

ADVANCING THE UNDERSTANDING OF WATER  
DISTRIBUTION SYSTEM CORROSION:  
EFFECTS OF CHLORINE AND ALUMINUM ON COPPER  
PITTING, TEMPERATURE GRADIENTS ON COPPER  
CORROSION, AND SILICA ON IRON RELEASE

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

Master of Science  
in  
Environmental Engineering

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July 24, 2002  
Blacksburg, Virginia

Keywords: Corrosion, Copper, Iron, Pitting, By-product release, Silica, Temperature, Chlorine, Aluminum

# **Advancing the Understanding of Water Distribution System Corrosion: Effects of Chlorine and Aluminum on Copper Pitting, Temperature Gradients on Copper Corrosion, and Silica on Iron Release**

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## **ABSTRACT**

When severe copper pitting problems impacted customers at a large utility, studies were begun to attempt to diagnose the problem and identify potential solutions. A series of tests were conducted to characterize the nature of pitting. Desktop comparisons of pinhole leak frequency and treatment practices at nearby utilities were also documented to identify treatment factors that might be influencing the initiation and propagation of leaks.

Factors identified included the presence of relatively high levels of free chlorine and aluminum in the distribution system. Experiments were conducted to examine the effect of these constituents on copper pitting under stagnant and flow conditions. That led to discovery of a synergistic redox reaction between chlorine, aluminum solids, and copper metal as evidenced by increased chlorine decay rates, non-uniform corrosion, and rising corrosion potentials.

Temperature changes had been suspected to increase copper pitting frequency and copper release to drinking water. Experiments examined the effect of temperature gradients on copper pipe corrosion during stagnant conditions. The pipe orientation in relation to the temperature gradient determined whether convective mixing would occur, which influenced temperature gradients within the pipe. This work is the first to demonstrate that temperature gradients lead to thermogalvanic currents, influences copper leaching and scale type.

Iron release from corroding water mains is another concern of many water utilities, but little is known about chemistry factors that influence the problem. In laboratory experiments, higher levels of silica caused more iron release to the water and decreased the size of suspended iron particles. Silica levels also changed during the experiment: it decreased through incorporation into a dense scale, and increased by release from cast iron during corrosion. Silica slightly decreased iron corrosion rates near the end of this 6-month test.

## **ACKNOWLEDGEMENTS**

Thanks to my advisor, Dr. Marc Edwards, for guidance and support, and for making this thesis and all of my accomplishments during graduate school possible. Thanks also to Dr. Laurie McNeill, who introduced me to research and taught me all of my good laboratory habits. Thanks also to the Virginia Tech Via Fellowship and the American Water Works Association for generous funding.

And finally, thanks to my loving family and friends, whose support and encouragement make everything possible.

# TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii
INTRODUCTION AND AUTHOR’S PREFACE.....	1
References.....	4
CHAPTER 1: ADDRESSING COPPER PINHOLE LEAKS IN CONSUMER TUBES.....	6
ABSTRACT.....	6
INTRODUCTION.....	6
CASE STUDY BACKGROUND.....	8
MATERIALS AND METHODS.....	9
RESULTS AND DISCUSSION.....	13
Desktop Comparison of Utility Experiences With Copper Pitting Problems.....	13
Chemical, Electrochemical, and Microbiological Analysis of Pitted Copper Pipe.....	15
A Focus on Aluminum and Silicates in the Water Distribution System.....	19
CONCLUSIONS.....	24
ACKNOWLEDGEMENTS.....	24
REFERENCES.....	25
CHAPTER 2: EFFECT OF ALUMINUM SOLIDS AND CHLORINE ON COLD WATER PITTING OF COPPER.....	37
ABSTRACT.....	37
INTRODUCTION.....	37

Review of the Chlorine and Aluminum Issue.....	38
MATERIALS AND METHODS.....	40
RESULTS AND DISCUSSION.....	43
The Effect of High Levels of Chlorine With and Without Aluminum Solids .....	43
Lower Levels of Chlorine and Non-uniform Corrosion .....	45
The Effect of Chlorine and Aluminum Under Alternating Flow and Stagnation.....	48
CONCLUSIONS.....	51
ACKNOWLEDGEMENTS.....	52
REFERENCES .....	52
CHAPTER 3: CONFIRMING THE ROLE OF ALUMINUM SOLIDS AND CHLORINE IN COPPER PITTING CORROSION .....	66
INTRODUCTION .....	66
MATERIALS AND METHODS.....	67
RESULTS AND DISCUSSION.....	68
Chlorine Decay Kinetics.....	68
Corrosion Potential and Polarization Resistance .....	69
Copper Release .....	70
Mass Change.....	71
Corrosion Rates.....	71
Visual Observations.....	71
CONCLUSIONS.....	72
REFERENCES .....	73
CHAPTER 4: THE ROLE OF TEMPERATURE GRADIENTS IN RESIDENTIAL COPPER PIPE CORROSION .....	80
ABSTRACT.....	80
INTRODUCTION .....	80

MATERIALS AND METHODS.....	82
RESULTS AND DISCUSSION.....	83
Pipe Orientation and Temperature Gradients .....	83
Copper Corrosion Byproduct Release .....	84
Temperature effect on Copper Scale.....	86
Thermogalvanic Currents.....	86
CONCLUSIONS.....	88
ACKNOWLEDGEMENTS.....	89
REFERENCES .....	89
CHAPTER 5: SOME EFFECTS OF AQUEOUS SILICA ON THE CORROSION OF IRON.....	97
ABSTRACT.....	97
INTRODUCTION .....	97
MATERIALS AND METHODS.....	98
RESULTS AND DISCUSSION.....	100
Iron and Silica Release to Water.....	101
Iron Corrosion Rates.....	103
Scale Composition and Morphology .....	104
Si Effects on Particle Size and Iron Oxidation Rates .....	106
CONCLUSIONS.....	108
ACKNOWLEDGEMENTS.....	109
REFERENCES .....	109
CHAPTER 6: SUMMARY KEY OF CONCLUSIONS .....	118
VITA.....	120

## LIST OF TABLES

Table 1-1. Frequency of pinhole leaks at WSSC and from other case studies. ....	28
Table 1-2. Summary of utility data and survey responses. ....	29
Table 1-3. Comparison of Copper Surfaces .....	32
Table 1-4. Characteristics of Sampling Locations for Tracking of Distribution System Aluminum. ....	35
Table 2-1. Conditions tested during the first phase of work. ....	40
Table 2-2. Conditions tested during second phase of work. ....	41
Table 2-3. Conditions tested during third phase of work. ....	43
Table 2-4. Critical pitting potentials for copper ( $E_{crit}$ ) in various studies. ....	45

## LIST OF FIGURES

Figure 1-1. Frequently asked questions about pinhole leaks .....	27
Figure 1-2. Repair of copper service lines due to copper pitting at a utility in Carroll County Maryland.....	30
Figure 1-3. A large isolated pit on WSSC residential copper tubing.....	30
Figure 1-4. Polarization scans of WSSC copper specimens .....	31
Figure 1-5. Effect of corrosion inhibitors on RMS noise measurements . .....	31
Figure 1-6. Perspectives on aluminum in treated water at WSSC.....	33
Figure 1-7. Monitoring results of finished water residual Al at the Potomac plant and yearly number of pinhole leaks reported to WSSC.....	33
Figure 1-8. Comparison of soluble aluminum data collected at the treatment plant during jar tests with expectations based on chemical model predictions .....	34
Figure 1-9. Aluminum at indicated sampling locations in the distribution system. ....	36
Figure 2-1. Dried copper surfaces after 10 weeks of exposure to WSSC water. ....	55
Figure 2-2. Free chlorine decay .....	56
Figure 2-3. Corrosion potential results ( $E_{\text{corr}}$ ) from first phase of experiments .....	57
Figure 2-4. Chlorine decay rates from 2 <sup>nd</sup> phase of experiments.. .....	58
Figure 2-5. Corrosion potential results for days 0-12 and 28-36. ....	59
Figure 2-6. Picture of dried copper surfaces after 6 month exposure to WSSC water .....	60
Figure 2-7. Typical corrosion potential response under flow or stagnant conditions.....	61
Figure 2-8. Corrosion Potential Results through day 209. ....	62
Figure 2-9. Corrosion potential measurements before and after 20 day period of constant flow. ....	63
Figure 2-10. Pictures of copper pipe surfaces in-situ during the experiment.....	64
Figure 2-11. Dried copper pipe samples at the end of the experiment. ....	65
Figure 3-1. Average chlorine decay rates .....	74

Figure 3-2. Percent increase in chlorine decay rate for given target dose with 2 mg/L aluminum solids present compared to same system without aluminum. ....	74
Figure 3-3. $E_{\text{corr}}$ results. ....	75
Figure 3-4. Polarization resistance data ....	76
Figure 3-5. $E_{\text{corr}}$ results from experiments with aluminum solids after day 20. ....	77
Figure 3-6. Average Copper Release ....	77
Figure 3-7. Average mass loss from copper samples ....	78
Figure 3-8. Average corrosion rate during day 23 with aluminum solids present.....	78
Figure 3-9. Copper samples cut in half after end of experiment. ....	79
Figure 3-10. Close up of corrosion byproducts formed on pH 9 sample exposed to aluminum solids and chlorine.....	79
Figure 4-1. Pipe setup and current measurement technique for pipe sample with PVC ball valve dielectric ....	91
Figure 4-2. Experimental rig set up. ....	91
Figure 4-3. Schematic illustrating how temperature differences on different ends of a copper pipe would set up convection currents that enhance or act to prevent mixing during stagnation. ....	92
Figure 4-4. External surface temperatures for copper pipes joined by PVC ball valve.....	92
Figure 4-5. Average copper release for days 42-98.....	93
Figure 4-6. Predicted cupric solid formation as function of temperature ....	93
Figure 4-7. Mechanism causing elevated particulate copper levels in pipe exposed to temperature gradients after stagnation. ....	94
Figure 4-8. Pictures of copper pipe surfaces at end of experiment.....	95
Figure 4-9. Thermogalvanic currents over two 48 hour periods, 14 weeks apart. ....	96
Figure 4-10. Thermogalvanic currents after oxygen removal ....	96
Figure 5-1. Iron (top) and silica (bottom) concentrations in 20 <sup>0</sup> C reactors. ....	112
Figure 5-2. Color difference in water ....	113
Figure 5-3. Total iron release in reactors at 5 and 20 <sup>0</sup> C.. ....	113

Figure 5-4. Iron coupon mass loss after 4 months.....	114
Figure 5-5. Silica loss from and incorporation in iron scale.....	114
Figure 5-6. Representative corroded iron coupons after end of experiment.....	115
Figure 5-7. Iron scale tubercle formation in 50 mg/L SiO <sub>2</sub> , 20 <sup>0</sup> C reactor.....	115
Figure 5-8. Particle size distribution.....	116
Figure 5-9. Ferrous oxidation in the presence of varying amounts of silica.....	116
Figure 5-10. Possible mechanism of iron release and “red water” formation.....	117

## INTRODUCTION AND AUTHOR'S PREFACE

Distribution system corrosion is among the most costly problems facing water utilities today, and the American Water Works Association estimates that 325 billion dollars will be spent by American water utilities over the next 20 years to repair and replace existing water distribution system infrastructure [1]. That estimate did not include corrosion related costs associated with plumbing in homes, which include pipe replacement, repair of leaks, associated costs of water damage, and higher homeowners insurance

Corrosion of water distribution materials can lead to lost water, increased pumping costs, disinfectant demand, and dissolved oxygen depletion. In addition, many problems of water quality, such as taste and odor problems, waterborne disease, red and blue water outbreaks, and copper pitting are the result of poorly understood reactions occurring within the distribution system between different materials and treated water [2]. From a regulatory standpoint, water utilities are most concerned about excess lead and copper release from plumbing materials; however, other corrosion problems can lead to a drop in consumer confidence in water quality. Finally, a large percentage of waterborne disease originates from corroding pipes or from contaminant intrusion into the distribution system [3, 4].

Although advances in water treatment over the past 100 years now allow us to attain virtually any standard of water quality at the treatment plant, very little is understood regarding even simple interactions between drinking water and the materials through which it flows. Under ideal circumstances, plumbing material can last many decades or centuries with little to no problems. However, as in the case of copper pitting, plumbing material can fail within months after installation or can cause release of heavy metals to the water. Although advances have been made in understanding how water chemistry influences some corrosion problems, it is still not possible to predict what will occur in practice. Because of this lack of understanding, water utilities are often caught off guard when problems do occur, and often must try to correct the problem through trial and error testing. Furthermore, when water treatment changes are made, other unexpected corrosion problems might surface.

One example of a rare but costly problem is the internal pitting corrosion of copper pipe that leads to the formation of pinhole leaks. Although the factors that cause this problem are still

unknown, it is well recognized that the chemistry of the water traveling through the pipes can influence the formation and propagation of pits [5]. Furthermore, when this problem is widespread throughout a utility's distribution system, consumer confidence in the quality of the treated water can decline, especially if there is sufficient publicity surrounding the problem. The following prominent newspaper headlines about the utility which served as the basis for this work are illustrative:

- LOOKING AT LEAKS: EXPERT SAYS PINHOLES MAY BE TIED TO NEW RULES, *Sandra Fleishman, Washington Post, April 20, 2002; Page H1*
- MYSTERY OF THE 'PINHOLE LEAK' DEEPENS; WSSC'S PROBE OF FAILING COPPER WATER PIPES SHIFTS FOCUS TO MINERAL DEPOSITS, *Sandra Fleishman, Washington Post, January 20, 2001; Page G1*
- PINHOLE-LEAK PROBLEMS SPREAD; 2 NEIGHBORHOOD GROUPS FIND A HIGHER RATE THAN WSSC ESTIMATES, *Sandra Fleishman, Washington Post, February 3, 2001; Page G1*
- NO ASSURANCES ON HOME INSURANCE; WHEN POLICIES ARE DROPPED, OWNERS HAVE OTHER WAYS TO GET COVERAGE, *Sandra Fleishman, Washington Post, October 21, 2000; Page G1*
- HOMEOWNERS VENT FRUSTRATIONS, OFFER QUICK FIXES, *February 3, 2001; Page G8*
- EXPERTS TO AID WSSC PROBE OF TINY LEAKS IN COPPER PIPES, *Sandra Fleishman, Washington Post September 16, 2000; Page G3*
- AND THE LEAKS GO ON, *Sandra Fleishman, Washington Post, July 1, 2000; Page G1*
- CUSTOMERS CALL ON PIPE LEAKS WSSC HEARS GRIPES, THEORIES ON COPPER PLUMBING PINHOLES, *Sandra Fleishman, Washington Post July 8, 2000; Page G1*

In addition to the obvious public relations problem, there is legal precedent that drinking water providers are financially responsible for damages. For all of these reasons, a recent outbreak of copper pitting problems in an area of Maryland served by the Washington Suburban

Sanitary Commission (WSSC) led to an effort to identify the nature, severity, and contributing factors to the problem. Chapter 1 details the work conducted as part of this effort.

That work demonstrated that aluminum levels were relatively high in WSSC treated water, and that aluminum based coagulants and cement linings were a significant source of aluminum leaching. Aluminum solids were also found deposited on the copper pipe walls and were therefore implicated as a possible cause of the copper pitting problems at WSSC. Surveys of other water utilities that treat essentially the same water as WSSC revealed few copper pitting problems. However, WSSC is the only utility in the area to use free chlorine in conjunction with poly-aluminum chloride to treat its water. Consequently, a study to determine the effect of free chlorine on copper pitting in the presence and absence of aluminum was conducted (Chapter 2).

There are many other theories as to the cause of copper pitting at WSSC. Plumbers who work in the area served by WSSC have noted a correlation between seasonal temperature changes and increased frequency of pinhole leaks [6]. Furthermore, others have suggested that temperature gradients on copper plumbing cause increased copper leaching under some circumstances [7]. It was deemed likely temperature gradients that develop along sections of pipe due to differences in external air temperature might be influential, and the first study ever conducted into these possible effects is presented in Chapter 3.

There is also evidence that leaching of other metals from distribution system materials can positively influence copper corrosion, whereas aluminum was believed to exert a negative impact. Specifically, in an early study of copper contamination of drinking water supplies, it was found when iron pipe materials were placed upstream of copper tube, copper release from the tube significantly decreased [8]. The general idea is that corroding iron pipe upstream releases iron to the water that becomes incorporated into a more protective copper scale layer on the pipe, a result seemingly confirmed very recently by others [9]. With this evidence in mind, copper corrosion and the pitting problems at WSSC might be influenced by the practice of relining old water mains, because less iron and more aluminum will be exposed to copper pipe. Iron release from corroding water mains, while possibly beneficial to copper corrosion, can cause other problems for utilities, including the formation of discolored or “red water” at the tap. This problem is the number one complaint from water consumers, and there is little known about the

water chemistry factors that influence the problem. Chapter 4 details work conducted to determine the role of silica in iron leaching and red water formation.

Most chapters of this thesis have been prepared in manuscript format according to the specifications of the journal to which it has been submitted. Chapter 1, “Addressing Copper Pinhole Leaks In Consumer Tubes,” will be submitted to *Water Science and Technology*. Chapters 2 and 4, “Effect of Aluminum Solids and Chlorine On Cold Water Pitting of Copper” and “The Role Of Temperature Gradients In Residential Copper Pipe Corrosion,” have been submitted to *Corrosion Science*. Chapter 5, “Effect of Silica on Iron Corrosion,” has been accepted for publication in *Water Research*. Chapter 3, “Confirming the Role of Aluminum Solids and Chlorine On Pitting Corrosion of Copper,” presents results of a single experiment designed to confirm several controversial hypotheses developed in Chapters 1 and 2. Additional research is necessary before it meets standards of a peer-reviewed article. Chapter 6 is a summary of conclusions from the work presented here.

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# **CHAPTER 1: ADDRESSING COPPER PINHOLE LEAKS IN CONSUMER TUBES**

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## **ABSTRACT**

Pinhole leaks in copper tubes are a major concern to homeowners, and a conscientious effort by utilities is recommended to diagnose the problem and identify potential solutions. In a case study at one utility, data was gathered and a methodology was followed that might prove to be a useful guide to addressing similar problems in the future.

## **INTRODUCTION**

Pinhole leaks caused by internal corrosion are relatively rare, but are a major cause of failures in residential copper plumbing. Over the half-century that this problem has been discussed in the literature (Campbell 1979), improvements to true understanding have been slow in coming and earned only after substantial effort. Recent work has merely served to highlight the poor existing level of practically relevant knowledge (Edwards, Ferguson et al. 1994; Sosa, Patel et al. 1999). The major deficiencies of existing knowledge are obvious upon reading a list of “frequently asked questions” developed for distribution to consumers afflicted with pitting problems (Figure 1-1).

Pinhole leaks are costly given the effort required to find and repair each leak, highly variable amount of water damage per occurrence, and loss of water resource from undetected leaks in service laterals. There is legitimate concern for consumers that one leak might soon follow another—insurance companies often raise insurance premiums or simply do not renew policies, and homeowners distraught over leaks can reach the point they do not feel comfortable leaving the house without first turning off the water. Homeowners may decide to re-plumb the entire house at costs that can exceed \$50,000 per residence. However, even a complete re-plumb with new copper tube does not guarantee that the problem will not recur after a period of time. A consumer confronting these problems must decide between fixing the leak by application of

external solder, replacing a small or larger section of tube, completely re-plumbing, replacing pipe with PVC or CPVC, or purchasing potential cures of dubious value such as magnets. A sound basis to guide consumer decision-making has never been rigorously established, and is likely to be dependent on experiences of other homeowners in the area, local plumbing codes, location and access to the leak, and other considerations.

Given the high costs, poor understanding, and obvious complexity of the problem, a response to a typical outbreak of pinhole leaks in a given area will develop through several phases, dependent on circumstance. The earliest phase, recognition of a problem, is perhaps the most variable. The fact that copper pipes occasionally develop leaks does not appear to surprise anyone. If they occur at a low enough rate, or residents in a given area are less communicative with one another on such issues, utilities are less likely to be informed of a problem. After all, the first inclination of someone experiencing a pinhole leak is to call a plumber, not the water utility. A critical mass is only achieved after several people in a single neighborhood learn they have shared a problem, or if utilities or plumbers are keeping careful records that they share with others, after which time the problem escalates to a noteworthy concern for a community. If a local newspaper runs a story on the issue, the odds of having a future leak reported to the utility increase markedly, sometimes making it appear there is an “epidemic” of leaks when it is possible only awareness has changed.

In the second phase of the process, parties including tube manufacturers, builders, homeowners and utility personnel typically gather, cooperate to varying degrees, and the usual suspected causes are “rounded up” for evaluation. Possible causes invariably include stray electrical currents, microbes, soldering flux, installation practice, water quality and assorted tube imperfections, as well as some more exotic and regionally popular ideas including lightning, cosmic radiation, cell phone use and fluoride addition. Occasionally some research is done in an attempt to prove or disprove one cause or another on behalf of a particular party, but since the problem of pitting has never been replicated under laboratory conditions, invariably only circumstantial evidence is gathered to support or refute certain viewpoints. Progress is greatly hindered by the long length of time, 3 months to 20 years dependent on circumstance, required to replicate the problem from its initiation through actual formation of a leak.

