the result of leftover aluminum from the coagulation process used in the Carvin’s Cove water treatment process. The increased levels of aluminum within the households may also be due to several other factors including leaching from concrete pipes and the wearing away of aluminum deposits from pipe walls during periods of higher flow. Aluminum may deposit on pipes within the distribution system during periods of stagnation or low flow and be carried away when higher flow returns.

The high levels of aluminum and chlorine in combination with high pH in the water leaving the Carvin’s Cove treatment plant may be combining to catalyze the pitting problem in the Roanoke area. While this is a preliminary conclusion, a more detailed study is needed to make a more thorough and complete conclusion.

NATIONAL SURVEY

Pinhole Leaks Around the Country and the Role of Aluminum

A substantial telephone survey of large utilities was undertaken. To accomplish this, plumbers were interviewed by telephone in areas served by the largest utilities in the U.S. The list of questions asked in the survey is presented in Appendix 1.A. In addition, an effort was made to determine if the combination of higher pH, aluminum and high residual disinfectant were present in other outbreaks of pitting around the country. The final step was to examine archival records of the Copper Development Association to determine whether the percentage of copper pitting failures associated with aluminum deposits had increased in the last few years.
Three types of data were collected to assess the extent and nature of recent pinhole leak outbreaks. In the first set of work, plumbers serving customers of many of the largest utilities in the U.S. were called by telephone. Names of plumbers were selected at random from a phone book and the survey questions in Figure 1 were asked of each individual. Several hundred phone calls were made to obtain 40 responses (Table 6-4).

At the outset, we note that this approach is subject to many problems in terms of quantifying the pinhole leak problem, even though it is the best information that could be obtained under the circumstances. Nonetheless, a key result is that all plumbers were seeing some level of pinhole leak activity. The highest activity was 10-12 leaks per month. These responses can be contrasted to an early survey (Edwards, 2002) in which plumbers at some other utilities had never even heard of the problem. Moreover, in the earlier study by Edwards, the frequency of pinhole leaks reported by 5 plumbers serving customers at WSSC ranged from “infrequent” to “2-3 leaks per week.” If this is any guide, a very rough estimate is that pinhole leak frequency at WSSC is only about 4 times higher than is typically observed for customers at other large utilities around the country. While it is true that a factor of 4 is of great concern, initial preconceptions were that customers at WSSC might be suffering an unprecedented outbreak for which pinhole leak frequency might be 10 to 100 times higher than was present elsewhere. Due to deficiencies with this approach, this is still possible, although it is clear that pinhole leaks are occurring at other large utilities. In fact, customers of the City of Chicago appear to be fixing pinhole leaks at the same rate as those at WSSC (pinholes repaired per week per plumber).

Additional information was collected based work tracking outbreaks of pinhole leaks at utilities in North Carolina, Virginia, Maryland (not WSSC), Florida, District of Columbia, Ohio, New Jersey, Wisconsin, Colorado and Arizona. These utilities did not give permission to release their data or their specific names, but they did allow the author to discuss general aspects of the problem. In still other instances, pipes and water samples were sent to the author directly by parties not associated with the utility. In 7 of 10 cases for which forensic analysis was conducted, significant amounts of aluminum were found to be associated with pits. At the utilities in Virginia, Florida, New Jersey and District of Columbia, samples of water were collected in the field and analyzed by the author or by utility personnel. One utility used a combination of free chlorine and chloramines (two treatment plants), two used chloramines, and one used free chlorine. In all cases where samples were collected, total chlorine residuals were above 2 mg/L, aluminum residuals were above 50 ppb, and pHs above 8.2 were detected in at least some water samples collected at the tap. In most cases the utilities expressed surprise at the aluminum results, since they had never tested for aluminum in the distribution system before. In summary, the combination of factors described by Rushing et al. (2002a; 2002b) including relatively high total chlorine residuals, pH above 8.2 and significant aluminum at the tap are occurring at many other utilities throughout the US, where customers are experiencing pinhole leaks.