After this educational experience, conscientious water utilities will often take the lead in finding a possible solution regardless of cause. There are two reasons for this. First and foremost, the only way to deliver a solution to all consumers at reasonable cost is by modifying the water in a manner that stops pinhole leaks from growing. Secondly, there are certain legal precedents for finding the utility legally liable for damages (Rambow and Holmgren Jr. 1966):

*“Water supplied by defendant to said subdivision was dangerous and defective, was not satisfactory for the particular use for which it was intended and required, and was not of merchantable quality, all by reason of being of corrosive quality and of such quality as to produce leaks within copper tubing.”*

Judgments as recent as 1997 have upheld this general premise (Amidei,1997). Given that the cause of the problem is unknown, the wisdom behind such legal precedent is perplexing to the authors, since it implies that it has been unambiguously established that the water is the cause.

The final phase involves evaluation and implementation of a possible solution, often after extensive trial and error testing that is guided more or less effectively by outside consultants. To aid in future desktop evaluations of these problems, this work attempts to summarize steps taken in the earlier phases of the work to document and identify the problem, make comparisons to other utilities, and evaluate possible solutions that might stop the problem.

## **CASE STUDY BACKGROUND**

The Washington Suburban Sanitary Commission (WSSC) operates two drinking water plants serving 1.6 million residents in Montgomery and Prince George’s Counties in Maryland. The larger of the plants ( $q_{\max} = 285$  MGD) draws water from the Potomac River while the smaller plant ( $q_{\max} = 72$  MGD) draws water from the Patuxent River. In 1998, plumbers in the areas served by these plants began to notice a surge in copper pitting problems (Fleishman 2000) prompting WSSC to begin asking consumers who experienced pinhole leaks to fill out surveys detailing the location of the leak, type (cold or hot water) and orientation of pipe, age and location of home. As of March 2002, over 4000 cases of pinhole leaks were documented. Out

of 400,000 customers served by WSSC, approximately 1% had reported at least one pinhole leak in their plumbing. Greater than 70% of the reported leaks occurred in cold water pipe, 60% in horizontal sections, and 80% in homes built before 1970.

As to the cause of the outbreak of this copper pitting problem, many theories were advanced and considered. After ruling out many of the possibilities and determining that the cause(s) might never be identified, a detailed investigation was begun to better understand how the chemistry of WSSC treated drinking water might be influencing the problem. In other words, regardless of the cause(s), the utility wanted to assist customers by stopping the propagation of pits. For this particular effort, the water chemistry and the role of aluminosilicates found on the interior walls of failed copper pipe were of interest, since these are the only factors that WSSC could hope to control either directly or indirectly, and because such deposits have been identified as a contributor to hot water copper pitting corrosion (Tunturi and Ylasaari, 1968). Reports of pinhole leaks also seemed to increase after poly-aluminum chloride use was initiated, although other changes were also made about the same time, including slightly increasing distribution system pH to control copper and lead leaching in the distribution system (Buglass, 2000). Some effort was also expended to characterize pits and tentatively identify promising solutions.

## **MATERIALS AND METHODS**

**Desktop Comparison of Utilities' Experience With Copper Pitting Problems.** Telephone surveys of water utilities and plumbers from selected cities were conducted during the first two weeks of May 2001. Survey questions for the water utilities were designed to better understand water treatment, corrosion control, water main cleaning and lining practices, and the utility's perception of copper pitting as a problem in their system. Utility water quality data was obtained from these interviews or consumer confidence reports. As a cross check, surveys were also designed to obtain the experiences of plumbers in the areas served by each utility. Plumbers' names were selected at random from phone listings. More details regarding the surveys can be found elsewhere (Edwards and Rushing 2001).

### **Chemical, Microbiological, and Electrochemical Characterization of Copper Pitting.**

Sections of pipe likely to contain active pits were collected by WSSC personnel in the field and shipped full of water to the Virginia Tech laboratories. Once delivered, these pipe sections were held vertically in a metal vise. A pipe cutter was used to collect 2-4 cm sections from the top of each tube for immediate processing, leaving the portions of pipe not under immediate study completely immersed in WSSC water.

Tubercles (mounds of corrosion products that cover active pits) were detached from each pipe section using a clean metal instrument, weighed on a microbalance, placed into 10 ml of 0.5 mM reagent grade  $\text{NaNO}_3$  solution and then crushed with a glass rod. The sample tube was then covered and mixed vigorously by hand for one minute before determining pH. After another 4 minutes of mixing, the pH was determined again, and the solution was either passed through a 0.45  $\mu\text{m}$  pore sized nylon syringe filter, or placed directly into microbial culture tubes supplied by Droycon Bioconcepts Inc. to check for the presence of classes of corrosion influencing bacteria including acid producing bacteria (APB) and fluorescing pseudomonads. The filtered samples were analyzed for  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  using ion chromatography per Standard Method 4110 C (AWWA, APHA et al. 1998).

The same process was followed for samples of scale collected by scraping areas of the pipe surrounding the pits. WSSC water from the shipped pipe samples were also tested in the microbial culture tubes. Additional tests were conducted for iron related, slime forming, heterotrophic aerobic, and sulfate reducing bacteria by removing 10 additional tubercles and dispersing them into 20 ml of WSSC water using a glass rod. This water was then distributed among four additional microbial test kits, also provided by Droycon Bioconcepts, diluted 1/10 with deionized and filter sterilized water. The microbial and chemical tests were conducted within 3 days after pipes were received.

Electrochemical tests were conducted at the HDR laboratory in Seattle, Washington. Copper tube samples were taken from three different residences experiencing high rates of pitting-type failures and were shipped filled with water by WSSC. Sections of pipe with isolated tubercle caps (an indication of a pit) were cut to 4 cm lengths and placed in a flow through electrochemical cell, through which 1 gallon of WSSC water, changed every fifth day, was

circulated at a rate of 0.5 gal per minute . Details of the polarization cell used in this work can be found in other reports (Reiber 1989). Each of the copper samples was ¾-inch type M copper tubing, with a total interior surface area of 20 cm<sup>2</sup>. Polarization scans were conducted at a scan rate of 1 mV/sec.

**Pipe Surface Analysis.** Pipe samples were collected from a variety of locations throughout the WSSC service area identified in the text. Each sample was first examined by eye to observe if large tubercles were present. Thereafter, the surfaces were scrutinized by scanning electron microscopy (SEM). Finally, x-ray photoelectron spectroscopy (XPS) was also used in conjunction with SEM to identify elements with atomic weights higher than that of oxygen.

**General Water Quality Analysis.** All pH measurements taken during plant sampling were performed with a bench top pH meter with combination electrode manually calibrated for temperature corrections. All pH measurements and temperature readings during distribution system sampling were collected using a portable pH meter with combination electrode and ATC probe. Dissolved O<sub>2</sub> was measured with a Horiba multi-probe per standard method 4500-O G (AWWA, APHA et al. 1998).

Soluble, colloidal and particulate metal samples were taken by passing samples through a 0.45 µm and/or 0.025 µm pore size nylon filters with a plastic vacuum filter apparatus with hand operated pump. Soluble and total metals samples were immediately acidified to 2% by volume using concentrated nitric acid after sampling and filtering and were analyzed using Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) according to Standard Method 3120 B (AWWA, APHA et al. 1998). The fraction of metal removed from samples by a 0.45 µm pore size filter is considered “particulate,” the fraction of metal removed by a 0.025 µm but not by the 0.45 µm pore size filter is termed “colloidal,” and the fraction of metal passing through the 0.025 mm pore size filter is termed “soluble.”

**Variations in Effluent Aluminum.** On 3/6/01 experiments were carried out at the WSSC Potomac Plant from continuously running taps located in the control room. Temperature, pH and dissolved O<sub>2</sub> were recorded when samples were collected for total and soluble metals from the different stages of the treatment process.

During the afternoon of the same day, three sets of experiments were performed using flocculated water in a jar test apparatus to examine effects of pH, temperature, silica and sulfate on soluble aluminum. The first test was designed to determine the effects of coagulation pH on solubility of aluminum at ambient temperature (about 10 °C), whereas the second test repeated the experiment at 25 °C using the same water. In the ambient temperature test, aliquots of flocculated water were adjusted to pH 7.5, 7.7, 7.9, 8.1, 8.3 and 8.5 using 1M HNO<sub>3</sub> or 1M NaOH and allowed to stir for 20 minutes at 30 rpm. Samples were then collected to characterize particulate, total and soluble metal. Concurrently, another plastic jug of flocculated water was warmed to 25 °C by contact with hot water in a nearby sink. Aliquots of this sample were adjusted to pH 7.7, 7.9, 8.1, 8.3 and 8.5, and then treated as before. One additional aliquot was spiked with 20 mg/L SiO<sub>2</sub> and adjusted to pH 8.1.

The third test examined the effects of higher sulfate at ambient temperature. Water for this test was collected 3 hours later than for the two earlier tests. 50 mg/L SO<sub>4</sub><sup>-2</sup> was spiked into each jar and the pH was adjusted to 7.5, 7.7, 7.9, 8.1, 8.3 and 8.5. Jars were then stirred and sampled as before.

**Distribution System Sampling.** On 3/7/01 drinking water samples were collected from several locations in the WSSC distribution system fed by the Potomac plant. These Montgomery County locations were selected by WSSC personnel based on an approximate 24-hour travel time from the Potomac plant, the goal being to sample the same water tested a day earlier at the treatment plant but after it passed through the distribution system. Cold water taps were flushed for 2 minutes and then sampled for particulate, colloidal and soluble metals, pH, temperature and dissolved O<sub>2</sub> measurements as described previously. At sampling locations in residential neighborhoods WSSC personnel opened a fire hydrant. Flow was adjusted such that the water hit the pavement a foot or so from each hydrant. After several minutes of flow with obvious rusty red water, the discoloration was no longer visible to the naked eye, and after about 45 seconds additional flow samples were collected for analysis.

## RESULTS AND DISCUSSION

### Desktop Comparison of Utility Experiences With Copper Pitting Problems

One goal of the work was to compile utility experiences in relation to copper pitting corrosion. The first task examined the frequency of pinhole leaks at other utilities based on literature reports. The second compiled experiences of utilities that have water quality similar to WSSC in terms of pH and alkalinity. As part of this evaluation, input from plumbers in the cities served by the utilities was also solicited.

#### *Comparison to Cases in Literature Where Pitting Was a Known Problem*

Since pitting corrosion is believed to be a relatively rare occurrence, a review of literature reports on pinhole leaks is expected to provide a worst-case perspective. It is noted at the outset that a large percentage of leaks might go unreported in a given case study, depending on the efforts expended to collect the data and the customer's willingness to supply it. It is accepted that all efforts at collecting this type of data are flawed to varying degrees.

Based on current WSSC data (2094 customers reporting at least one leak from 10/23/00-5/29/01, an estimated 21,000 miles of copper pipe in the WSSC customers' houses, and about 400,000 customers), it is calculated that about 1% of WSSC customers have reported at least one leak each year, with an average of 0.04 leaks per WSSC customer and about 0.04 leaks for every 100 meter of copper tube. Comparing these rates to other instances where pitting was reported to be a problem (Table 1-1), it is noted that WSSC customers are experiencing between 2.5-52 times lower frequency of pinhole leaks. The exception is Orlando, where the reported frequency of pinhole leaks is at least 16 times lower than for customers at WSSC. It is possible that homeowners in Orlando might be less likely to report pinhole leaks to utilities since the local belief is that these problems are caused by lightning strikes (Dunham and Russell 1997). In summary, while it appears that WSSC customers are experiencing a troublesome level of pinhole leaks, there are clearly instances where customers seem to have had a greater frequency of problems.

In the WSSC case study, additional efforts were expended to determine underreporting, and that analysis suggests that 27 - 53% of the homes served by WSSC may have experienced pinhole leaks (Zhou, Mathew et al. 2002). Thus, the problem may be much worse at WSSC and the other utilities in Table 1-1 than the less detailed evaluations indicate.

### *Comparison To Utilities With Similar Water Quality*

A telephone survey was conducted of 14 utilities that produce finished water with approximately the same pH and alkalinity as the WSSC Potomac and Patuxent water treatment plants (pH 8.0 +/- 0.5, 30-90 mg/L alkalinity as CaCO<sub>3</sub>). The original list of utilities was generated from a 1992 American Water Works Association Survey (Dodrill and Edwards, 1995) and other utilities were added based on input from these telephone calls. Utilities treating water from the Potomac River, the source water for the larger of the two treatment plants WSSC operates, were a special focus of this investigation.

The plumber and utility surveys supported the general idea that utilities producing water with similar pH and alkalinity to WSSC typically have very few problems with cold water copper pitting. For instance, the plumbers interviewed in Gadsden AL, Fort Collins CO, and Lexington KY, had never encountered pinhole leaks in copper (Table 1-2), and while plumbers in York PA said they had encountered such leaks they were only in homes served by private wells. Anchorage AK plumbers said they encountered pinhole leaks about 2-6 times per year, but most of these were found in hot water recirculating systems that are generally known to have a higher likelihood of pinhole leaks. In Sacramento CA, plumbers fixed 1 or 2 leaks per year, but most of these were in hot water lines. In Denver CO, the plumbers interviewed encountered pinhole leaks with varying frequency, but the problem was relatively rare and predominantly in hot water tubing. Utility personnel in each city confirmed that there was no or only a small problem with pinhole leaks (Table 1-2).

Surveys also clearly supported the general idea that customers at WSSC are experiencing more leaks than customers at other utilities. Four of the five plumbers working in the WSSC area said they were fixing between 4 to 16 pinhole leaks in cold water pipe every month and that they have been fixing leaks at this rate for several years. It is also interesting to note that

plumbers working in Washington D.C., which borders the area served by WSSC but for which a different utility (Dalecarlia) provides water, were also reporting some pitting. The frequency of pinhole leak repairs in this area ranged from never to one leak per day, but 3 of the plumbers felt that the problem was getting worse in D.C.. Interestingly, 2 of the plumbers working in D.C. said they found more pinhole leaks in hot water and recirculating systems while the other half said they found more in cold-water tubing. Officials at WSSC were certainly aware of pitting as a problem, but this was not the case for utility personnel at Dalecarlia, which treats water for D.C.. It is possible that the proximity of the WSSC service area to Washington D.C. could have influenced the results of the plumber surveys for this area, because they might work in both areas.

Even more interesting, perhaps, is the apparent higher frequency of pitting at WSSC compared to Fairfax, Rockville and Leesburg (Table 1-2), since they all draw essentially the same water from the Potomac River and there are no noteworthy differences in the ages of the communities. This suggested that subtle differences in treated drinking water treatment and distribution are responsible for the problems in the WSSC service area, or that water itself has nothing to do with initiation of the pinhole leak problem. Of the utilities surveyed, Carroll County and WSSC are the only ones to have a significant cold water copper pitting problem. In terms of the key variables, these are 2 of the 3 utilities surveyed that use poly-aluminum chloride (PACl) in combination with free chlorine disinfectant. The third utility using this combination is Rockville, but they also feed a very low dose of polyphosphate to control red water complaints. It was deemed possible that the phosphates act to prevent pitting corrosion in waters of this pH and alkalinity, especially since Carroll County provided data that showed decreased copper pitting frequency (after an initial spike) in their service lines after zinc phosphate had been dosed for a few months (Figure 1-2).

### **Chemical, Electrochemical, and Microbiological Analysis of Pitted Copper Pipe**

Experiments were conducted to determine the chemical and biological characteristics of the tubercles that cover copper pits and surrounding scale found in pipes that have pitting problems. This is of interest because the chemistry and biology within the pipes can provide insight into the processes that are propagating pits. For instance, in some cases of pitting

corrosion the tubercles are believed to be highly acidic compared to the surrounding pipe, which can help support pinhole leak propagation (Sosa, Patel et al. 1999). Similarly, if relatively high concentrations of sulfate reducing bacteria (SRB) or acid producing bacteria (APB) are present on the pipe, it might imply they are involved in pitting. Additional experiments were conducted to determine the electrochemical characteristics of an actively pitting copper pipe in WSSC water.

#### *Chemistry of Detached Tubercles and Scale*

In general, active pits are expected to contain relatively high concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  compared to the bulk water, since these ions must move into pits as the attack on copper proceeds (Lucey 1967). In addition, the water within the tubercles is often observed to be about pH 2.7-3.0, which is an indication of an active pit. For samples from homes at WSSC, there was only a slight change in pH when the tubercles or scale were placed in pure water, and when there was a significant change the pH increased (probably due to the alkalinity of the WSSC water in the tubercle relative to pure water). Only one sample showed a significant chloride or sulfate content. This tubercle was at least 4%  $\text{Cl}^-$  and 0.4% sulfate by weight, since it is not certain that all  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in the pit was released by the test protocol. Although it was not quantified, this pit also contained a significant concentration of  $\text{F}^-$ . In conclusion, the pH in the pits was not highly acidic, and only one of six tubercles tested contained high concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , suggesting that only a fraction of the tubercles present on the copper pipes were actively growing. These results also suggest pits are not propagating via classic concentration cells (Sosa, Patel et al. 1999).

#### *Electrochemical Characterization of Copper Pitting*

Copper tubing sections have, as do all metal specimens, a characteristic polarization curve that under appropriate circumstances can reveal information about the underlying corrosion processes. From an electrochemical perspective, copper is a particularly desirable material to work with because its polarization curves are usually predictable, repeatable and can be readily interpreted.

For a WSSC copper pipe sample with a large tubercle cap (Figure 1-3), which typically covers a pit, the polarization scan is distinctive in the hysteresis it shows in the anodic region immediately above the null current (Figure 1-4). While interpretation of the scan is currently unclear and beyond the scope of this paper, it is currently believed that this type of electrochemical response is typical of specimens with active pitting sites. After the initial scan, the tubercle cap was carefully removed from the active pit site leaving the rest of the pipe and the material within the pit undisturbed, and polarization scans were repeated. The absence of the cap and the exposure of the pit interior quickly began to change the electrochemical response of the specimen, and after 96 hours the polarization curve was indistinguishable from scans made on uniformly corroding surfaces (Figure 1-4). This result suggests that removal of the tubercle cap will stop copper pitting. The presence of a tubercle cap did not guarantee the polarization curve response considered typical of pitting specimens. Most samples with tubercle caps produced a conventional polarization curve, which did not change after the tubercle cap was removed. This seems to again confirm that only a fraction of tubercle caps were associated with active pits on a pipe.

One of the possible benefits of adding a phosphate or silicate based corrosion inhibitor to a water in which pitting is occurring, is that the inhibitor might dissolve or weaken the tubercle cap to a sufficient degree that pit propagation will stop. To test this hypothesis, tubercle caps from WSSC pipes were removed and placed in beakers containing WSSC water with high concentrations of polyphosphate (100 – 100,000 mg/L as  $\text{PO}_4$ ). At the highest level of polyphosphate, nearly 100% of the copper in the tubercle cap was dissolved in solution, compared to approximately 10% at the lowest concentration. This suggests that polyphosphates might be helpful in stopping pitting with the detriment of higher soluble copper in the water (Edwards, Hidmi et al. 2002).

Polarization scans were then conducted on active and non-pitting copper samples before and after being exposed to polyphosphate, orthophosphate, and a silicate based corrosion inhibitor. An indication that the inhibitor is effective would be the same shift in polarization response seen when the tubercle cap was removed from an actively pitting sample (Figure 1-4). The RMS (Root Mean Square) noise index was used to mathematically assess the degree to which polarization scans differed from the theoretical response for uniform corrosion, and

therefore, the tendency for the surface to be pitting. It is believed that the greater the RMS noise value, the more likely pitting is occurring on the surface.

The RMS data for the high dosage (60 mg/L as PO<sub>4</sub>) of orthophosphate test showed a substantial decrease in pitting activity on the active pitting specimen, but little effect on the non-pitting samples (Figure 1-5). High dosage of polyphosphate (60 mg/L as PO<sub>4</sub>) produced similar results, with a pronounced impact on the active specimen, but little effect on the non-pitting specimens. The silicate inhibitor showed only a minor impact on RMS noise level of the active pitting specimen and no effect on non-pitting. A full discussion of the electrochemical tests conducted is beyond the scope of this paper and can be found in other reports (Reiber 2001), but the tests indicate that both types of phosphate corrosion inhibitors at high concentrations show a positive effect in terms of decreasing copper pit behavior, whereas the silicate based inhibitor had little effect. Orthophosphate addition to WSSC water might prove to be an effective strategy to control copper pitting at WSSC without causing problems with metal release (Edwards, Hidmi et al. 2002).

#### *Microbial Testing of Tubercles and Attached Scale.*

Microbial tests were made for acid producing bacteria (APB), fluorescing pseudomonads, iron related, slime forming, heterotrophic aerobic, and sulfate reducing bacteria in tubercles, samples of scale collected from outside the tubercles, and bulk water from the pipes with copper pitting. A previous bacterial culture conducted by WSSC indicated that *Pseudomonas aeruginosa* were present on pipe surfaces, and preliminary tests of a water sample by WSSC personnel for APB were positive. Bacteria are believed by some as contributing factors to copper pitting. All test results from this study except those for APB were negative.

For the APB test kits used, presence of these bacteria is indicated by a color change in the test vial from purple to yellow. It was later determined that a total color shift was obtained with nothing but filter sterilized deionized water. In other words, the color change had nothing to do with the presence of APB but rather lack of buffer capacity in a sample. We speculate that this false positive was because the pH of pure water in equilibrium with indoor atmospheric CO<sub>2</sub> is about 5.0-5.6, whereas the pH of buffered WSSC water is higher. Future researchers should be

aware of this deficiency. In summary, it was deemed unlikely that bacteria are responsible for forming or propagating pits in WSSC water.

### **A Focus on Aluminum and Silicates in the Water Distribution System**

The goal of this phase of research was to determine the origins of aluminum in coatings on pipes of WSSC consumers, and to obtain preliminary insights as to their potential benefits or detriments in copper corrosion at WSSC. This stage of the work was conducted in three phases. The first involved a comparison between the aluminosilicate films formed at WSSC and the films formed on the pipes in previous tests with Denver water (Kvech and Edwards 2001). The second phase involved a comparison between pipes in consumers' homes with and without pinhole leaks at WSSC. The third phase examined the sources of aluminum in WSSC water.

#### *Comparison Between Denver and WSSC Pipe Samples*

Until recently, the conventional wisdom was that aluminosilicate films formed on pipe should be beneficial to aspects of cold-water copper corrosion. However, recent research indicated that these films worsened aspects of copper corrosion by-product release in Denver water (Kvech and Edwards 2001). While pitting was not a focus of the Denver laboratory investigation, the original pipe samples from that experiment were obtained and studied carefully. The copper pipe samples included those generated after a 14 week exposure to the ambient aluminosilicate solids in Denver water at pH 8.0, versus the same condition after these solids had been removed by filtration.

The pipes were examined by eye, SEM, and XPS. A particular focus was to determine whether the aluminosilicate solids caused formation of micro-pits, or non-uniform corrosion, compared to the same water with low concentrations of aluminosilicates. If so, it would suggest that the aluminosilicate solids promote pitting. In contrast, it might be that the aluminosilicates prevented micro-pitting and non-uniform corrosion, in which case it would support the idea that these films are protective to copper pitting. In addition, the surface composition of aluminosilicates on the pipes from the Denver system was compared to those from WSSC using

electron backscatter techniques. Water from the Moffatt plant in Denver has roughly similar pH and alkalinity as that from the WSSC Patuxent plant (Table 1-2).

The visual analysis of Denver pipes indicated that copper pipes exposed to a higher concentration of aluminum solids at pH 8.0 had more non-uniform blue green scale on their surfaces than other pipes. However, in this 14-week test this effect was only obvious if the solids concentration was about 1.2 mg/L Al.

The surfaces of the copper samples were then examined using SEM for evidence of pitting. In all cases where the Al solids were added to water, discrete particles could be observed attached to the surface and projecting into solution. In other words, the aluminosilicate films did not uniformly coat the surface. However, discounting micro-pits that were consistently about 1  $\mu\text{m}$  in diameter, no large pits were present on samples. Micro-pits were not more prevalent on tubes with aluminosilicate films when compared to tubes without aluminosilicate films. Thus, while the Al deposits seemed to increase the buildup of copper and aluminum scale on the surface as determined by eye and SEM, they did not seem to increase the likelihood of copper pitting. Copper pipe samples exposed to filtered Denver water for 14 weeks had nearly undetectable levels of Al and Si on the pipe surface. For pipes exposed to unaltered Denver water, Al and Si comprised as much as 9.5 and 28% of the surface elemental composition by weight, respectively. These levels are comparable to the amounts found on non-pitted areas of WSSC samples (Table 1-3). In summary, this work demonstrates that the solids forming on pipes at WSSC are probably not that unusual compared to those forming elsewhere.

#### *Comparison Between Samples from Homes with and without Pitting*

In order to try to understand why pitting is occurring in some homes and not others serviced by WSSC, surface deposits on pipes were analyzed from homes in both categories. To facilitate this analysis, WSSC staff collected pipe samples from a few homes that had and had not experienced copper pitting corrosion. Some samples were sent to Virginia Tech directly by WSSC consumers who volunteered to do so. The pipes were all drained of water before shipment to Virginia Tech, except for sample 2 which was collected fresh and sent full of water.

There were no obvious pit tubercles on the pipes collected from non-pitting areas and when surface deposits were removed pits, were not visible underneath. On the other hand, in pipe samples collected from homes where pitting had occurred, or where a pit has broken through the pipe, it was not uncommon to observe as many as 8-10 pit tubercles per foot of pipe. The pits often contained very high chloride, exposed pure copper metal, and undetectable aluminum and iron. Some silica could also be detected in pits.

A comparison of unpitted surfaces of pipe collected from homes highly subject to pitting with pipe surfaces collected from homes or areas without serious pitting problems showed no apparent differences. Aluminum on the pipes from pitting areas ranged from 0-39% of the weight fraction (Table 1-3), whereas the pipes from areas without pitting contained 4-33% aluminum. Iron ranged from 0-12% on pipes from pitting areas compared to 0-19% from non-pitting areas. Silica ranged from 0-30% on pipes from pitting areas compared to 0-28% in non-pitting areas. Similar comparisons are possible for the minor constituents detected in samples including S, Ca, Mg, Mn, K and P. In summary, there is nothing that was detected on the surfaces of pipes from consumer's homes at WSSC that seems to correlate with the frequency of pinhole leaks, including aluminosilicate deposits by themselves. This seems to call into question the conventional wisdom about these deposits driving copper pitting, at least without other contributing factors.

#### *Sources of Aluminum in WSSC Water*

Possible sources of aluminum and silica observed on pipes in the WSSC service area include the river water, coagulant chemicals added during treatment, and cement pipes in the distribution system. Aluminum occurs naturally in waters as clay (an aluminosilicate) or soluble species such as  $Al^{+3}$ . In addition, because WSSC uses aluminum-based coagulants (poly-aluminum chloride at the Potomac plant, and aluminum sulfate at the Patuxent plant), aluminum found in the distribution system might come from this source. Finally, cements in the water distribution system, from concrete transmission lines or cement re-lining of iron mains, can contain between 5-36%  $Al_2O_3$ , which can leach to the water in significant concentrations

(AWWA, 1996). Silica will also occur naturally in the influent water, as clay or as soluble silica, and will leach from cement. Leaching of both silica and aluminum is greatest from new cement.

To explore the relative importance of each source at WSSC, several experiments and sampling events were conducted to examine changes in aluminum concentration as water flowed from the treatment plant and through the distribution system at WSSC. Before discussing the actual sampling results, it is useful to put the aluminum issue into perspective for the treatment plants at WSSC and nationally. Aluminum is not a regulated contaminant, and it is monitored mainly because it can form white solids that can cause water discoloration and consumer complaints. Iron containing coagulants were used at the Potomac treatment plant from 1984-1993, then aluminum and iron based coagulants were tested, and after 1995 the Potomac treatment plant switched to poly-aluminum chloride coagulant. Prior to 1984, aluminum sulfate (alum) was used at WSSC; the Patuxent treatment plant has always used alum.

Data collected from WSSC was compiled for these key time frames and plotted in a frequency distribution, along with data from a national survey of aluminum in finished drinking water (Letterman and Driscoll 1988) (Figure 1-6). The y-axis label corresponding to 0.5 indicates the median concentration reported in each data set. Using this to describe a “typical” result, median aluminum in the finished drinking water of the Potomac plant increased from about 0.046 to 0.060 mg/L after the change from ferric to PACl coagulant. The median aluminum in the Patuxent plant is typically only 0.030 mg/L whereas the median aluminum in finished drinking water nationally is 0.090 mg/L. Thus, while some increase in treated water aluminum occurred in 1995 at the Potomac treatment plant when PACl use began, median aluminum levels are still about 1/3 less than those observed nationally, and 2/3 less than those observed nationally at the Patuxent plant.

On the other hand, as indicated by measurements of effluent aluminum from the WSSC Potomac treatment plant (Figure 1-7), it is clear that there are “spikes” of aluminum leaving the treatment plant that were not present when ferric coagulant was used. This is not uncommon at treatment plants using alum or PACl coagulants.

Water Treatment Plant Results of jar testing using flocculated water indicated that soluble aluminum is strongly controlled by the temperature and pH of the water (Figure 1-8). As a general rule, lower pH decreased soluble aluminum, consistent with the fact that the dominant

soluble species in this pH range is  $\text{Al}(\text{OH})_4^-$ , and its formation is favored at higher pH and temperature as predicted by the computer program Mineql+ (Figure 1-8). For samples collected at the plant that were near 6 °C, the model and data agree very closely. In the presence and absence of sulfate near 11 °C, most predictions are within a factor of two of actual data. Near 25 °C the agreement is very good for the point collected near pH 7.7, but the model tends to over predict soluble aluminum as pH increases. These trends in aluminum solubility with temperature and treated water pH provide a good explanation for why WSSC sees spikes in effluent aluminum during the summer when temperatures and algal blooms raise pH.

Water Distribution System On March 7, 2001, one day after sampling at the Potomac plant, samples were collected at various locations in the distribution system that corresponded to an approximate 24 hour travel time from when the water left the plant; the goal being to sample approximately the same water from the day before. A variety of sampling locations were selected (Table 1-4) to represent water that had flowed through water mains of various classifications as it traveled to consumers homes, including 1) mains that had been never been cleaned and lined, or cleaned and lined at least 5 years previously, and 2) mains that had been cleaned and lined more recently. If pipes that were relined with cement do leach significant amounts of aluminum, there should be an increase in aluminum levels in the water at these locations. However, given that water in a distribution system can reach a location through a variety of paths, it cannot be certain that the information in Table 1-4 is perfectly representative of the type of mains involved, but it is the best that could be done under the circumstances.

The effluent sample collected the day before at the Potomac plant indicated this water had a concentration of 0.042 mg/L total Al before entering the distribution system. The lowest level of total Al was 0.045 mg/L in the samples collected from the distribution system, which shows that no net aluminum was removed from the water between the treatment plant and the sampling locations (Figure 1-9). The locations that had total aluminum above 0.065 mg/L included Silver Spring#2, Olney, Airpark, Gaithersburg, and Silver Spring #3. Samples with less than 0.065 mg/L total aluminum included Hillandale, Silver Spring#1, and Glendale. Of the 3 locations with the lower total aluminum, water either had little chance of passing through mains that were cleaned and lined, or in one case could have passed through one block of re-lined main. In the other locations where aluminum was above 0.065 mg/L, the water likely passed through a

main that had recently been cleaned and lined, or had passed through many miles of cement transmission line. This data strongly implies that concrete is serving as a significant source of aluminum in the WSSC distribution system. Moreover, 50% or more of the aluminum leached to the water is particulate, although soluble aluminum also appears to be increasing in some circumstances.

## **CONCLUSIONS**

- There are no proven causes for pinhole leaks in residential plumbing, only hypotheses that are supported to varying degrees by scientific data, and some that are outright speculation. Pinhole leaks have never been produced in the laboratory under conditions that are scientifically reproducible.
- It is 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.
- An array of chemical, biological and electrochemical tests can shed light on the problem and assist efforts to find a solution. However, these tests require expertise and sometimes provide faulty guidance. Desktop studies of pinhole leak frequency and practices at nearby utilities can also serve as a valuable guide.
- The analysis suggests that dosing of orthophosphate might solve the problem in at least some circumstances.
- The role of aluminum in pitting corrosion deserves future study. While aluminum deposits clearly do not cause pitting by themselves, the effect of a combination of aluminum solids and chlorine on copper pitting is deemed of particular interest.

## **ACKNOWLEDGEMENTS**

The authors acknowledge the financial support of WSSC, who funded this research, and in particular the efforts of Bob Buglass, Mike Woodcock, and Mohammed Habibian.

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Figure 1-1. Frequently asked questions about pinhole leaks

**What is corrosion?** “Corrosion” refers to the degradation of a material, such as those used in home plumbing, by chemical reactions.

**Why are metals used for pipe materials if they corrode?** Metals used in home plumbing possess a unique combination of strength, durability, corrosion resistance and low cost. In most cases, we also have decades of experience with the materials, and those that failed to perform are no longer used. Some metals such as gold do not corrode but they too expensive.

**Is corrosion of plumbing, including the copper pipes in my house, to be expected?** When immersed in water, all commercially available metal pipe materials will corrode. In the vast majority of cases, however, corrosion proceeds very slowly, and it is not a significant concern.

**What are the consequences of corrosion?** The two main consequences of corrosion that might concern homeowners include loss of pipe material, with loss of strength, possibly leading to burst or leaking pipe, and release of metal to drinking water in low concentrations as a result of corrosion.

**Why isn’t plastic pipe used to avoid these problems?** Use of plastic pipe may eliminate certain corrosion problems; however, there are other problems have been associated with plastic. For example, under some circumstances plastic pipe more readily supports bacterial growth, certain chemicals can migrate to drinking water through plastic, and indeed some potentially harmful chemicals also leach to water from plastic. In addition, because plastic is non-conductive to heat and electricity, plastic pipes are more prone to freezing in cold weather and cannot be used to ground electrical appliances. This list is not meant to discourage use of plastic plumbing, which obviously has its own merits, but it does show that there is no perfect plumbing material that could be economically used in all situations.

**Explain the difference between pitting corrosion and normal corrosion?** On a copper pipe, corrosion usually eats away at the surface slowly and uniformly -- in the case of copper pipe it will normally last hundreds if not thousands of years. “Pitting” is said to occur when excessive corrosion occurs at a very small area on the pipe surface, causing the pipe to fail in as little as a few months under some very rare instances.

**What causes copper pitting corrosion to start?** There are many ideas on this subject. The list includes factors arising from improper installation, bacteria, electrical grounding, pipe manufacture, water quality, or a combination of these and other factors. Over the years, most of the promising ideas have been directly tested in my university laboratory, and none have ever caused a pit to form. Obviously, *there is a cause*, because pitting does occur—the problem is that the very unusual circumstances that cause this have not yet been scientifically identified.

**What can I do if I have a pitting corrosion failure?** Unfortunately, other than replacing the pipe section when it fails or considering re-plumbing, not much can be done.

**If I have had a pitting corrosion failure, does that mean I will have more?** No. There are many cases where only one leak from pitting corrosion has occurred, the affected pipe section has been replaced, and that is the end of the problem. On the other hand, if you have had one pitting failure, you are more likely to have another.

**If my neighbor has experienced copper pitting corrosion, does that mean I will too?** No. One of the most perplexing aspects of this problem is that two houses can be built next to each other at about the same time, the pipes can be installed by the same plumber and purchased from the same manufacturer, and pipes are filled with the same water--yet one home might develop a serious pitting problem while the other does not.

**If I replace all my copper pipe with new pipe, will that guarantee I will not have problems in the future?** Replacing all your pipes will buy you a few months to a year during which time new pinhole failures will not occur. It might even solve the problem for a much greater time period; however, in my experience with other "outbreaks" of pinhole leaks it has not solved the problem once and for all. Your own decision to replace plumbing should weigh the total cost versus these possible benefits.

**Who is responsible for this problem?** Since scientists studying this problem have never identified a cause, it is not possible to say who or what is to blame.

**Is the situation hopeless?** No. While scientists have never identified what starts pitting, it is currently believed that in some cases, adjustments to water chemistry are possible that can “kill” existing pits. Again, to use a tire analogy, some unusual types of tires can be purchased that are self-healing. Not much is known about how to kill pits, and as a result, these factors have to be investigated on a case by case basis before a “cure” can be identified

Table 1-1. Frequency of pinhole leaks at WSSC and calculated values from other case studies where pitting was deemed a problem.

Name	Frequency	Reference	Relative Frequency*	Other comments
Unidentified area in Colorado	11% of all homes with pinholes each year	Edwards (unpublished)	11 times worse than WSSC	Less than 80 homes served by well water, data collected over 3 year time period.
California Utility	on average 1 leak per customer	(Rambow and Holmgren Jr. 1966)	25 times worse than WSSC	Houses built in 1961-1963, and data is frequency through Nov. 1964
Texas utility	on average 0.1 leak per customer in area of 900 homes	(Reiber 2001)	2.5 times worse than WSSC	Some trailers with relatively little plumbing, many occupied part time.
Scottish Hospital	64 total leaks	(ICA 1990)	NA	Mostly cold water
Saudia Arabian Hospital	657 leaks (avg. 2.1 leaks/100 meter of pipe)	(ICA 1990)	52 times worse than WSSC	Hot and cold water over a 4-7 year time span.
City of Orlando	0.06% of customers reporting a copper corrosion problem each year	(Reiber, Poulson et al. 1997)	16 times better than WSSC	Includes blue water complaints.

\*The cited pitting frequency estimated in the case study compared to the same relative frequency estimated at WSSC.

Table 1-2. Summary of utility data and survey responses. “ND” indicates no data available.

	Raw Water Source	Final pH target	Disinfectant type residual	Final Alkalinity (mg/L)	Final Hardness (mg/L)	Current Coagulant	Previous Coagulant	Residual Al Range (ppb)	Relining?	Corrosion Inhibitor	# of service connections	Pitting Problem? Utilities Opinion:
WSSC, Potomac	Potomac	7.5	1.5-2.1 mg/L chlorine	82	130	PACl	1960-79 Alum; 1979-94 FeCl3	102 (33-185)	yes	none	400,000	yes, it's a problem
WSSC, Patuxent	Patuxent River	7.5-8.5	1.4-2.2 mg/L chlorine	33	57	Alum	Alum	35 avg. 9-102	yes	none	400,000	somewhat less a problem than Potomac plant
Fairfax (VA)	Potomac and Occoquan	7.1-7.9	2.1-5.3 Cl-NH3	43-82	ND	PACl	Alum before 1998	25-35	none	ND	213215	none
Dalecarlia (DC)	Potomac	7.7-8.4	4 mg/L, Cl-NH3	81.1	136.3	Alum	Alum	31-106	trans. mains only	none (pH control w/lime)	1,000,000 customers	None
Leesburg (VA)	Potomac	7.5-7.8	2.5 mg/L Chlorine	118	130	Ferric Chloride	No previous	none	no	pH control	10,000	None
Carroll County (MD)	Liberty Reservoir	8.5	1.2 mg/L Chlorine	43	ND	PACl	ferric chloride before 1996	64	no	ZnPO4	7000	Yes. Based on repair of copper service lines.
Baltimore (MD)	Liberty Reservoir Plant	8.1	1 mg/L chlorine	ND	ND	Alum	No previous	60 (50-100)	Yes	No	1.8 million customers	None
Anchorage PWS (AK)	Surface	8.0	1 mg/L, Cl2	96	115	Ferric Sulfate	Alum till 1985	-	no	none (pH control)	150,000	No known widespread problem
Fort Collins Water Utilities (CO)	Surface	7.9	0.5 mg/L chlorine	37	51.1	Alum	Alum	48-72	no	none (pH control)	34775	Not a known problem
Gadsden Water and Sewer Board (AL)	Surface	8.1	2 mg/L chlorine	60	ND	Alum	Lime and Alum	ND	no	Sodium Phosphate	19000	Not a known problem
City Of Sacramento (CA)	Surface/gro und	8.4	0.6 mg/L chlorine	24	42	Alum	Alum	50-60	no	none (pH control)	150000	Not a problem
York Water Company (PA)	Surface	8.1	1.2 mg/l Cl-NH3	46.8	84	Alum	Alum	75	yes (concrete)	none (pH control)	50,000	Not a known problem
Kentucky American Water Company (KY)	Surface	7.3	2.5-3.0 mg/L Cl-NH3	74	186	PACl/FeCl (2plants)	FeCl3 for both till 90	46	no	zinc ortho phosphate	100000	Not a known problem
Denver, Moffat Plant (CO)	Surface	7.8	1.4-1.6 mg/L Cl-NH3	28	42	Alum	Alum	0-230	yes (concrete)	pH control	>1,000,000	None

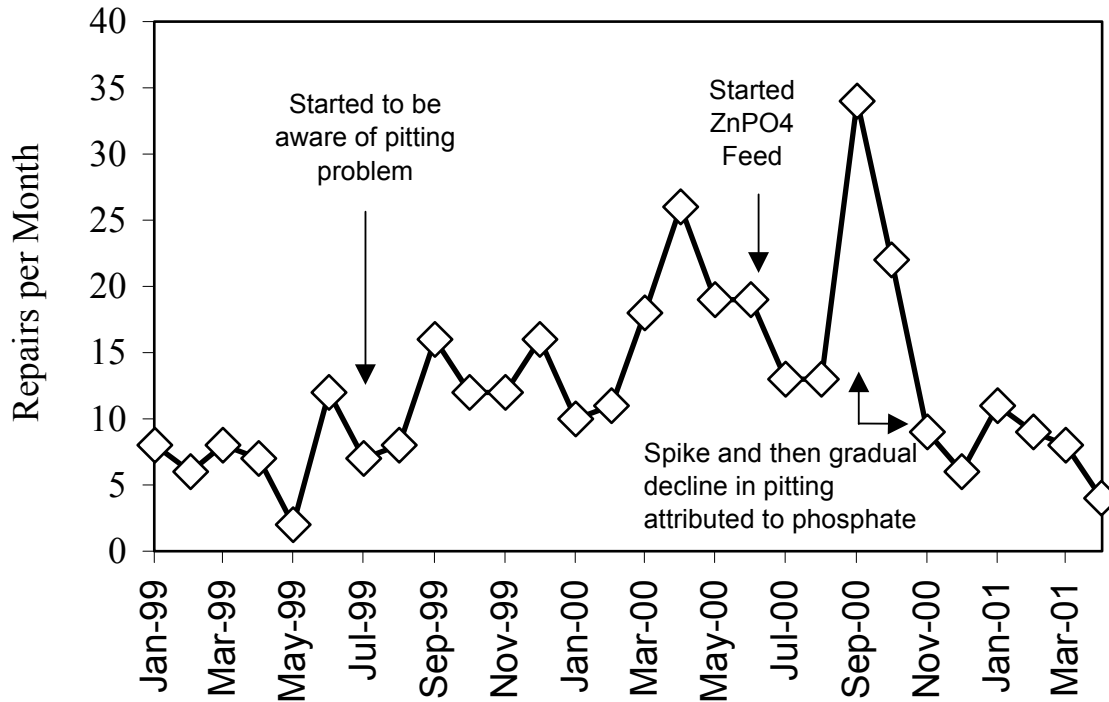


Figure 1-2. Repair of copper service lines due to copper pitting at a utility in Carroll County Maryland. In 1996, Zinc orthophosphate dosing was discontinued. In 1997, coagulant was changed from ferric chloride to poly-aluminum chloride. Pitting frequency was just a few leaks per month at that time. Data courtesy of Charles Singer, Carroll County.