A final set of information was gathered by Andy Kireta from the Copper Development Association (Kireta, 2003). Mr. Kireta reviewed a forensic database of pipe samples sent to them. According to Mr. Kireta, before the mid to late 1990’s, aluminum was only detected in hot or cold water pits in only a very small percentage of cases. However, from 1998 onwards, it is clear that aluminum was detected in pitted samples in well over 40% of the cases each year. This information also seems consistent with the Rushing et al. (2002a; 2002b) hypothesis regarding aluminum, and as a whole the data suggest that relatively recent changes to water quality or treatment practice might also be contributing factors.
CONCLUSIONS

Pitting is occurring at a significant frequency at other large utilities across the US. The combination of high residual aluminum, relatively high total chlorine residuals, and pHs above 8.2 are also observed when pitting is associated with aluminum deposits. The importance of this type of pitting attack may have increased since the early to mid 1990’s.

ACKNOWLEDGEMENTS

This work was supported by the Roanoke County and Roanoke City water utilities. The authors also acknowledge Paul Gantzer for his efforts in sampling and correspondence between the Roanoke County and Roanoke City water utilities. Opinions and findings expressed herein are those of the authors and do not necessarily reflect the views of the Roanoke County and Roanoke City water utilities.

REFERENCES


Plumber’s Questionnaire

Questions:

1. Are you familiar with pinhole leaks in copper piping? yes no (if not, explain)

2. Do you service homes that receive water from <water utility>?

3. In homes served by the <water utility>,
   how many leaks per week per plumber or per month per plumber,
   do you repair that have this problem?
   
   per week per plumber
   per month per plumber

If there are leaks...

4. In what parts of the service area do they see these problems?

5. Do the impacted homes use public water? yes no most some

6. What percentage are hot water pipes? %

7. What percentage of the pipes are within 3 inches of the joint? % no pattern

8. Any feel as to the approximate age of the plumbing failure?
   years months

If they seem like talking...

9. How long have you been a plumber in the area? years months

10. Do you have any other input that may be useful?

---

Figure 6-1. Questionnaire for plumber’s survey.
Table 6-1. Summary of results from plumber survey.

<table>
<thead>
<tr>
<th>Plumbing Company</th>
<th>Familiar with Copper Pinhole Leaks</th>
<th>Serves homes using water utility of interest</th>
<th>Frequency of Leaks</th>
<th>Most problematic service area</th>
<th>Impacted homes on public water</th>
<th>% Hot Water Leaks</th>
<th>% Leaks within 3 inches of Joint</th>
<th>Age of Pipe in Failure</th>
<th>Plumber’s Experience in the Area</th>
<th>Additional Useful Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>yes</td>
<td>yes</td>
<td>difficult to determine because leaks are not just in homes</td>
<td>South West Roanoke County, Bent Mountain area.</td>
<td>These homes were on wells and now on public water source.</td>
<td>85%</td>
<td>65-75%</td>
<td>most 10-15 years old</td>
<td>45 years</td>
<td>A lot of new houses are using type M pipe. This is a thinner pipe. Types L or K should be used instead.</td>
</tr>
<tr>
<td>#2</td>
<td>yes</td>
<td>yes (both commercial and home plumbing)</td>
<td>25 per week</td>
<td>Majority in South West, newer plumbing</td>
<td>yes, small amount on wells.</td>
<td>65-70%</td>
<td>75% (especially in recirculating lines)</td>
<td>20-30 years old</td>
<td>20 years</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>yes</td>
<td>yes, most leaks in acid water. Sometimes in &quot;M&quot; piping.</td>
<td>2 per week</td>
<td>South West County and Botetourt Area</td>
<td>sometimes homes use public water.</td>
<td>mostly cold water.</td>
<td>20% varies, pinhole can be anywhere. About 95% of pinholes occur in the thinner, &quot;M&quot;, piping.</td>
<td>10-20 years</td>
<td>40 years</td>
<td>Suggests home owners do not use &quot;M&quot; piping. Sometimes there are pinholes at the joints</td>
</tr>
<tr>
<td>#4</td>
<td>yes</td>
<td>yes</td>
<td>2 per year</td>
<td>homes, but no area sticks out</td>
<td>yes, most. Very few on well water.</td>
<td>no correlation</td>
<td>varies</td>
<td>as little as 1 year</td>
<td>45 years</td>
<td></td>
</tr>
</tbody>
</table>

CARVIN’S COVE:

- raw water → rapid mix → flocculation and sedimentation → filter → clearwell #1
- clearwell #1 → clearwell #2 → combined flow to distribution system
- potassium permanganate → chlorine gas and orthophosphate → fluoride and NaOH

SPRING HOLLOW:

- raw water → rapid mix → clarifier → filter → wet well #1
- wet well #1 → wet well #2 → combined flow to distribution system
- chlorine dioxide and ferric sulfate → GAC (granular activated carbon) → fluoride and chlorine gas

Figure 6-2. Flow Diagrams of simplified treatment processes at both the Carvin’s Cove and Spring Hollow water treatment facilities.
Figure 6-3. Sampling results for Spring Hollow and Carvin’s Cove treatment facilities.
Table 6-2. Comparison of Spring Hollow and Carvin’s Cove water sources.

<table>
<thead>
<tr>
<th>Treatment Plant</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Free Chlorine (ppm)</th>
<th>particulate Al (ppm)</th>
<th>soluble Al (ppm)</th>
<th>PO4-P (mg/L)</th>
<th>K (mg/L)</th>
<th>Ca (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring Hollow</td>
<td>14.2</td>
<td>7.61</td>
<td>1.43</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.889</td>
<td>39.5</td>
</tr>
<tr>
<td>Carvin’s Cove</td>
<td>16.4</td>
<td>8.68</td>
<td>1.00</td>
<td>0.0193</td>
<td>0.119</td>
<td>0.334</td>
<td>1.075</td>
<td>11.95</td>
</tr>
</tbody>
</table>
Figure 6-4. Concentrations of Potassium, Phosphate-P, Calcium, and Aluminum throughout the day in residents previously experiencing a copper pitting corrosion problem.
Figure 6-5. Aluminum at indicated sampling locations in the WSSC distribution system. Categories denote amount of aluminum that passed through a filter of that pore size in μm. Total samples not filtered before analysis.

Figure 6-6. Total and soluble aluminum concentrations obtained during sampling of the Roanoke water distribution system and treatment plants.
Figure 6-7. Comparison of soluble aluminum data collected at the treatment plant during jar tests with expectations based on chemical model predictions.