Figure 1-3 A large isolated pit on WSSC residential copper tubing typical of the type used to develop polarization scans. The mound, or tubercle, is formed by rapid copper corrosion underneath the pit.

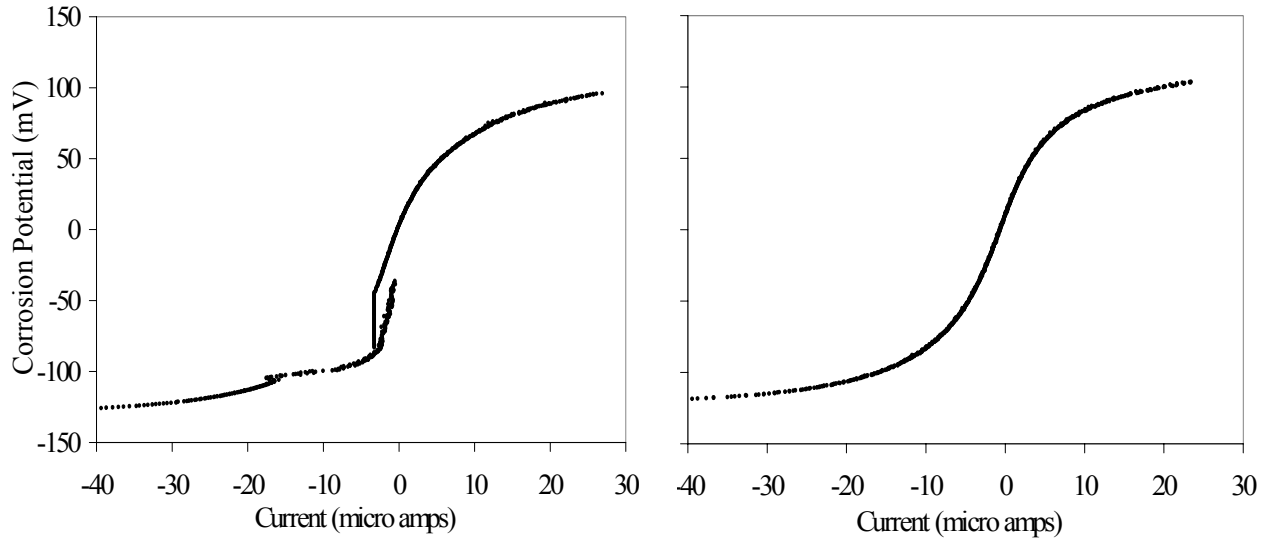


Figure 1-4. Polarization scans of WSSC copper specimens. Left: Actively pitting copper with tubercle cap in place. Right: Same sample 96 hours after tubercle cap removal. The scan on the right is also typical of copper corrosion in pipes without pits.

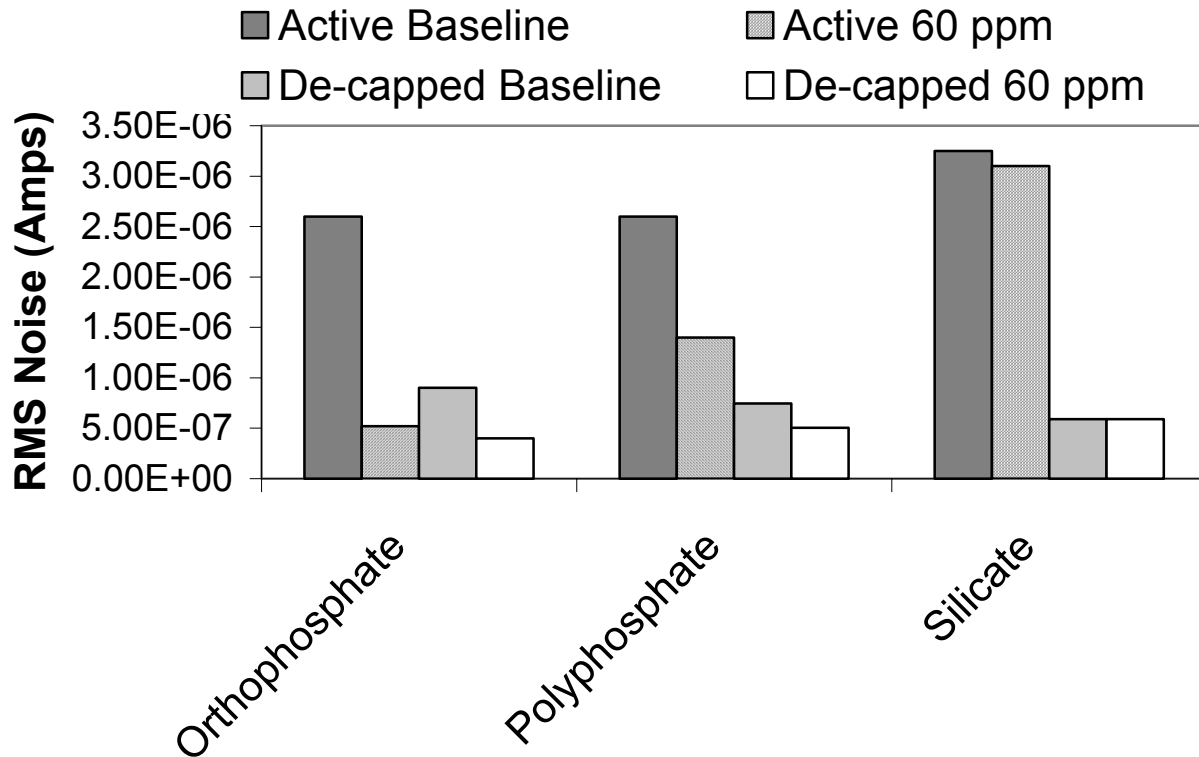


Figure 1-5. Effect of corrosion inhibitors on RMS noise measurements for samples with active pits and removed tubercles before and after 60 mg/L of corrosion inhibitor dosing.

Table 1-3. Comparison of Copper Surfaces between Homes with and Without Frequent Pinhole Leaks

Sample Number	Comment	(n) <sup>@</sup>	% Al	% Fe	% Si	% Cl	% S	% Cu	% Sn	% Ca	% P
The following pipe samples were collected from an area/homes where pitting was relatively common											
1a*	Pitted (In pit)	3	0	0	2.2-4.3	1.3-4.3	0-8	0-100 <sup>#</sup>	34-93 <sup>#</sup>	0	0
1b*	Pitted (Near pit)	8	8.2-32	0-6.4	6.2-23	0-0.4	0	32-47	0	0	0
2a	Unpitted Sample	10	0-30	0-12	0-20	0	0	28-93	0	0-3.5	0
2b	Pitted (in pit)	5	0	0	0-15	0-41	0	59-97	0	0	0
2c	Pitted (Near Pit)	5	15-31	0-9	17-30	0-1.5	0	27-61	0	0-2	0
3a	Pitted (in pit)	4	0	0	0	0-2.1	0	98-100	0	0	0
3b	Pitted (Near Pit)	7	5-22	0-3	9-28	0-0.1	0	50-86	0	0-2	0
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.											
4a	Pitted (in pit)	5	0	0	0	3-43	0	59-97	0	0	0
4b	Pitted (Near Pit)	8	0-39	0-11	0-23	0-3	0-4	27-95	0	0-3	0
5a	Pinholes Uncommon	6	7-23	3.2-19	7-26	0	0	25-80	0	1-3	0
The following pipe samples are from an area/homes where pinholes are relatively uncommon											
6a	Pinholes Uncommon	7	9-24	0-2	0-28	0	0	47-100	0	0-2	0
7a	Pinholes Uncommon	6	4-24	0-4	2-22	0-2.8	0	40-94	0	0-2	0
8a	Pinholes Uncommon	6	13-33	0-4	10-23	0	0-4	29-80	0-7	1-2	0-5

#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.

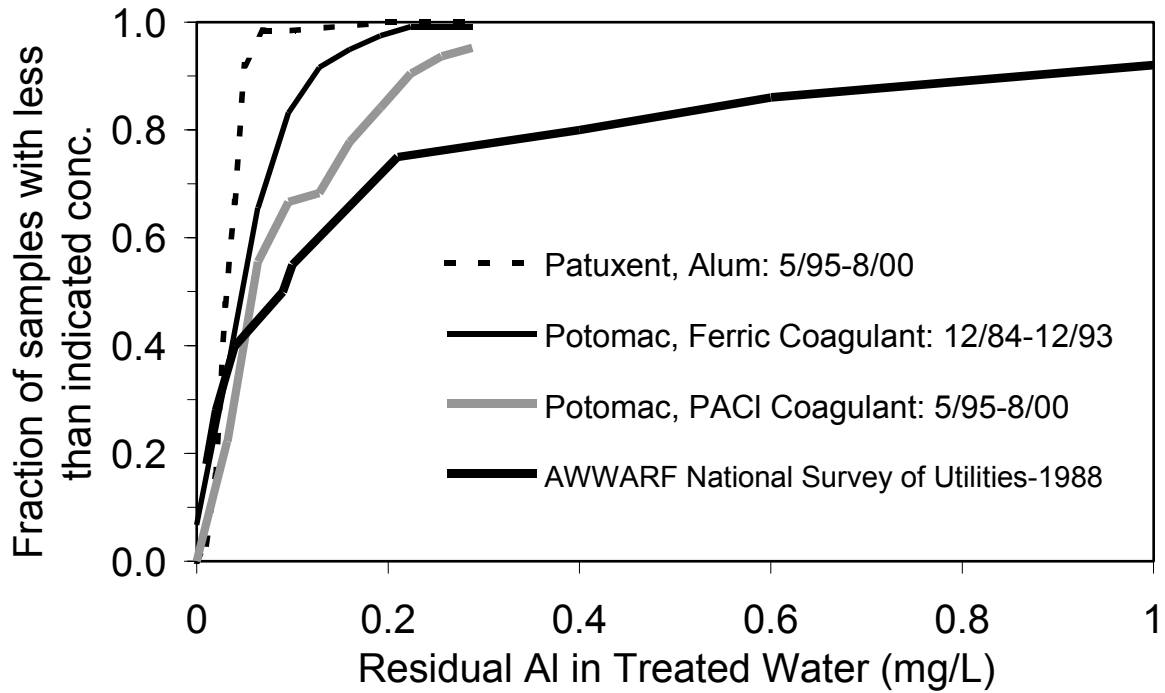


Figure 1-6. Perspectives on aluminum in treated water at WSSC.

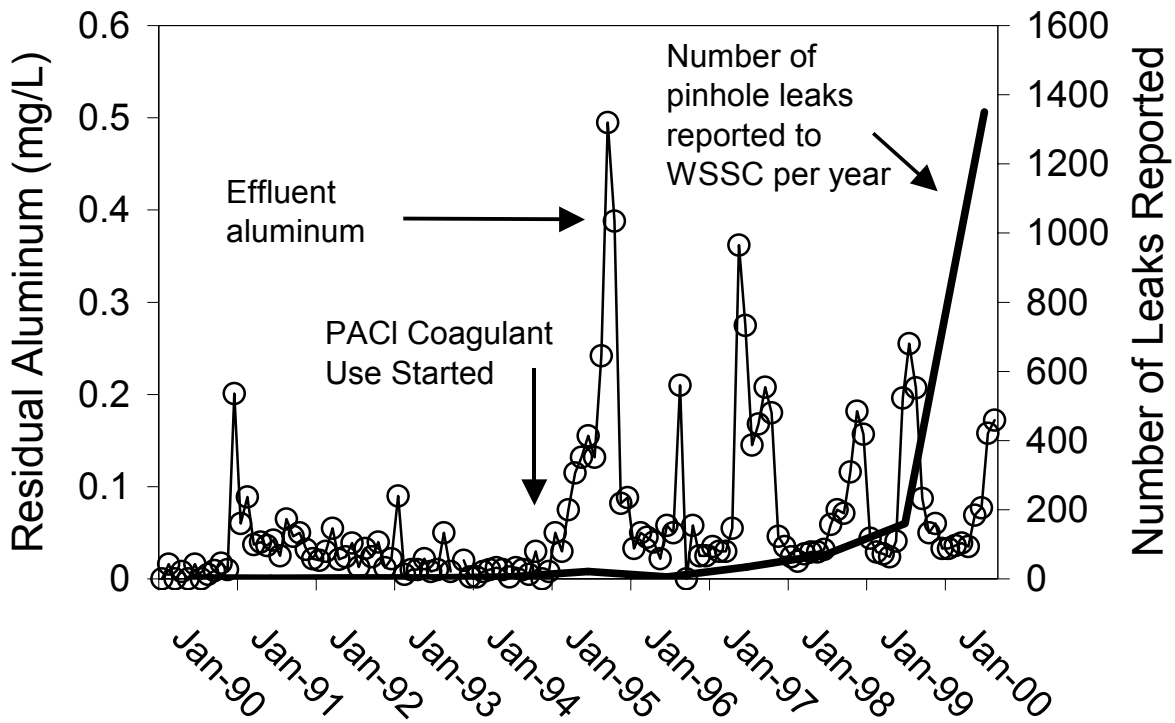


Figure 1-7. Monitoring results of finished water residual Al at the Potomac plant and yearly number of pinhole leaks reported to WSSC.

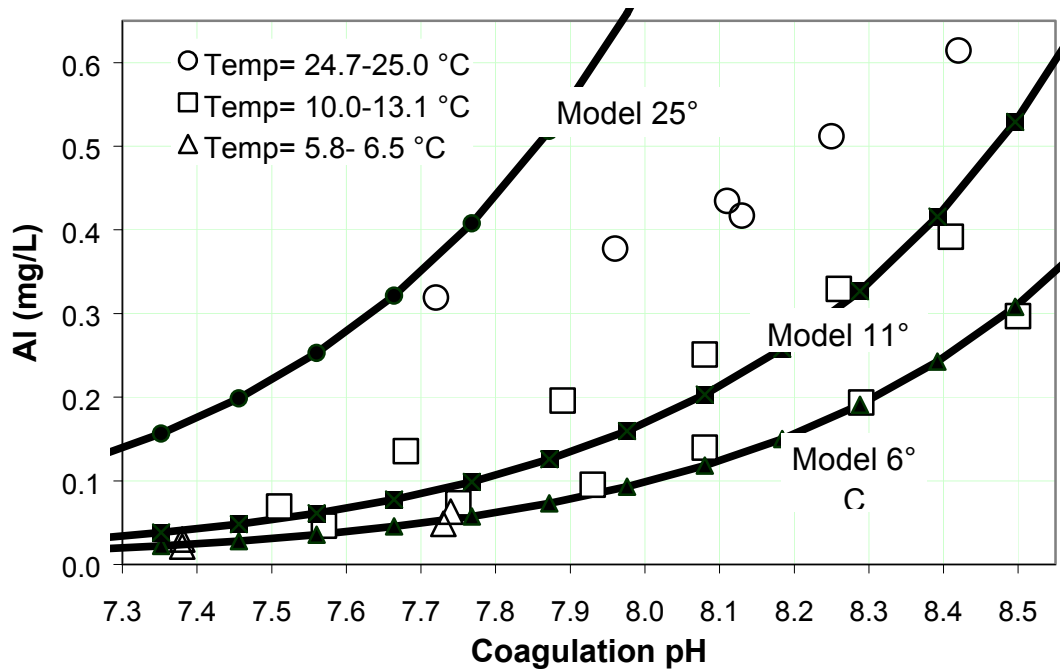


Figure 1-8. Comparison of soluble aluminum data collected at the treatment plant during jar tests with expectations based on chemical model predictions

Table 1-4. Characteristics of Sampling Locations for Tracking of Distribution System Aluminum. The term “clean/lined” refers to the belief that water traveled through a water main that was cleaned and then lined with concrete within the last 5 years or so. “Dead end” means that the main is ending, and “extreme point” means that the sampling location is within 1 mile of a dead end or pressure zone.

	Sampling Location		DO	Approx age of system in area	System clean/lined in area?	Passed through some clean/lined or new?	Dead end/ extreme pt.?
Area		pH	mg/L O <sub>2</sub>				
HILLANDALE	10230 New Hampshire Ave.	7.32	9.90	40	No	No/No	No/No
Silver Spring#1	8301 Fenton St.	7.51	10.60	50-80	Possible*	(1)/No	No/Yes
Glenmont	2315 Randolph Rd.	6.88	10.33	40-50	No	No/No	No/No
Silver Spring#2	12808 Saddlebrook Rd.	7.10	10.70	35	Yes	Yes/No	Yes/Yes
Olney	18040 Georgia Ave.	7.44	10.11	30-40	No	Possible@	No/Yes
Airpark	7889 Cessna Ave.	7.72	*	25-30	No	Possible#	No/Yes
Gaithersburg	19388 Montgomery Village Ave.	*	*	30	No	Possible#	No/Yes
Silver Spring#3	10711 Ordway Dr.	6.86	*	50	Yes	Yes/No	No/No

\*one block of main re-lined in 1999

# the water probably flowed through 2-3 miles of 10-12 yr old and 1 mile of one year old cement lined transmission (48" & larger) main

@ the water probably flowed through about 6 miles of one year old cement lined transmission main

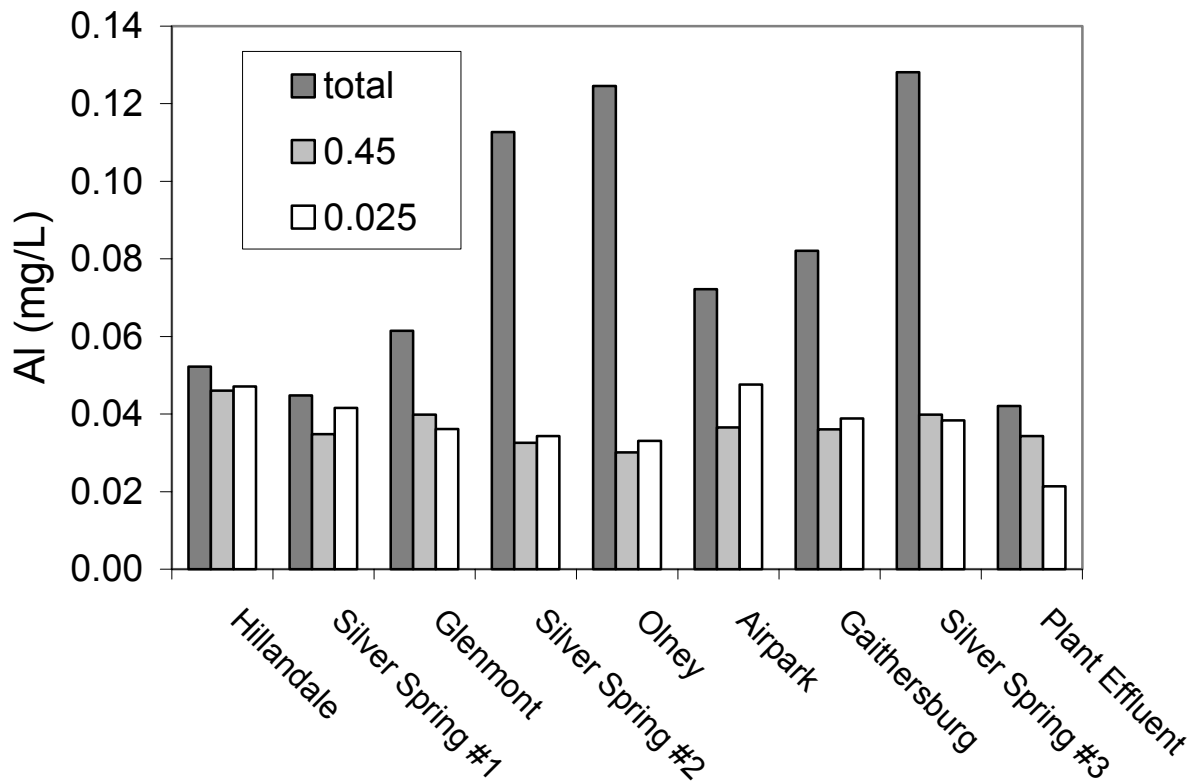


Figure 1-9. Aluminum at indicated sampling locations in the distribution system. Categories denote amount of aluminum that passed through a filter of that pore size in  $\mu\text{m}$ . Total samples not filtered before analysis.