Figure 6-8. Comparison of drinking water from houses experiencing copper pitting corrosion and the treated water entering the distribution system from both the Spring Hollow and Carvin’s Cove treatment facilities.
<table>
<thead>
<tr>
<th>Water Utility</th>
<th>Plumber</th>
<th>Time in area (yrs)</th>
<th>Freq. of pinhole repairs per plumber</th>
<th>Hot vs. Cold pipe</th>
<th>With-in 3 inches of joint?</th>
<th>Problem getting worse?</th>
<th>Replace a section or solder to fix?</th>
<th>Cost to replace/repair one section of pipe</th>
<th>Cost to replumb and when is it necessary?</th>
</tr>
</thead>
<tbody>
<tr>
<td>City of New York DEP</td>
<td>1</td>
<td>25</td>
<td>1 per month</td>
<td>DK</td>
<td>most</td>
<td>no</td>
<td>replace</td>
<td>$200</td>
<td>$1,500 – if old pipes</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15</td>
<td>1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>$1,500 – if old galvanized</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23</td>
<td>0-1 per month</td>
<td>Hot</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>N/a</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10</td>
<td>0-1 per month</td>
<td>DK</td>
<td>Most</td>
<td>No</td>
<td>Replace</td>
<td>$180</td>
<td>$1,600 – rarely recom.</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8</td>
<td>2 per month</td>
<td>Mostly hot</td>
<td>No</td>
<td>No</td>
<td>Replace</td>
<td>$200</td>
<td>$1,500 – rarely recom.</td>
</tr>
<tr>
<td>Metro Water District of Southern CA</td>
<td>1</td>
<td>15</td>
<td>1-2 per month</td>
<td>DK</td>
<td>DK</td>
<td>no</td>
<td>replace</td>
<td>$120</td>
<td>$4,000 – rarely recom.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15</td>
<td>1 per month</td>
<td>About the same</td>
<td>DK</td>
<td>No</td>
<td>Either</td>
<td>$150</td>
<td>$2,500</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>12</td>
<td>1-2 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$125</td>
<td>$2,000</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>45</td>
<td>0-1 per month</td>
<td>Both</td>
<td>Sometimes</td>
<td>No</td>
<td>Replace</td>
<td>$125</td>
<td>$2,000</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25</td>
<td>1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$125</td>
<td>N/a</td>
</tr>
<tr>
<td>Chicago Water Depart.</td>
<td>1</td>
<td>55</td>
<td>3-5 per month</td>
<td>DK</td>
<td>DK</td>
<td>no</td>
<td>replace</td>
<td>$125</td>
<td>$3,000 –if old pipes</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>55</td>
<td>10-12 per month</td>
<td>DK</td>
<td>DK</td>
<td>no</td>
<td>either</td>
<td>$100</td>
<td>$1,500 – rarely recom.</td>
</tr>
<tr>
<td>City of Los Angeles</td>
<td>1</td>
<td>25</td>
<td>2 per month</td>
<td>Mostly hot</td>
<td>DK</td>
<td>No</td>
<td>Either</td>
<td>$125</td>
<td>n/a</td>
</tr>
<tr>
<td>---------------------</td>
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<td>----</td>
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<td>-----</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20</td>
<td>2 per month</td>
<td>DK</td>
<td>Most</td>
<td>No</td>
<td>Either</td>
<td>$200</td>
<td>$3,000 – rarely recom.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7</td>
<td>1 per month</td>
<td>Mostly hot</td>
<td>No</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>$2,500</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>15</td>
<td>1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$125</td>
<td>$2,000 – if old pipes</td>
</tr>
<tr>
<td>City of Detroit Water and Sewer</td>
<td>1</td>
<td>55</td>
<td>2 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>n/a</td>
<td>$200</td>
<td>$2,500</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>0-1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$175</td>
<td>$3,000</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10</td>
<td>1 per month</td>
<td>DK</td>
<td>Not necessarily</td>
<td>No</td>
<td>Replace</td>
<td>$175</td>
<td>$1,500</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>15</td>
<td>2 per month</td>
<td>Mostly cold</td>
<td>no</td>
<td>no</td>
<td>Either</td>
<td>$200</td>
<td>$2,000</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25</td>
<td>3-5 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>$2,500</td>
</tr>
<tr>
<td>San Francisco</td>
<td>1</td>
<td>17</td>
<td>1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>N/a</td>
<td>N/a</td>
</tr>
<tr>
<td>Department</td>
<td>Year</td>
<td>Frequency</td>
<td>Monthly</td>
<td>Condition</td>
<td>Action</td>
<td>Cost</td>
<td>Cost Range</td>
<td></td>
<td></td>
</tr>
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<td>--------</td>
<td>--------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cisco Water Dept.</td>
<td>2</td>
<td>20</td>
<td>3-4 per</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>N/a</td>
<td>$150</td>
<td>$3,000 – rarely recom.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15</td>
<td>1-2 per</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>$2,000 – rarely recom.</td>
</tr>
<tr>
<td>City of Houston, Main System</td>
<td>1</td>
<td>50</td>
<td>3-5 per</td>
<td>DK</td>
<td>Don’t pay attention to it</td>
<td>No</td>
<td>Either</td>
<td>$100</td>
<td>$2,000 – if old pipes</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30</td>
<td>3-5 per</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>$1,500 – if old pipes</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21</td>
<td>1-2 per</td>
<td>Hot</td>
<td>DK</td>
<td>No</td>
<td>n/a</td>
<td>n/a</td>
<td>N/a</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>12</td>
<td>2-3 per</td>
<td>DK</td>
<td>Most</td>
<td>No</td>
<td>Replace</td>
<td>$150</td>
<td>$1,500 – rarely recom.</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>15</td>
<td>1 per</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$120</td>
<td>$1,000</td>
</tr>
<tr>
<td>Philadelphia Water Depart</td>
<td>1</td>
<td>25</td>
<td>1 per</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Either</td>
<td>$200</td>
<td>$3,500</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13</td>
<td>1-2 per</td>
<td>DK</td>
<td>Most</td>
<td>No</td>
<td>Replace</td>
<td>$175</td>
<td>$2,500 – rarely recom.</td>
</tr>
<tr>
<td>Miami-Dade Water and Sewer</td>
<td>1</td>
<td>50</td>
<td>5-7 per</td>
<td>DK</td>
<td>DK</td>
<td>Yes – older pipes</td>
<td>Replace</td>
<td>$150</td>
<td>$3,000 – if old pipes</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>25</td>
<td>2-3 per</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>replace</td>
<td>$150</td>
<td>$2,500 – if old pipes</td>
</tr>
<tr>
<td>NJ-American Water Comp. Short Hills</td>
<td>1</td>
<td>55</td>
<td>2-3 per month</td>
<td>Both</td>
<td>Sometimes</td>
<td>No</td>
<td>replace</td>
<td>$120</td>
<td>$2,500 – rarely recom.</td>
</tr>
<tr>
<td>------------------------------------</td>
<td>---</td>
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<td>-----</td>
<td>----------------------------</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$125</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>22</td>
<td>2 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$135</td>
<td>$2,000 – rarely recom.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>1 per month</td>
<td>DK</td>
<td>DK</td>
<td>No</td>
<td>Replace</td>
<td>$120</td>
<td>n/a</td>
<td></td>
</tr>
</tbody>
</table>
Table 6-4. Comparison of Copper Surfaces between Homes with and Without Frequent Pinhole Leaks

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Comment</th>
<th>(n)</th>
<th>% Al</th>
<th>% Fe</th>
<th>% Si</th>
<th>% Cl</th>
<th>% S</th>
<th>% Cu</th>
<th>% Sn</th>
<th>% Ca</th>
<th>% P</th>
</tr>
</thead>
</table>

The following pipe samples were collected from an area/homes where pitting was relatively common

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Comment</th>
<th>(n)</th>
<th>% Al</th>
<th>% Fe</th>
<th>% Si</th>
<th>% Cl</th>
<th>% S</th>
<th>% Cu</th>
<th>% Sn</th>
<th>% Ca</th>
<th>% P</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Comment</th>
<th>(n)</th>
<th>% Al</th>
<th>% Fe</th>
<th>% Si</th>
<th>% Cl</th>
<th>% S</th>
<th>% Cu</th>
<th>% Sn</th>
<th>% Ca</th>
<th>% P</th>
</tr>
</thead>
</table>

Pipe sample 4 was collected from an area/home where pinholes were common, and the resident did not believe there were any pinholes, but a pinhole was discovered when collecting the sample. Sample 5 was from an area where pinholes are common, but the resident has not had pinholes.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Comment</th>
<th>(n)</th>
<th>% Al</th>
<th>% Fe</th>
<th>% Si</th>
<th>% Cl</th>
<th>% S</th>
<th>% Cu</th>
<th>% Sn</th>
<th>% Ca</th>
<th>% P</th>
</tr>
</thead>
</table>

The following pipe samples are from an area/homes where pinholes are relatively uncommon

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Comment</th>
<th>(n)</th>
<th>% Al</th>
<th>% Fe</th>
<th>% Si</th>
<th>% Cl</th>
<th>% S</th>
<th>% Cu</th>
<th>% Sn</th>
<th>% Ca</th>
<th>% P</th>
</tr>
</thead>
</table>

#High Sn and low Cu due to solder repair in one sample.