## **CHAPTER 2: EFFECT OF ALUMINUM SOLIDS AND CHLORINE ON COLD WATER PITTING OF COPPER**

Jason C. Rushing and Marc Edwards

### **ABSTRACT**

Both aluminum solids and chlorine are often present in potable water systems, but their effect on copper corrosion and pitting is not well understood. Circumstantial evidence from one system with copper pitting problems suggested that high chlorine residuals and aluminum solids might be contributing factors. To test this hypothesis, a series of experiments were conducted to examine their effect on copper corrosion under stagnant and flow conditions. Although chlorine alone impacted copper corrosion, a synergistic reaction was discovered between chlorine and aluminum solids when exposed to copper. Evidence for this effect was seen in increased chlorine decay rates, increased non-uniform copper corrosion, and rising corrosion potentials during exposure. It is likely this reaction is involved in pit initiation.

### **INTRODUCTION**

Copper pitting is the primary cause of copper tube failure in potable water lines, and while research to date has been able to identify characteristics and some mechanisms that propagate copper pitting [1, 2], many theories regarding pit initiation have not been confirmed in scientific experiments. For instance, carbon films left from the manufacturing process were once thought to be the primary cause of nearly all copper pitting problems, but they have been shown to be unnecessary for pitting to occur [3-6], and there are other noteworthy contradictions in the literature summarized elsewhere [7]. In fact, a recent test of key initiation factors including combinations of copper pipe with and without exposure to flux and carbon films, exposed to six different waters, found that none of these factors initiated pits in a nine month laboratory experiment [8]. The current level of understanding is obviously not sufficient to effectively predict or prevent pit initiation. Earlier field studies suggested it might be productive to clarify

the role of two common constituents in drinking water distribution systems, chlorine and aluminum solids, in contributing to pitting tendencies [9].

### **Review of the Chlorine and Aluminum Issue**

Chlorine is the most commonly used disinfectant by water utilities in the United States. To control re-growth of microorganisms, chlorine residuals are maintained throughout many water distribution systems. Although chlorine is not essential for pitting to occur, it is a stronger oxidant than oxygen, and some researchers have shown a relationship between free chlorine and copper pitting. For instance, Fuji et al demonstrated that residual chlorine levels of 2-3 mg/L as  $\text{Cl}_2$  in Tokyo tap water caused copper pitting in hot water systems [6], while Atlas et al noted a possible correlation between high rates of pitting failure and chlorinated water in Amherst, MA [10]. However, research directly examining the role of free chlorine on cold water copper pitting is currently lacking.

In terms of the effect of chlorine on general copper corrosion, more information is available. Free chlorine has been shown to cause corrosion rates to increase during short-term exposures [11, 12], but decrease aspects of copper corrosion in other water types [13], including those that cause blue water [14]. Furthermore, free chlorine also can decrease corrosion rates of certain copper alloys in drinking water [15]. Free chlorine generally increases the amount of copper leaching to water [10, 16, 17]. While metals leaching from plumbing material is not necessarily related to the corrosion rate of the metal, it is still a concern to water utilities. Combined chlorine (chloramines) has also recently been shown to increase corrosion rates and copper leaching to water [18].

Aluminum is also commonly present in water distribution systems. Aluminum can come from the untreated source water, aluminum based coagulants, and cement based distribution system materials [9, 19, 20]. A 1988 national survey of water utilities that use aluminum based coagulants found the median level of aluminum in finished drinking water in the United States was 0.09 mg/L, and 10% of the surveyed utilities had levels as high as 1 mg/L [21]. Aluminum in the water distribution system can exist in soluble and insoluble forms. Dissolved aluminum

can precipitate as aluminosilicate solids, (a generic term for any mineral containing both aluminum and silica) which are sometimes found in surface films of copper plumbing materials. The literature is not clear regarding the role of such films in copper corrosion, much less cold water pitting corrosion. For instance, one author opined that Al deposits on pipe can be a cause of hot water copper pitting, and mentioned that a level of 0.1 mg/L Al in the finished water was associated with increased frequency of pinhole leaks [22]. In contrast, others have felt that the aluminosilicate deposits coated pipes and reduced lead and copper corrosion in Denver drinking water [23]. However, in a direct relatively short-term test of this hypothesis, it was discovered that the aluminosilicate particles actually worsened aspects of copper leaching from pipes [24].

Aluminum solids have also been circumstantially implicated as a possible cause of copper pitting problems in the service area of Washington Suburban Sanitary Commission (WSSC) [9, 25]. A study conducted by the water utility found significant amounts of aluminum solids on the surfaces of the copper pipes in its water distribution system. Furthermore, the outbreak of pitting problems experienced in this area started a short time after the water utility started to use an aluminum based coagulant (poly-aluminum chloride; PACl) in treatment and instituted an aggressive water main cement relining program, both of which caused increased levels of aluminum in the distribution system [9]. This utility also maintains relatively high chlorine residuals (up to 4 mg/L as Cl<sub>2</sub>) throughout its distribution system due to its long length. Of further interest, few copper pitting problems have been reported by other nearby utilities that treat essentially the same water, and WSSC is the only utility in the area to use free chlorine in conjunction with poly-aluminum chloride to treat its water.

The purpose of this research was to answer the question: do chlorine and aluminum, acting together or separately, contribute to initiation of copper pitting? To answer this question, a series of experiments were conducted to examine the effect of chlorine and aluminum on copper corrosion and pitting tendencies under stagnant and flow conditions. Tests under stagnant conditions were performed using treated drinking water from WSSC. Other work utilized synthetic water with similar water quality characteristics to WSSC water under alternating flow/stagnation conditions. Chlorine decay rates, electrochemical analyses, and visual analysis of non-uniform corrosion were utilized as part of these analyses.

## MATERIALS AND METHODS

At the start of the work, the conventional wisdom was that stagnant conditions are most conducive for pit initiation to occur [7]. Therefore, the first phase of work determined the effect of chlorine and aluminum solids on the corrosion of copper without flow in WSSC water. WSSC finished water has a typical pH of 7.5-8.0, 80 mg/L alkalinity as CaCO<sub>3</sub>, 40 mg/L calcium, 40 mg/L sulfate and 340 µS conductance

Each test cell contained a rectangular pure copper sheet to which a cylindrical Plexiglas section was glued using silicon sealant. This resulted in an apparatus that exposed 2 liters of water to an 18 cm diameter circular section of copper metal. WSSC water added to cells 1-3 was pre-filtered through a 0.45 µm pore size nylon membrane filter. Water added to cells 4-6 was unfiltered, to which 30 mg/L of preformed aluminum solids as Al were dosed (Table 2-1). Finally, free chlorine was added to the targeted value in each cell and pH was immediately adjusted to 8.0 +/- 0.1 with 1.0 M HCl or NaOH. The cells were then covered with black plastic to exclude light. Free chlorine disappeared (decayed) from the bulk water during the experiment but was re-adjusted to its target value 3 times per week with minimal stirring.

Table 2-1. Conditions tested during the first phase of work, pH = 8.0.

	Cell #1	Cell #2	Cell #3	Cell #4	Cell #5	Cell # 6
Cell Reference Name	No Cl <sub>2</sub>	2 mg/L Free Cl <sub>2</sub>	10 mg/L Free Cl <sub>2</sub>	No Cl <sub>2</sub> , 30 mg/L Al solids	2 mg/L Free Cl <sub>2</sub> , 30 mg/L Al solids	10 mg/L free Cl <sub>2</sub> , 30 mg/L Al solids

Water used in the experiment was collected from the WSSC Potomac water treatment plant, mailed to our laboratories, and stored in the dark at 5°C. The water was warmed to room temperature before use. The stock solution of aluminum solids was created by raising the pH of the PACl coagulant to pH 8.0 using NaOH. The solids were repeatedly washed with reagent grade water (followed by solids settling) until the conductivity of the solution was equal to that

of WSSC water. Liquid bleach (6% NaOCl) was used for chlorine addition. Chlorine was measured using the DPD colorimetric test per standard method 4500-Cl G. Corrosion potentials ( $E_{\text{corr}}$ ) were measured versus Ag-AgCl reference electrodes, which were routinely maintained and checked for accuracy. The maximum difference between any two reference electrodes used in all phases of this work was 10 mV. Corrosion potential data was collected twice daily using a Gamry electroanalysis system.

The first phase of testing was of 10-week duration. During the first 5 weeks, a siphon was used to drain old water from the upper 5/6 of each cell and fresh water was added, leaving behind an accumulation of aluminum solids at the bottom of cells 5-7. After week five, “old” solids were completely removed from the cells each week by gentle rinsing with the test solutions, before spiking in a fresh solution of WSSC water made up as described above. After 8 weeks aluminum solids were no longer added to the cells, and a fresh bleach solution was used, which increased the concentration of free chlorine in the water by a factor of two.

The purpose of the second phase of work was to determine the effect of different doses of free and combined chlorine (chloramines) in the presence of aluminum solids in WSSC water (Table 2-2). The experiment lasted 6 months and followed the basic set up and procedure as the first phase. A siphon was again used to change the water every week, but new aluminum solids were not routinely added with each water change, although the original solids dosed (30 mg/L) were left undisturbed on the surface of the copper. A complete water change, with rinsing of the copper surface and dosing of new aluminum solids, was performed every 10 weeks.

Table 2-2. Conditions to be tested during second phase of work. Copper in cell #1-4, 6 and 7 had imperfections imposed on the copper. Copper in cell #5 and #8 had no imperfections for comparison. All cells contained 30 mg/L Al solids. pH = 8.0

	Cell #1	Cell #2	Cell #3	Cell #4	Cell #5	Cell #6	Cell #7	Cell #8
Cell Reference Name	No Cl <sub>2</sub>	1.2 mg/L Free Cl <sub>2</sub>	2.4 mg/L Free Cl <sub>2</sub>	3.6 mg/L Free Cl <sub>2</sub>	3.6 mg/L Free Cl <sub>2</sub>	2.5 mg/L combined Cl <sub>2</sub>	5.0 mg/L combined Cl <sub>2</sub>	5.0 mg/L combined Cl <sub>2</sub>

Chloramines were formed by dosing concentrated HOCl to an equal molar concentration of NH<sub>3</sub>OH and then pouring the solution into the reactor. Target levels of chloramine were confirmed during the first week of the experiment by measuring free and combined chlorine with a colorimetric test. Free chlorine measurements were less than 10% of the total chlorine dosed, indicating that chloramine formation was essentially complete. Surface imperfections were also crudely imposed manually on some of the copper sheets as noted in Table 2-2. A roughly linear scratch of approximately 5 cm length was created with a metal file. In addition, 0.04 g of copper phosphide and 0.01 g of graphite was rubbed onto the same copper surfaces before the first batch of water was placed in the cells.

The third phase of work utilized synthetic water designed to replicate WSSC water chemistry under alternating flow/stagnation conditions through actual copper pipes obtained from a local hardware store. The water contained 50 mg/L HCO<sub>3</sub><sup>-</sup>, 50 mg/L SO<sub>4</sub><sup>2-</sup>, 40 mg/L Cl<sup>-</sup>, and 40 mg/L Ca<sup>2+</sup> added as reagent grade sodium or calcium salts to filter sterilized deionized water. 16 L of this water was circulated through two 1-foot copper tube sections with a centrifugal pump at a rate of 6 L/min for a five minute period every three hours. The first section of tube consisted of a 3/4" type L copper pipe split along its length, to which an 1/8" thick piece of Plexiglas was affixed using silicon sealant, allowing visual changes of the copper surface to be tracked throughout the course of the experiment. An Ag-AgCl reference electrode with a flexible barrel was inserted in the plastic tubing immediately in front of this copper pipe, with the barrel of the electrode extending 3 cm under the Plexiglas window and within 1 mm of the copper surface. A second pipe section consisted of a whole 1-foot section of 3/4" soft copper tube. Tygon type R-3603 brand tubing was used to join the pipes and create the rest of the flow loop.

Four rigs were used to test the various conditions (Table 2-3). Water was completely changed every two weeks, and chlorine levels and pH adjustments were made 3 times per week. Corrosion potential measurements ( $E_{\text{corr}}$ ) were also made three times per week by bridging the reference electrode and the external surface of the split copper pipe with a handheld voltmeter with a precision of 0.1 mV and an input impedance of 10 MΩ. This experiment was run for 250 days.

Table 2-3. Conditions tested during third phase of work, pH = 8.0.

	1	2	3	4
Cell Reference Name	No Cl <sub>2</sub> , No Al solids,	No Cl <sub>2</sub> , 1 mg/L Al solids	4 mg/L Cl <sub>2</sub> , No Al solids	4 mg/L Cl <sub>2</sub> , 1 mg/L Al solids

## RESULTS AND DISCUSSION

Results are presented in sections representing the three phases of work discussed earlier. They include 1) the effect of high levels of chlorine in presence and absence of aluminum solids on copper corrosion under stagnant conditions, 2) the effect of a range of realistic levels of free chlorine and combined chlorine (chloramines) in the presence of aluminum solids on copper corrosion under stagnant conditions, and 3) the effect of chlorine and aluminum solids on copper corrosion under alternating flow and stagnation.

### The Effect of High Levels of Chlorine With and Without Aluminum Solids

This first phase of work clearly demonstrated that WSSC water along with Al(OH)<sub>3</sub> solids and high levels of Cl<sub>2</sub> could promote aspects of non-uniform copper corrosion. The evidence for this was visual, chemical, and electrochemical. The visual evidence indicated that while both Al(OH)<sub>3</sub> and Cl<sub>2</sub> each had a slight influence on copper corrosion, they also worked in combination to promote corrosion. After 10 months, non-uniform corrosion was visibly much more severe when copper was exposed to high levels of chlorine and aluminum solids compared to aluminum or chlorine alone (Figure 2-1).

The chemical evidence for chlorine and aluminum promoting non-uniform corrosion was based on the chlorine decay kinetics within the test cells. When chlorine is placed in water, it is known to decompose slowly over time. Furthermore, because chlorine is a strong oxidant, the rate of decay will occur faster as it reacts with the metal surface [11]. However, free Cl<sub>2</sub> decay of the 10 mg/L dose in the presence of copper metal was more rapid in the cells with Al(OH)<sub>3</sub> solids compared to the cells without, suggesting that these solids enhanced the ability of Cl<sub>2</sub> to

react with (corrode) the copper metal (Figure 2-2, top). Furthermore, during week 10, five weeks after the aluminum solids were completely removed from the test cells that previously had contained the aluminum solids, the chlorine decay rates for a given level of chlorine were indistinguishable (Figure 2-2, bottom). Since beaker tests (no copper metal present) conducted with chlorine with and without aluminum solids showed that aluminum solids alone did not increase the decay rate of chlorine, the increased rate of chlorine decay is clearly linked to a synergistic interaction among the aluminum solids, chlorine, and the copper metal. This mechanism was supported by the visual differences between the copper samples shown in Figure 2-1.

In addition to the chlorine decay and visual changes, corrosion potential ( $E_{\text{corr}}$ ) was used to electrochemically monitor the pitting propensity of the different conditions tested in this experiment. As background to interpretation of  $E_{\text{corr}}$ , it is known that new copper immersed in essentially pure water near pH 7.0 will increase in corrosion potential over a few days, rising slightly to a stable value versus a reference electrode. Potentials remain at this level under normal circumstances or in non-pitting waters. Under unusual circumstances leading to pitting, however, the potential rises continuously to a critical level ( $E_{\text{crit}}$ ) that is seemingly dependent upon specific water quality at which point pits are initiated [5, 6, 26-29]. Dependent on the water, this critical level has been reported to vary between 49-495 mV versus an Ag-AgCl reference electrode (Table 2-4). In general, it is believed that if  $E_{\text{corr}}$  decreases slowly versus time, the pipe surface is passivating, whereas if  $E_{\text{corr}}$  is increasing with time it is activating towards pitting. An abrupt decrease in  $E_{\text{corr}}$  is suspected by some to indicate the onset of pitting corrosion. It is important to note that it is difficult to draw definitive conclusions about pitting behavior from electrochemical interpretations because of the complexity and poor understanding of the underlying mechanisms of copper pit initiation and growth. However, the technique is still considered a useful tool for monitoring pitting in practice.

In this first phase of experiments, there is no question that the presence of  $\text{Al}(\text{OH})_3$  solids and  $\text{Cl}_2$  had dramatic impacts on  $E_{\text{corr}}$  (Figure 2-3). For example, in waters with no  $\text{Cl}_2$  or  $\text{Al}(\text{OH})_3$  solids,  $E_{\text{corr}}$  remained relatively constant with time. While potential was initially higher in the presence of 2 mg/L  $\text{Cl}_2$  but without  $\text{Al}(\text{OH})_3$ , it gradually declined to below -20 mV. However, when  $\text{Al}(\text{OH})_3$  was present by itself or with 2 mg/L free chlorine,  $E_{\text{corr}}$  was higher

initially and remained above  $-20$  mV with time. Finally, when both  $\text{Al}(\text{OH})_3$  solids and a very high level (10 mg/L) of free chlorine was present,  $E_{\text{corr}}$  was much higher at +100-125 mV during the first few weeks of the experiment, before dropping down to the lower levels typical of free chlorine alone. This type of behavior, with a high  $E_{\text{corr}}$  and a sudden drop, is often interpreted as indicating the onset of copper pitting corrosion. Obviously, the data are open to considerable interpretation, but the trends were considered worthy of follow-up study at more realistic levels of free chlorine.

Table 2-4. Critical pitting potentials for copper ( $E_{\text{crit}}$ ) in various studies.

Reference	Type of Pitting	$E_{\text{crit}}$ (vs Ag-AgCl)
[5]	Soft-water	495
[29]	Soft-water	49
[6]	Hot-Water	195
[27]	Cold-Water	215
[28]	Cold-Water	145-215
Lucey (unpublished)	Cold Water	105

### Lower Levels of Chlorine and Non-uniform Corrosion

The primary goal of the second phase of work was to identify a realistic level of free  $\text{Cl}_2$  in WSSC's water that would not contribute to non-uniform copper corrosion. To this end, the effect of 0, 1.2, 2.4 and 3.6 mg/L free chlorine as  $\text{Cl}_2$  was tested. The effect of chloramines was also tested using two levels of combined chlorine: 2.5 and 5.0 mg/L as  $\text{Cl}_2$ . The work also had the goal of determining whether imperfections imposed on the copper surfaces had any obvious effect on copper corrosion reactions in WSSC water. It is believed by many that imperfections or deposits on copper tube surfaces can cause conditions that will initiate pinhole leaks in copper

tube if certain water quality conditions are simultaneously met [1, 20]. To examine this possibility, graphite deposits, copper phosphide inclusions, and surface scratches were imposed on some of the copper surfaces. The different conditions tested are listed in Table 2.

During the first 2 weeks of the experiment chlorine levels were measured every 24 hours, and 1-day decay rates were calculated (Figure 2-4). There was not a significant difference in chlorine or chloramine decay for a given level of disinfectant exposed to the copper with and without imperfections. Likewise, the more free or combined chlorine, the faster the rate of decay, consistent with anticipated pseudo-first order decay kinetics. The rate of decay for the container with 2.5 and 5.0 mg/L combined chlorine was roughly equivalent to the decay rate for 1.2 and 3.6 mg/L free chlorine, respectively (data not shown). This is consistent with the fact that combined chlorine is a weaker oxidant and thus is more stable in water than free chlorine.