@number of measurements on the sample represented in reported range

*This sample was mailed directly from the consumer to Virginia Tech. The consumer had experienced 1 leak in 1999, 2 in 2000, and 3 by March 2001.
Figure 6-9. Perspectives on aluminum in treated water at WSSC compared the Roanoke system. The shaded area represents the range in aluminum levels measured in areas of the Roanoke system experiencing copper pitting.
CHAPTER 7: SUMMARY OF KEY CONCLUSIONS

- There is a concentration effect of aluminum solids at pH 9.0, in that higher concentrations cause a rising $E_{corr}$ much faster if sufficient chlorine is present. There does not seem to be a “safe” level of aluminum, in that higher aluminum is leading to a higher tendency for pitting.

- The synergistic impacts of aluminum and chlorine on copper pitting are confined to pH between 8.0 to somewhere below 10.0.

- Utility practices in terms of coagulant selection, aluminum carryover, concrete lining, pH control and disinfectant dose needs to be reconsidered in light of these startling results.

- The presence of free chlorine leads to higher and more erratic corrosion potentials. Severe pitting was observed in the presence of free chlorine and aluminum at pH 9.2, whereas no pitting was observed in the absence of aluminum.

- In the presence of free chlorine, pitting corrosion is more likely to occur at higher flow frequencies.

- The location of bends and pipe orientation had complicated impacts on corrosion tendencies. All pits formed after bends in pipe and consistent with the notion that particles settling and sticking to the pipe bottom can catalyze the cathodic reaction, both visual and electrochemical analyses indicate that the bottom horizontal sections tended to be more cathodic.

- Surface imperfections from manufacturer are not a likely cause of pitting corrosion in waters of this type, nor are do lines of pits indicate that surface imperfections are involved. It remains possible that surface imperfections could be an indirect contributor to pitting, but that remains to be proven.

- Phosphates reduced electrochemical indications of pitting in the synthetic water at the pH of 8.3 compared to synthetic water without phosphate. Phosphates had lesser benefits at higher pH even in synthetic water, but they were clearly having impacts on scale formation. Overall, even at pHs as high as 10, some benefits from orthophosphate dosing are anticipated.

- There is a natural inhibitor to pitting corrosion in WSSC water that is not present in the synthetic water. Silica and NOM seem to be the most likely candidates.

- The higher chloride concentration in the water after ferric chloride was dosed at the treatment plant may have reduced the pitting propensity of the water. This could be due to higher chloride in the water, or reduced aluminum, or both.

- Water treated by alum and ferric chloride exhibit major differences in non-uniform copper corrosion behavior.

- Pitting is occurring at a significant frequency at other large utilities across the U.S. The combination of high residual aluminum, relatively high total chlorine residuals, and pHs above 8.2 are also observed when pitting is associated with aluminum deposits. The importance of this type of pitting attack may have increased since the early to mid 1990’s.
BECKI JEAN MARSHALL  
bemash1@vt.edu  

Current address: 1301 Westover Dr., Blacksburg, VA 24060  
(540) 953-2870  
Permanent address: 480 Winding Hills Rd., Montgomery, NY 12549  
(845) 361-1251  

OBJECTIVE: Civil and Environmental Engineer; interest in consulting, design, research, field, and lab work.  

EDUCATION: Masters in Environmental Engineering, expected May 2004  
GPA: 3.77/4.0  
Virginia Polytechnic Institute and State University, Blacksburg, VA  
The Thesis Topic: An Electrochemical Study of Copper Corrosion  
Advisor: Marc Edwards  

Bachelor of Science in Civil Engineering, Concentration in Environmental Engineering, May 2002 GPA: 3.78/4.0  
Bucknell University, Lewisburg, PA  
EIT Certified  

Senior Design Project: Detailed analysis of various engineering methods for phosphorous removal from a DuPont Company industrial waste stream to meet upcoming Environmental Protection Agency (EPA) discharge limits.  

WORK EXPERIENCE: Research Assistant, Virginia Tech, Blacksburg, VA (July 2002- April 2004)  
• Developed techniques to analyze the electrochemistry of copper corrosion and determine possible inhibitors.  
• Worked directly with the Washington Suburban Sanitary Commission (WSSC) and Roanoke Water Utilities to mitigate recent corrosion problems within their distribution systems.  
• Learned to effectively work directly with a client (Roanoke Water Utilities) to determine causes of corrosion problems in a distribution system.  
• Gained effective technical and formal report writing skills as well as thorough laboratory experience.  
IWA Conference on Scaling and Corrosion: London, UK (March 2003)  

Research Assistant, Mohonk Preserve, Inc., New Paltz, NY (Summer 2000, 2001)  
• Developed detailed study of trail use impacts on the environment while using Global Positioning System (GPS).  
• Utilized Standard Method lab techniques to measure Phosphorus concentrations of surrounding water bodies and analyze possible sources of eutrophication, or nutrient loading.  

Engineering Intern, Taconic Engineering Designs, Newburgh, NY (Summer 1999)  
• Gained fieldwork experience including on-site inspections and cost analysis, perk tests, and surveying.  
• Became proficient in Auto CAD drafting and design.
LEADERSHIP EXPERIENCE: Team Captain, Bucknell University (Fall 2000- Spring 2002) Division I Cross Country and Track and Field

- Develop teamwork skills; act as a role model for over 50 female college athletes.

Treasurer, Bucknell University (Spring 2001- Spring 2002) Tau Beta Pi Engineering Honors Fraternity

- Balanced organization’s social and academic agendas with financial and economic resources.

COMPUTER SKILLS: Proficient in PC and Macintosh operating systems. Applications include: Microsoft Word, Microsoft Excel, Powerpoint, Auto CAD, CAD Key, GPS, Arc View, and SPSS.

ACADEMIC HONORS: Virginia Tech VIA scholar (Fall 2002-Present)
Dean’s List (seven out of eight semesters at Bucknell )
Academic All American Athlete (Spring 2002)
Eastern College Athletic Conference Academic Medallion (Fall 2001)
All Academic Team, Women’s Intercollegiate Coaches Association (Fall 2001)
Patriot League Academic Athlete of the Year for all sports (2000-2001)
Patriot League Scholar Athlete (Fall 1999, Fall 2000, Spring 2001, Fall 2001)
Cross Country Academic All-American Conference/ National Qualifier (Fall 1999)

ACTIVITIES: Student Action Committee (SAC), (September 2002- Present)
Virginia Tech Triathlon Team, (September 2002- Present)
Tau Beta Pi Engineering Honor Society Member, (October 2000- Present)
ASCE (American Society of Civil Engineers) Member, (February 1999- Present)

Alpha Lambda Delta National Academic Honor Society Member, (Spring 1999- Present)

Athletic Awards:

- ECAC Star Athlete (eight times in collegiate running career)
- All Conference Team Honors (Fall 1998, Fall 1999, Fall 2000, Fall 2001)
- Patriot League Cross Country and Track Champion (8 individual and 11 team championship titles, 6 obtained while captain)
- Most Outstanding Patriot League Athlete (Fall 1999, 2000, 2001)
- Cross Country All-District Team (Fall 1999, 2000, 2001)

References available upon request.