Analysis of the corrosion potential data revealed several factors that can contribute to variations in corrosion potential during an experiment. Before discussing general trends in  $E_{\text{corr}}$  data as a function of chlorine dose, it is worthwhile to examine the factors shown to influence corrosion potential based on experimental changes. It was clear that the corrosion potential temporarily increased whenever chlorine residuals were returned to target levels or during periodic water changes which are indicated by the dashed and solid vertical lines on Figure 2-5. Approximately one day after each water change or chlorine addition, the potential continued to drop at an ever-decreasing rate, until the next addition of chlorine. This jump in corrosion potential did not occur during most water changes in the control cell that did not contain chlorine, suggesting that this behavior is related to diffusion of chlorine to the surface of the copper. In other words, if the corrosion potential were a function of chlorine brought into contact with the copper surface, it would be highest during water changes and chlorine additions when the solution was mixed and free chlorine concentrations were highest. As the system stagnates and transport of chlorine via diffusion becomes less significant, the potential drops.

However, the relative level of the corrosion potential was not a function of absolute level of disinfectant. During the first 36 days (Figure 2-5), copper exposed to 1.2 mg/L  $\text{Cl}_2$  exhibited the lowest corrosion potential, while all other conditions were higher including the condition with no chlorine. From 70 to about 90 days, this general trend held (data not shown).

Interestingly, during this time the corrosion potential for the 1.2 mg/L free chlorine experiment showed a temporary but marked decrease after water changes, in contrast to the behavior of the higher free chlorine conditions where corrosion potential temporarily increased. It appears that the copper exposed to 1.2 mg/L free chlorine was responding fundamentally differently to the addition of more oxidant. From day 82 through the end of the experiment, the 0 mg/L Cl<sub>2</sub> condition had the highest potential, the 1.2 mg/L free Cl<sub>2</sub> had the next highest potential, and the higher chlorine doses had the lowest corrosion average potential (data not shown). Peak measurements of E<sub>corr</sub> remained highest for the copper exposed to higher levels of free chlorine, however, and these consistently occurred during the water changes or chlorine additions. With the exception of these observed spikes, corrosion potential measurements for all conditions were consistently between 20 and 80 mV versus an Ag-AgCl reference electrode throughout the experiment. There were no major differences in corrosion potential results seen between the copper samples with and without imperfections.

The same general trends were seen in corrosion potential for the copper exposed to chloramines as those exposed to chlorine. First, when chloramines were added to the system, corrosion potential increased temporarily and then fell to a relatively stable level until the next chloramine addition (data not shown). With some exceptions, the copper exposed to chloramines also exhibited a higher corrosion potential than all other conditions. This may be due to the greater stability of chloramines in water. Because the decay of combined chlorine is slower, more oxidant is able to reach the surface of the copper where it causes an increase in corrosion potential.

Although the differences in average corrosion potential among the different conditions were relatively small, the decreasing trend in potential during the first month did suggest that the copper exposed to 1.2 mg/L free chlorine was behaving differently than the other conditions. This result was supported by the visual changes of the copper as it corroded. After one month, the surface of the copper exposed to 1.2 mg/L free chlorine appeared markedly more uniform than any other condition, where as the sample exposed to 3.6 mg/L free chlorine looked markedly worse than the others. Photos taken at the end of the experiment after 6 months further support this trend (Figure 2-6). Additionally, there was no visual evidence to support the idea that the imperfections imposed on the copper surfaces had a significant impact on copper

corrosion at either 3.6 mg/L free chlorine or 5.0 mg/L combined chlorine. Furthermore, chloramines visually appeared to be just as aggressive to copper as chlorine, albeit they were present at higher levels.

The visual results and electrochemical data from these two phases of work suggest that copper corrosion is greatly impacted by the level of chlorine present in the system. In terms of preventing non-uniform copper corrosion (and possibly pitting) in this water, a level of 1.2 mg/L free chlorine appeared to be optimal among the conditions tested, and chloramines had no beneficial effect relative to free chlorine with respect to copper pitting and non-uniform corrosion.

### **The Effect of Chlorine and Aluminum Under Alternating Flow and Stagnation**

The first two phases of work examined the role of chlorine on the corrosion of a large surface area exposed to 2 L of stagnant water. The spikes in corrosion potential during water changes and chlorine addition suggested that the diffusion of chlorine to the copper surface controls many important corrosion reactions. Considering these results it was expected that copper exposed to chlorine and aluminum under flowing conditions would behave much differently than copper exposed to stagnant conditions. The next phase of work was designed to test this premise and to better approximate what happens in practice by alternating flow and stagnation conditions through actual copper pipe samples. A flow cycle of 5 minutes every three hours was used. The other major difference between this and the two earlier phases of work was that synthetic water was used that had approximately the same alkalinity, sulfate and chloride concentration, and calcium hardness, as the “real” water from WSSC. Also, a more realistic aluminum solids concentration of 1 mg/L was used. The conditions tested are summarized in Table 2-3.

From the beginning of the experiment, flow had a large effect on the corrosion potential measurements for the waters with chlorine residuals. Soon after the five-minute flow period began, the corrosion potential typically jumped by 50-100 mV and reached a peak value after 1 to 2 minutes (Figure 2-7). Figure 2-7 shows a typical measured response during a 3-hour cycle

for a container with chlorine residuals. The potential slowly declined until the flow stopped, when the potential decreased rapidly, and reached a relatively stable value after approximately 1 hour. This asymptotic decrease in corrosion potential after flow stopped is suspected to be caused by a rapid decrease in chlorine available to react with the copper as the system stagnates due to mass transfer limitation. The increase in potential during flow, therefore, would be the result of an increase in the available level of chlorine being exposed to the copper surface due to enhanced mass transfer due to the water flow. Interestingly, in previous work with copper pitting and Belgium tap water periodic stagnant conditions caused the corrosion potential to drop during the period that pitting corrosion started to occur [27]. However, it is important to note that neither chlorine nor aluminum solids were a focus of that work, although they might have been present. In the experiments without chlorine residual in this work, flow typically caused an immediate small drop in the corrosion potential.

Throughout the 7-month experiment, two different corrosion potential measurements were taken 3 times per week for each condition (Figure 2-7). The “rest potential” was taken during a period of stagnation, a few minutes before the five-minute flow period began. The “flow potential” was taken during the five-minute flow period, and depending on the condition, the peak or steady state value was recorded. All  $E_{\text{corr}}$  values listed are versus an Ag-AgCl reference electrode.

For the control condition (no chlorine and no Al solids) the rest potential ranged from 30 to 50 mV throughout the experiment, and potentials during onset of flow were usually around 20 mV lower (Figure 2-8). There were no major differences in the rest potential for the condition with only aluminum, but the flow potentials were typically only about 5 mV lower than the rest potential. This suggests that aluminum solids alone are not drastically affecting the underlying corrosion reactions occurring in this system.

On the other hand, the presence of chlorine with and without aluminum solids had a large effect on rest and flow corrosion potentials over the course of the experiment (Figure 2-8). For the condition with only chlorine, the rest potential rose from 25 mV to 75 mV over 200 days. The flow potentials were always significantly larger than the rest potentials by 25 – 50 mV. And although aluminum solids alone did not cause a significant effect on corrosion potential, chlorine

and aluminum together had a significant effect, producing the largest magnitude of corrosion potential seen in the four systems. Over 200 days, the rest potential increased from 25 to 100 mV, while the flow potential was 75 to 100 mV higher. Toward the end of the experiment, the upward trend in corrosion potential measurements was not as rapid and appeared to be stabilizing in both systems. Although no actual pits were apparent on the surfaces in these relatively short-term experiments, a slow rise of corrosion potential measurements is often times considered a sign of a copper surface that is activating towards pitting.

On day 209 it was decided to allow the water in all the rigs to flow continuously for 21 days, during which time potential measurements were routinely taken. After this period of constant flow, the original on/off cycle was continued for another 20 days. The period of constant flow had no notable effect on the corrosion potential measurements in the systems without chlorine (data not shown), but did impact the corrosion potentials in the two systems with chlorine (Figure 2-9). During the first week of constant flow, potential dropped by approximately 100 mV in both systems and remained relatively stable during the remaining 2 weeks of constant flow. It is unclear what led to the rapid decrease in corrosion potential for the conditions with chlorine during the period of constant flow. Although the chlorine in these systems was observed to decrease at a faster rate, chlorine levels were maintained more often so that the levels in the systems were consistent with those found during the first 200 days. Furthermore, no spike in corrosion potential occurred when fresh chlorine was added to the system during this time period. This suggests that the copper surfaces were fundamentally changed by being constantly exposed to fresh chlorine. After the original on/off cycle was restarted, the flow potentials increased slightly versus rest potentials, but neither the magnitude nor the difference between the rest and flow potentials were as large as immediately before the 3 week period of constant flow was begun. Thus, the change in the copper surface caused by constant flow had long-term impacts.

The visual differences among the copper samples exposed to different conditions were also striking. The experimental setup allowed photographs to be taken of the corroding copper pipe surfaces through a Plexiglas view port while the experiment was in progress (Figure 2-10). The copper pipe exposed to no chlorine or aluminum, and the copper pipe exposed to only aluminum, slowly turned dullish brown as the experiment progressed. However, white deposits

were easily visible after a few weeks in the container with 1 mg/L aluminum solids. Chlorine had a more drastic effect on the copper surfaces. Soon after the beginning of the experiment, the surface turned brown, and dark streaks were visible on the surface. After 13 days, the copper exposed to chlorine and aluminum was more discolored, and developed bluish streaks. Aluminum deposits were also visible on the surface. As is shown in the day 78 pictures, the copper exposed to only chlorine developed non-uniform blue spots on its surface with dark streaks running the length of the tube. The day 208 photos show that the surfaces of the pipe exposed to chlorine or chlorine and aluminum began to look more similar, characterized by a dark brown surface with blue streaks running along the length of the pipe. At the end of the experiment, the Plexiglas window was removed, the copper pipe samples were dried, and final photographs were taken (Figure 2-11). The differences among the surfaces are most obvious in this picture.

It is clear that the synergistic effect between aluminum solids and chlorine on copper corrosion is strongly impacted by flow regimes imposed on the system and it can be expected that similar results would be obtained in consumers homes based on usage patterns. Also, realistic levels of aluminum solids (1 mg/L) significantly impact copper corrosion. Although no copper pitting was observed to occur, the electrochemical results for the conditions with chlorine and aluminum at the very least indicate large differences in the underlying corrosion mechanisms, and at the worse, could indicate a system that is activating towards pitting compared to systems without these compounds.

## CONCLUSIONS

- Chlorine and aluminum solids together can enhance non-uniform corrosion of copper under both stagnant and flow conditions compared to either constituent alone.
- The concentration of chlorine is important in determining its effect on copper; lower doses appear to be beneficial compared to either no chlorine or higher chlorine when aluminum solids are present.

- Flow has an important impact on the corrosion potential of copper exposed to chlorine, or chlorine and aluminum solids. Large jumps in potential ( $\approx 100$  mV) are observed when flow starts.
- The gradual increase in corrosion potential as copper is exposed to chlorine under alternating flow and stagnation experiments are likely indicative of a copper surface activating towards pitting.
- The synergistic interaction between aluminum and chlorine shown to occur in this work is of particular interest, and it would be worthwhile to see if other solids in water caused similar effects on copper.
- More work is needed to determine how flow and different levels of chlorine and aluminum affect copper corrosion and pitting behavior. It is of particular interest to determine the impact of pH on this reaction, since data not shown here strongly suggested the reaction is worse at higher pH.

## ACKNOWLEDGEMENTS

This work was made possible through funding from the Washington Suburban Sanitary Commission (WSSC) and the Copper Development Association (CDA). The authors would also like to thank Steve Kvech and Nestor Murray for laboratory assistance.

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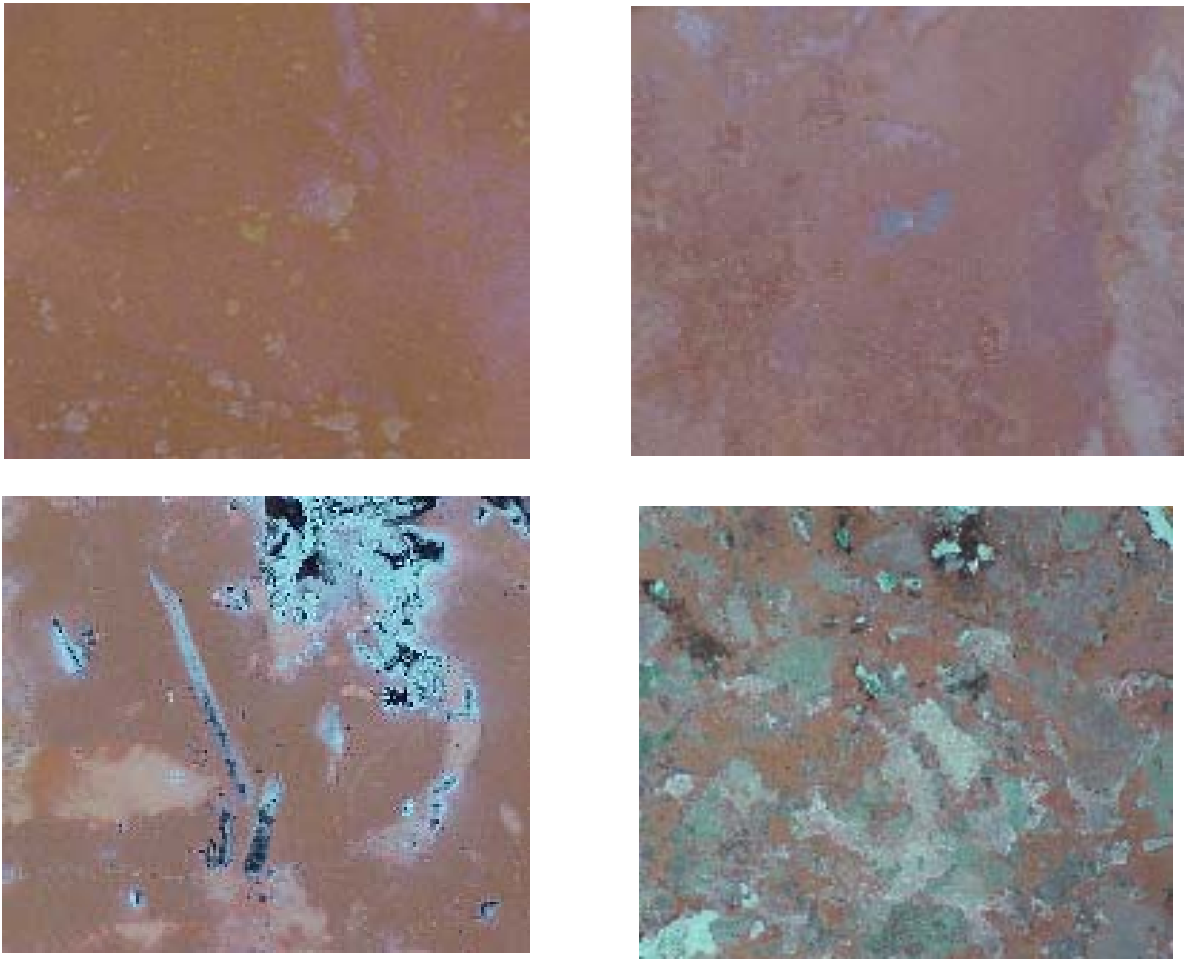


Figure 2-1: Dried copper surfaces after 10 weeks of exposure to WSSC water. Top left: No chlorine or aluminum solids. Top right: Aluminum solids only. Bottom left: 10 mg/L free chlorine as  $\text{Cl}_2$ . Bottom right: 10 mg/L free chlorine as  $\text{Cl}_2$  plus aluminum solids. Surface areas of each picture are approximately  $100 \text{ cm}^2$ .

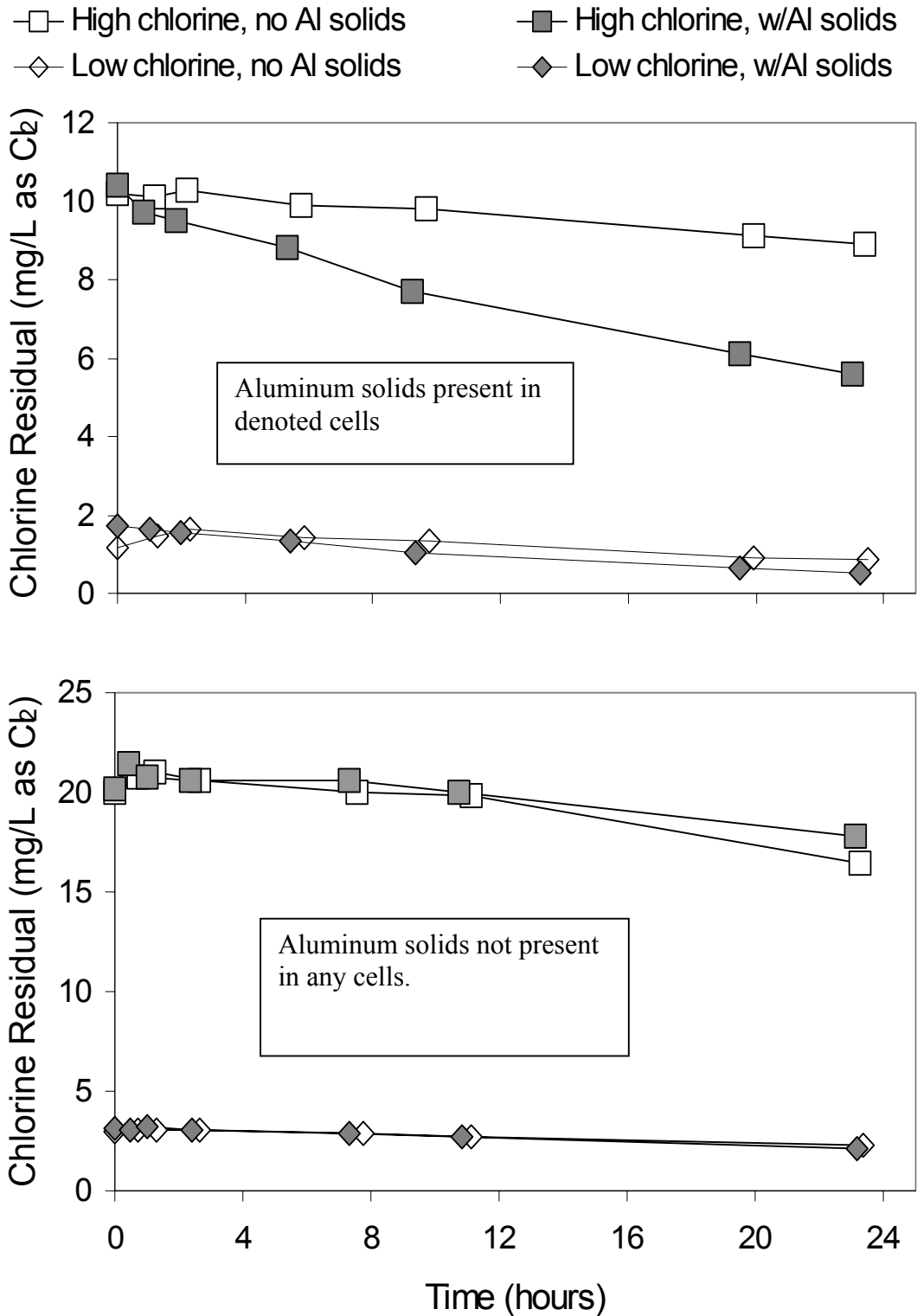


Figure 2-2: Free chlorine decay during week 4 (top) and week 10 (bottom). Aluminum solids were removed from cells during week 5. Cl<sub>2</sub> in bulk water (residual) in bottom graph is greater due to the use of a fresh bleach solution.

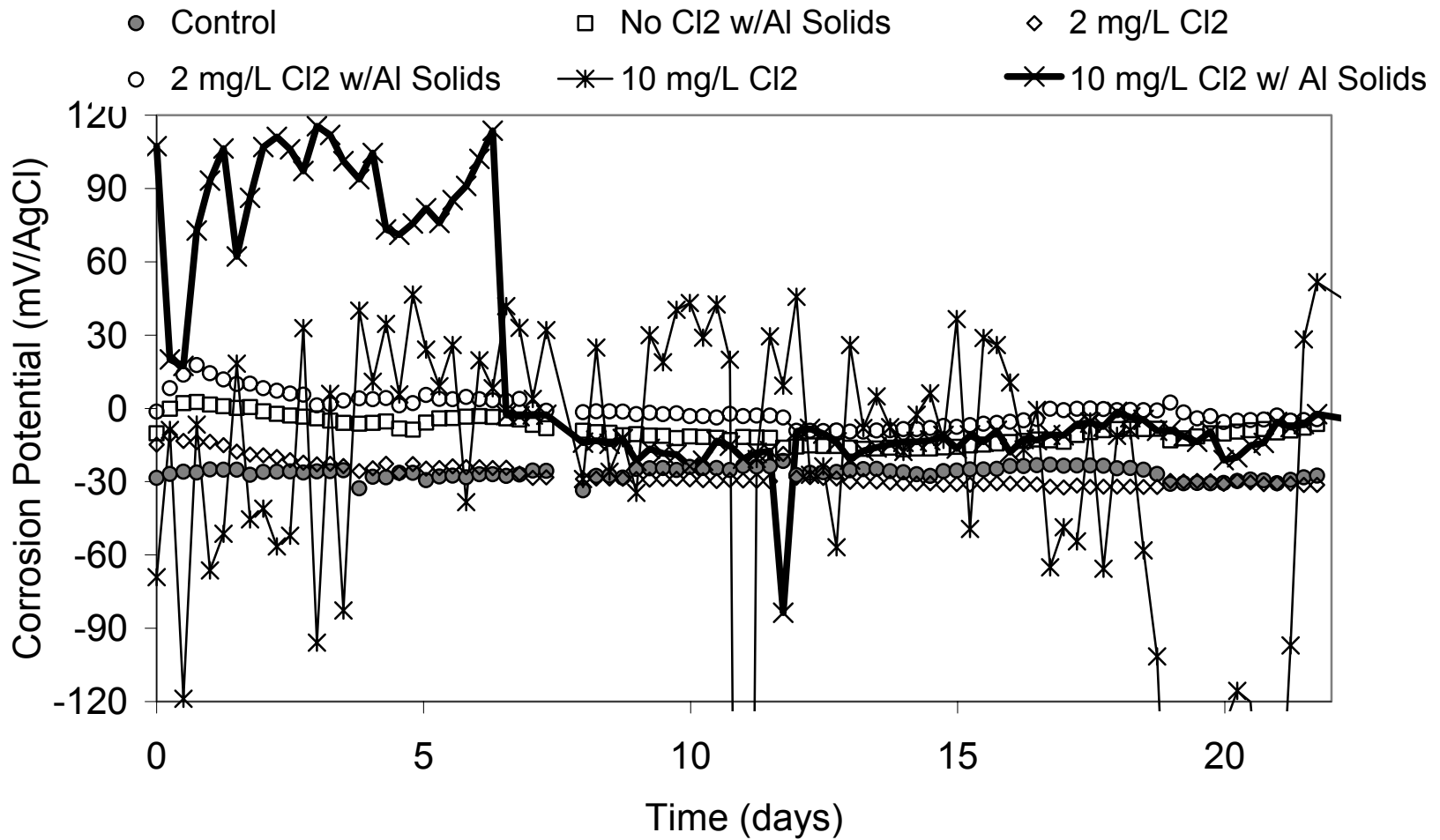


Figure 2-3: Corrosion potential results ( $E_{corr}$ ) from first phase of experiments with chlorine and aluminum.

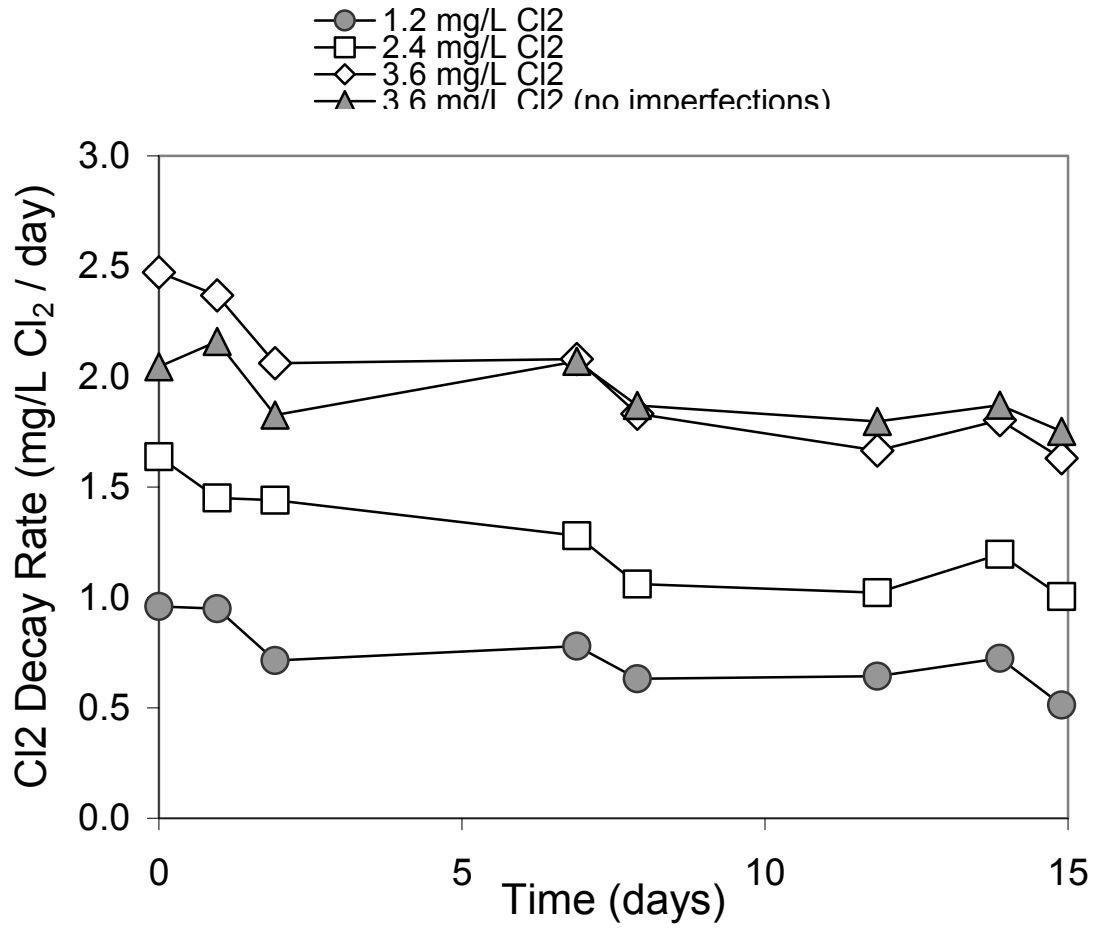


Figure 2-4: Chlorine decay rates from 2<sup>nd</sup> phase of chlorine and aluminum experiments. Rates calculated from amount of free chlorine decay over 24 hours.

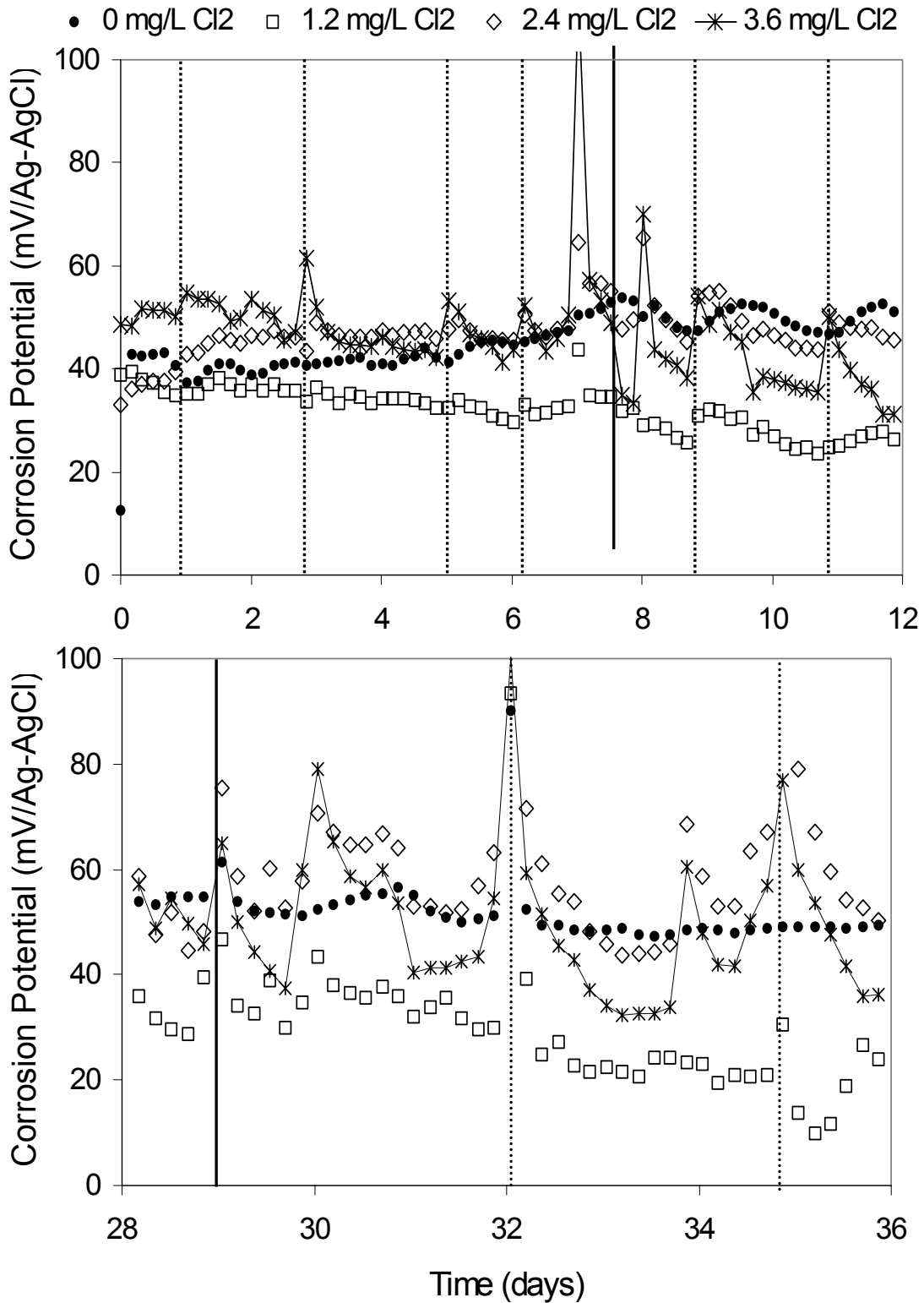


Figure 2-5: Corrosion potential results for days 0-12 and 28-36. Vertical dashed and solid lines correlate with time of chlorine dose and water change, respectively.

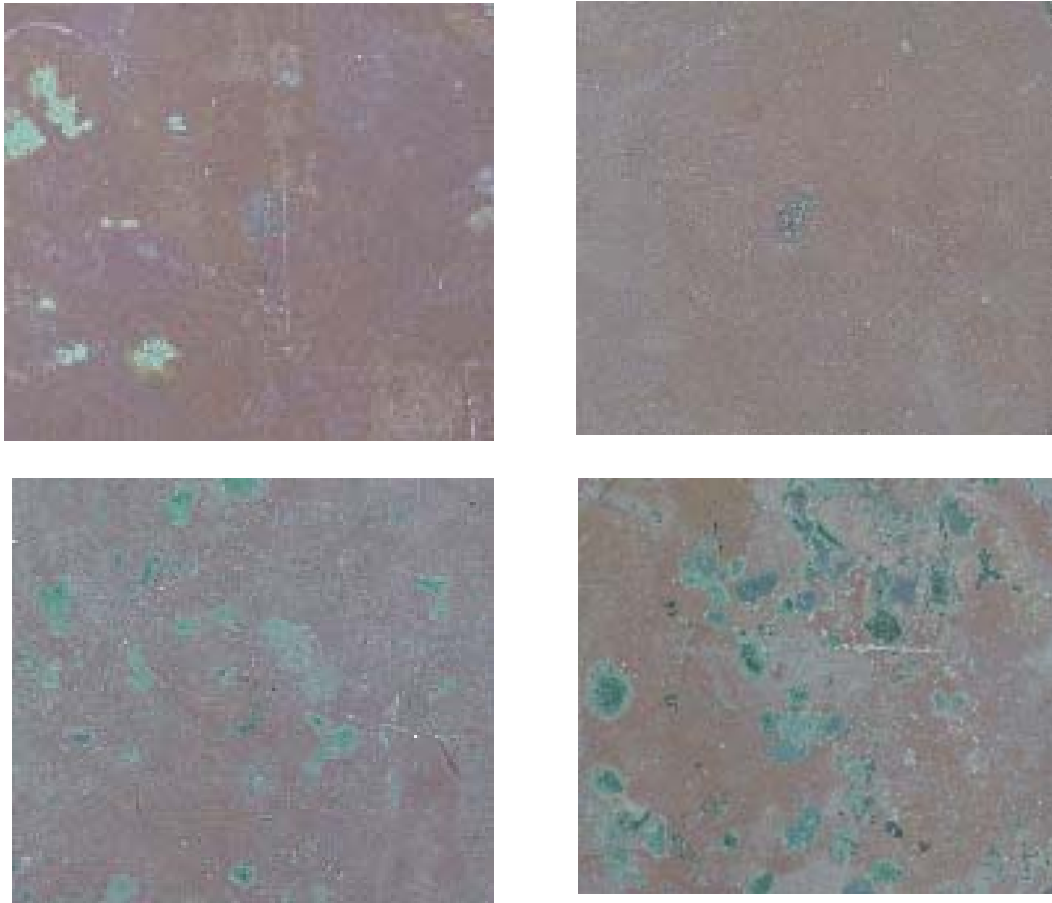


Figure 2-6: Picture of dried copper surfaces after 6 month exposure to WSSC water and aluminum solids. Top left: 0 mg/L free chlorine. Top right: 1.2 mg/L free chlorine. Bottom left: 2.4 mg/L free chlorine. Bottom right: 3.6 mg/L free chlorine. All samples exposed to 30 mg/L aluminum solids. Surface areas of each picture are approximately 100 cm<sup>2</sup>.

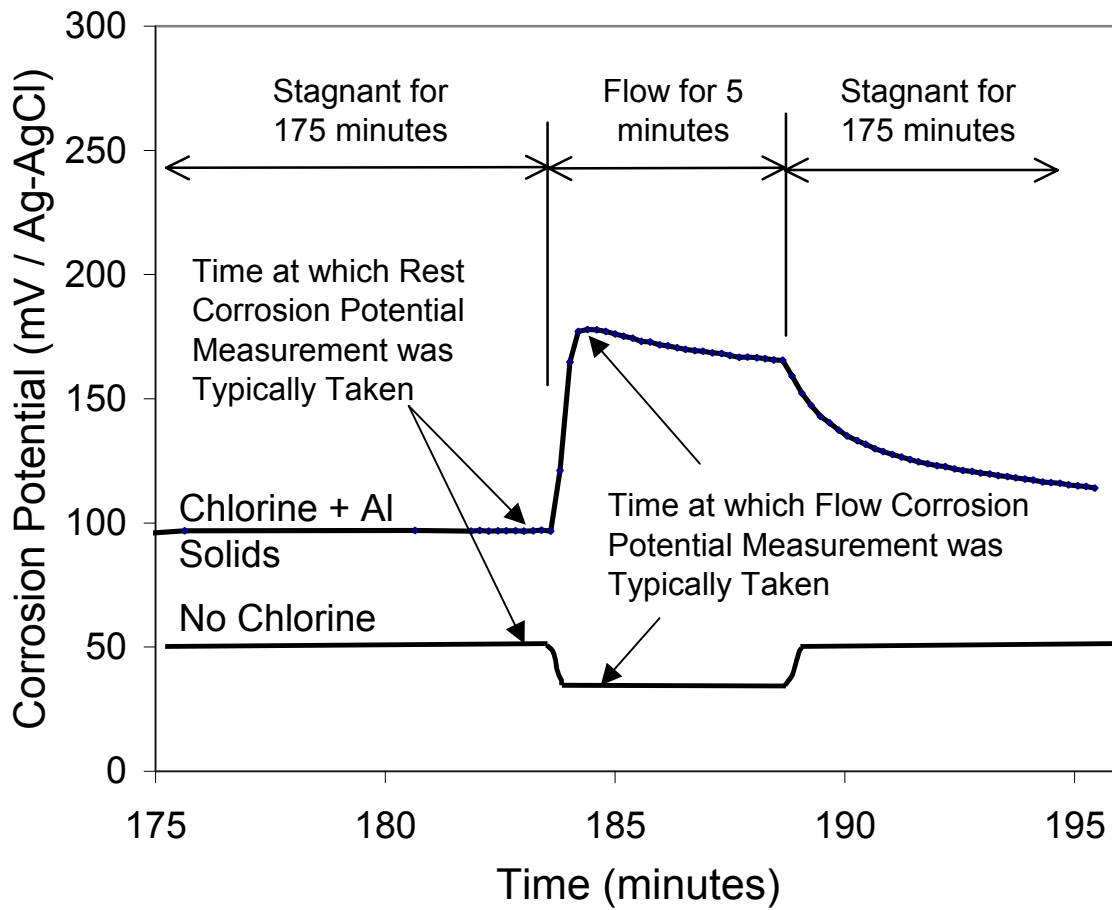


Figure 2-7. Typical corrosion potential response under flow or stagnant conditions for conditions with  $\text{Cl}_2$  and Al solids, and no  $\text{Cl}_2$  and no Al solids after 3 months of exposure. Arrows correspond to times flow and at rest corrosion potential measurements typically taken.

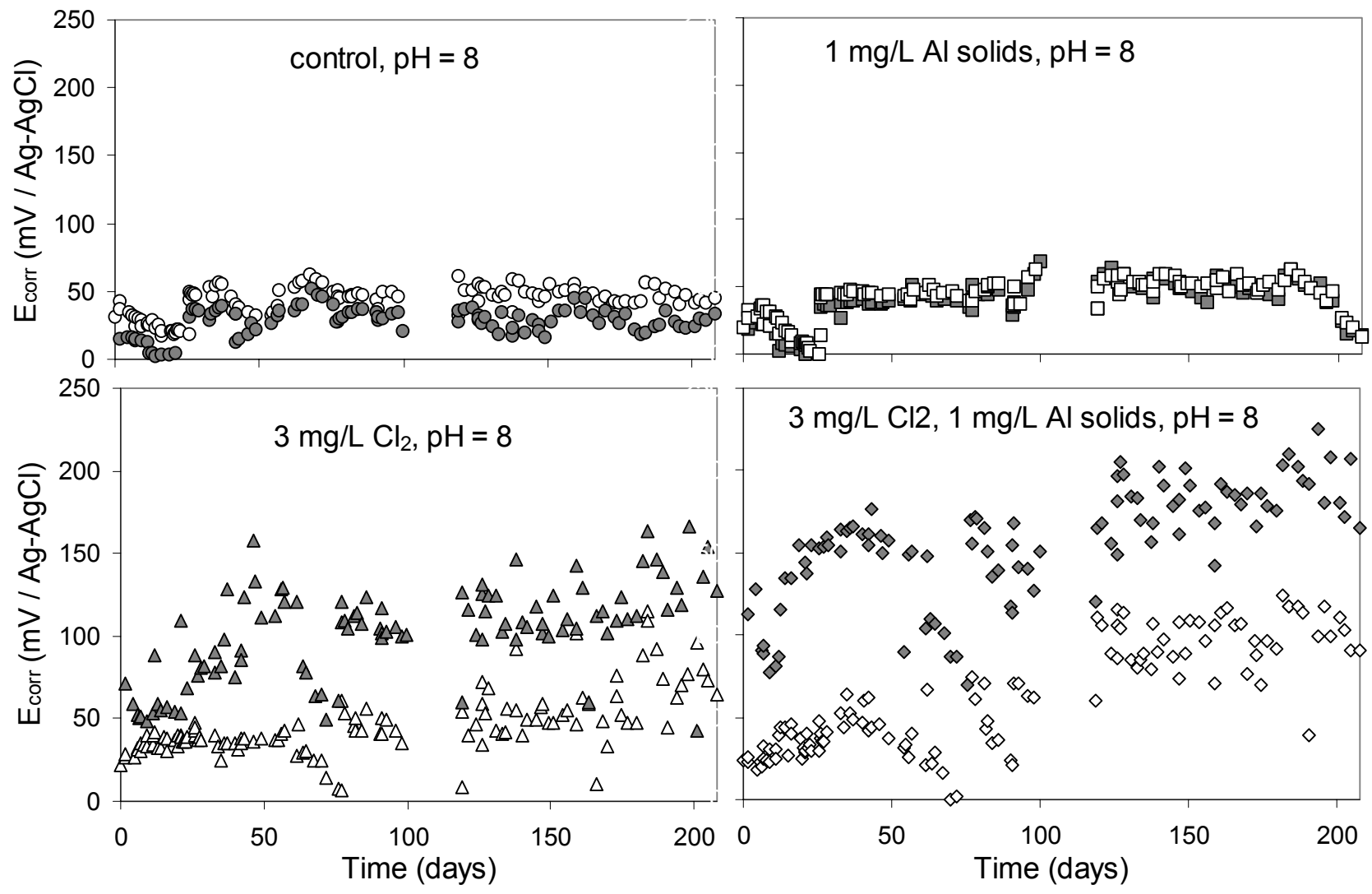


Figure 2-8: Corrosion Potential Results through day 209. Filled and unfilled shapes denote  $E_{corr}$  during flow and stagnation, respectively.

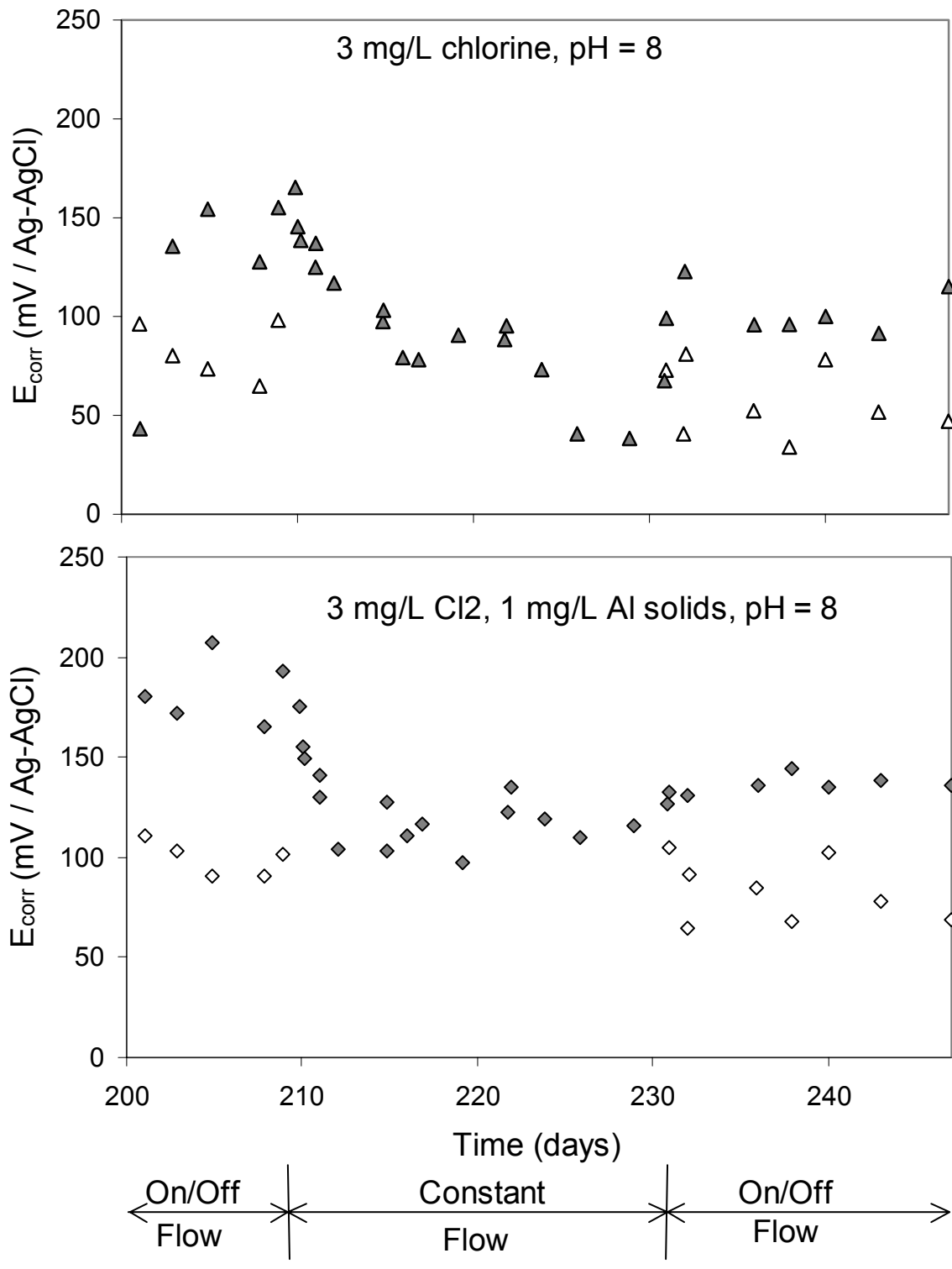


Figure 2-9: Corrosion potential measurements before and after 20 day period of constant flow. Filled and unfilled shapes denote E<sub>corr</sub> during flow and stagnation, respectively.

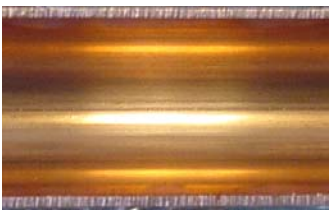



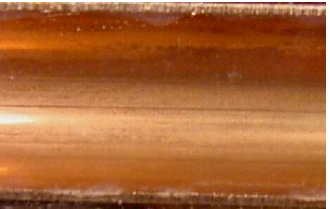




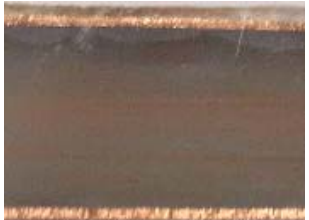
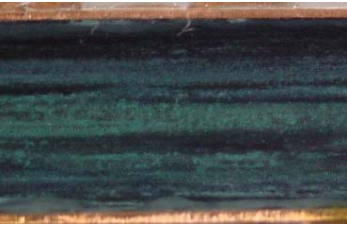

Day	Control	1 mg/L Al	3 mg/L Cl <sub>2</sub>	1 mg/L Al and 3 mg/L Cl <sub>2</sub>
13				
78				
208				

Figure 2-10: Pictures of copper pipe surfaces in-situ during the experiment. Photos were taken through a Plexiglas view port when pipes were full of water.



Figure 2-11: Dried copper pipe samples at the end of the experiment. From top to bottom: Control, 1 mg/L Al, 3 mg/L Cl<sub>2</sub>, 1 mg/L Al plus 3 mg/L Cl<sub>2</sub>.

# **CHAPTER 3: CONFIRMING THE ROLE OF ALUMINUM SOLIDS AND CHLORINE IN COPPER PITTING CORROSION**

Jason C. Rushing

## **INTRODUCTION**

Previous work indicated that there is an important synergistic effect between aluminum solids and chlorine on pitting corrosion of copper. The initial evidence for this link was found in extensive studies of treatment practices and household plumbing at Washington Suburban Sanitary Commission (WSSC), which is experiencing a high frequency of copper pitting problems (Chapter 1). That work proved that use of poly-aluminum chloride coagulant (PACl) and cement-based distribution system materials led to higher levels of soluble and particulate aluminum in the distribution system, which in turn formed deposits on copper pipes. Use of PACl, concrete pipe lining, and WSSC corrosion control practices have also led to a slight increase in the pH of WSSC water. Furthermore, this utility is unique in comparison to other nearby water suppliers, in that it uses relatively high levels of free chlorine (up to 4 mg/L as Cl<sub>2</sub>) for its distribution system disinfectant residual in conjunction with PACl.

Bench scale experiments were then conducted to investigate the influence of aluminum solids and chlorine on copper corrosion (Chapter 2), 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 showed increased chlorine decay and non-uniform corrosion when aluminum solids and chlorine were exposed to copper metal. Other experiments at this pH demonstrated that under alternation 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]. Corrosion potentials were largely unaffected by chlorine and aluminum solids under stagnant conditions, which is surprising given that current theories regarding copper pitting suggest that pitting is more likely to occur during stagnant conditions [4]. In addition, when the same alternating flow experiment was repeated at pH 7 in the presence of aluminum solids and chlorine (data not shown), 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. However, 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 cause copper pitting is controversial to say the least, since recent work has indicated that all these factors are beneficial to aspects of copper corrosion. Therefore, an experiment was 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 and under constant flow conditions.

## MATERIALS AND METHODS

5/8" nominal size copper couplings (surface area = 20 cm<sup>2</sup>) 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 HCO<sub>3</sub><sup>-</sup>, 50 mg/L SO<sub>4</sub><sup>2-</sup>, 40 mg/L Cl<sup>-</sup>, and 40 mg/L Ca<sup>2+</sup> 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. Free chlorine was increased incrementally every two days from zero to 4.8 mg/L as Cl<sub>2</sub> 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 Cl<sub>2</sub>. Targeted pH values of 6,7,8, and 9 were tested in duplicate (8 cells total), and the pH was adjusted and Cl<sub>2</sub> residuals were replenished twice daily. pH values were kept within 0.3 units of the target value.

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 ( $E_{\text{corr}}$ ) 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.

This experiment was repeated in parallel with the addition of 2 mg/L of Al(OH)<sub>3</sub> solids, the stock solution for which was created by raising the pH of a 3000 mg/L AlCl<sub>3</sub> 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. The same chlorine dosing schedule was used, except an additional level of 6.0 mg/L Cl<sub>2</sub> was added 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. After 18 hours, corrosion rates were measured using potentiodynamic scans and Tafel analyses. The pH for all conditions was then raised to 9.0 and corrosion potential and polarization resistance were measured for another 2 days.

Copper samples were weighed before and after each experiment to assess mass changes. At the end the experiment, samples were cut in half using a hacksaw and photographs were taken of the corroded copper surfaces using a digital camera.

## **RESULTS AND DISCUSSION**

### **Chlorine Decay Kinetics**

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 3-1). 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 larger in all systems compared to the lower doses of chlorine for a given pH, consistent with anticipated first order or higher kinetics.

When aluminum solids were present the chlorine decay behavior significantly changed compared to the tests without the solids. For all doses of chlorine, 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:

$$100* [ (\text{decay rate w/ Al} - \text{decay rate w/o Al}) / \text{decay rate w/o Al} ]$$

( 0% would indicate an equal decay rate)

it is clear that aluminum caused much higher chlorine decay rates at higher pH (Figure 3-2).

### **Corrosion Potential and Polarization Resistance**

Electrochemical data were collected for each pH condition in duplicate, and since the duplicate measurements for a given pH value were always very close to one another, only one set of data is presented.

Corrosion potential ( $E_{\text{corr}}$ ) was affected by both pH and chlorine in the system (Figure 3-3). 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.  $E_{\text{corr}}$  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 chapter 2.

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  $E_{\text{corr}}$  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 < 25% lower than target values).

Polarization resistance ( $R_p$ ) data was also collected in all the systems (Figure 3-4).  $R_p$  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 with higher pH, indicating a greater corrosion rate at lower pH values, consistent conventional wisdom. 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 lead to higher corrosion rates at pH 9. In other words, if aluminum is present,  $R_p$  values suggest that copper corrodes as fast at pH 9 as it does at pH 6 without aluminum.

Additional tests were conducted on the samples exposed to after 20 days (Figure 3-5). 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 23<sup>rd</sup> 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 release for all pH levels, but was most apparent at pH 6 (Figure 3-6).

### **Mass Change**

The amount of mass loss or gain of the copper samples was affected by pH and the presence of aluminum solids (Figure 3-7). 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 3-8). 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 measurement from the pH 6 condition is ignored. Besides the pH 9 result, 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 trends in  $R_p$  discussed earlier.

### **Visual Observations**

Aluminum and pH had profound impacts on the visual characteristics of copper corrosion (Figure 3-9). 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 3-10). 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 pitting corrosion.

## **CONCLUSIONS**

The short-term experiments described here clearly confirm the controversial conclusions from earlier work: chlorine and aluminum solids lead to increased susceptibility to copper pitting corrosion. Since pinholes generally take several years to develop and cause leaks in pipes, the results at pH 9 after a few weeks are quite remarkable especially given that the result runs so contrary to expectations before this research was conducted. Although this work indicates that the problem is most severe at higher pH, it is possible that long-term exposure at lower values such as pH 8 could lead to the same results. 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.

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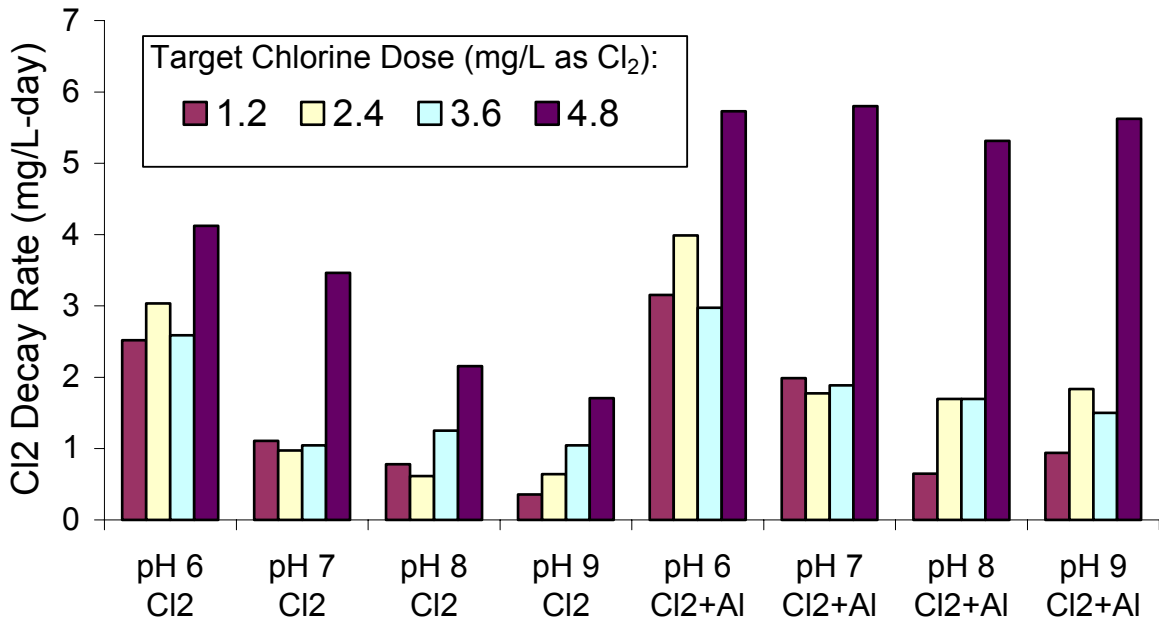


Figure 3-1. Average chlorine decay rates based on duplicates for various target chlorine doses. Chlorine decay measured over an 8-hour period, and rate is presented in mg/L Cl<sub>2</sub> lost per day.

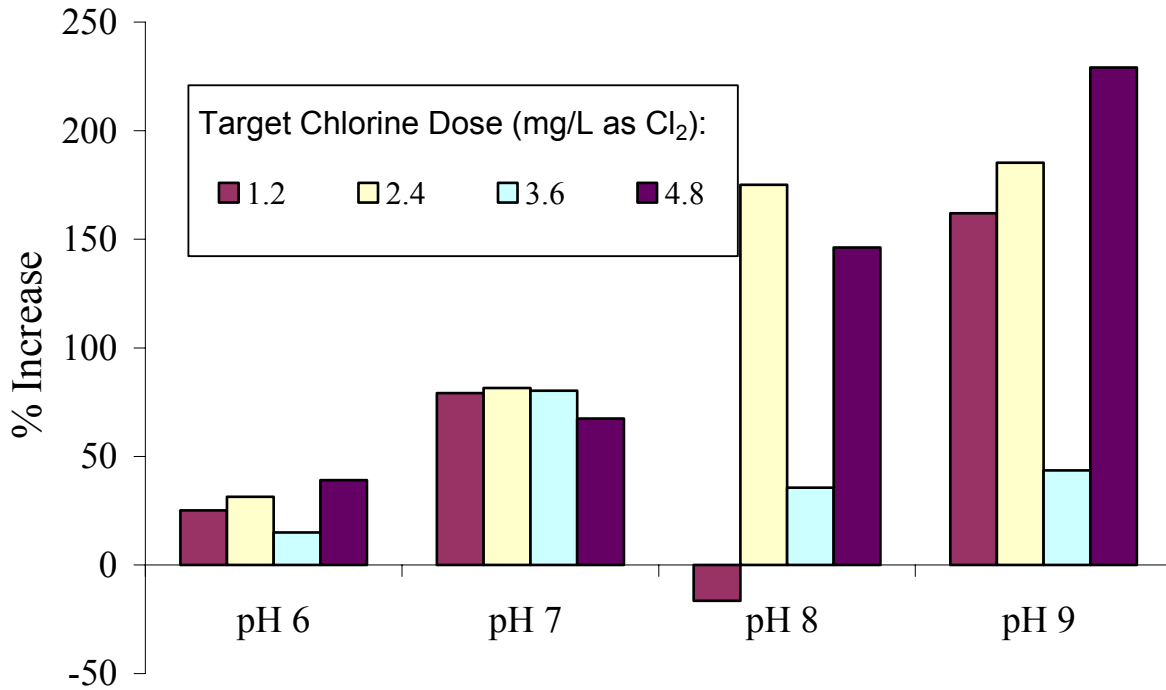


Figure 3-2. Percent increase in chlorine decay rate for given target dose with 2 mg/L aluminum solids present compared to same system without aluminum.

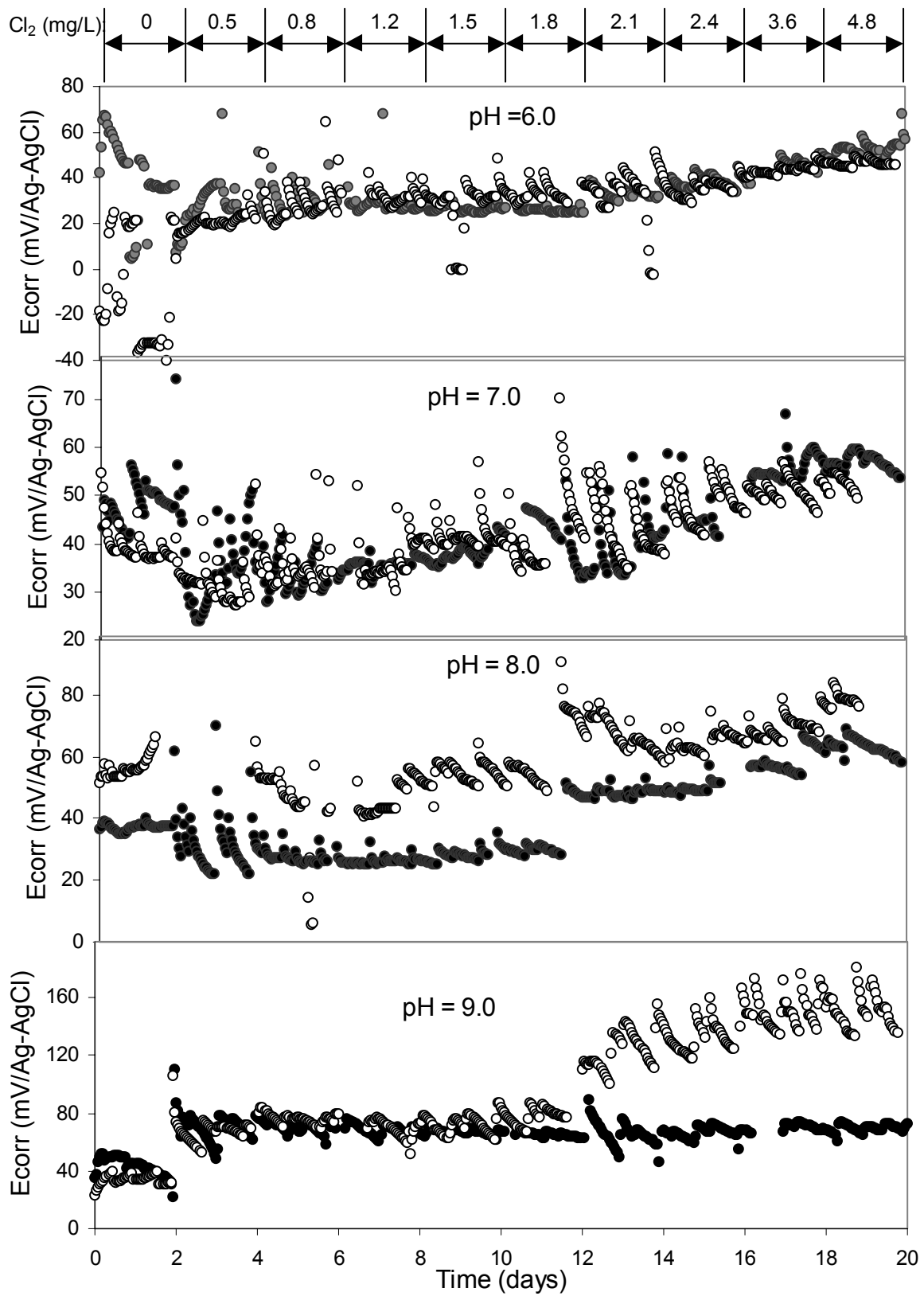


Figure 3-3:  $E_{\text{corr}}$  results. Open and closed circles denote with and without aluminum solids, respectively. Complete Water change on Day 12.

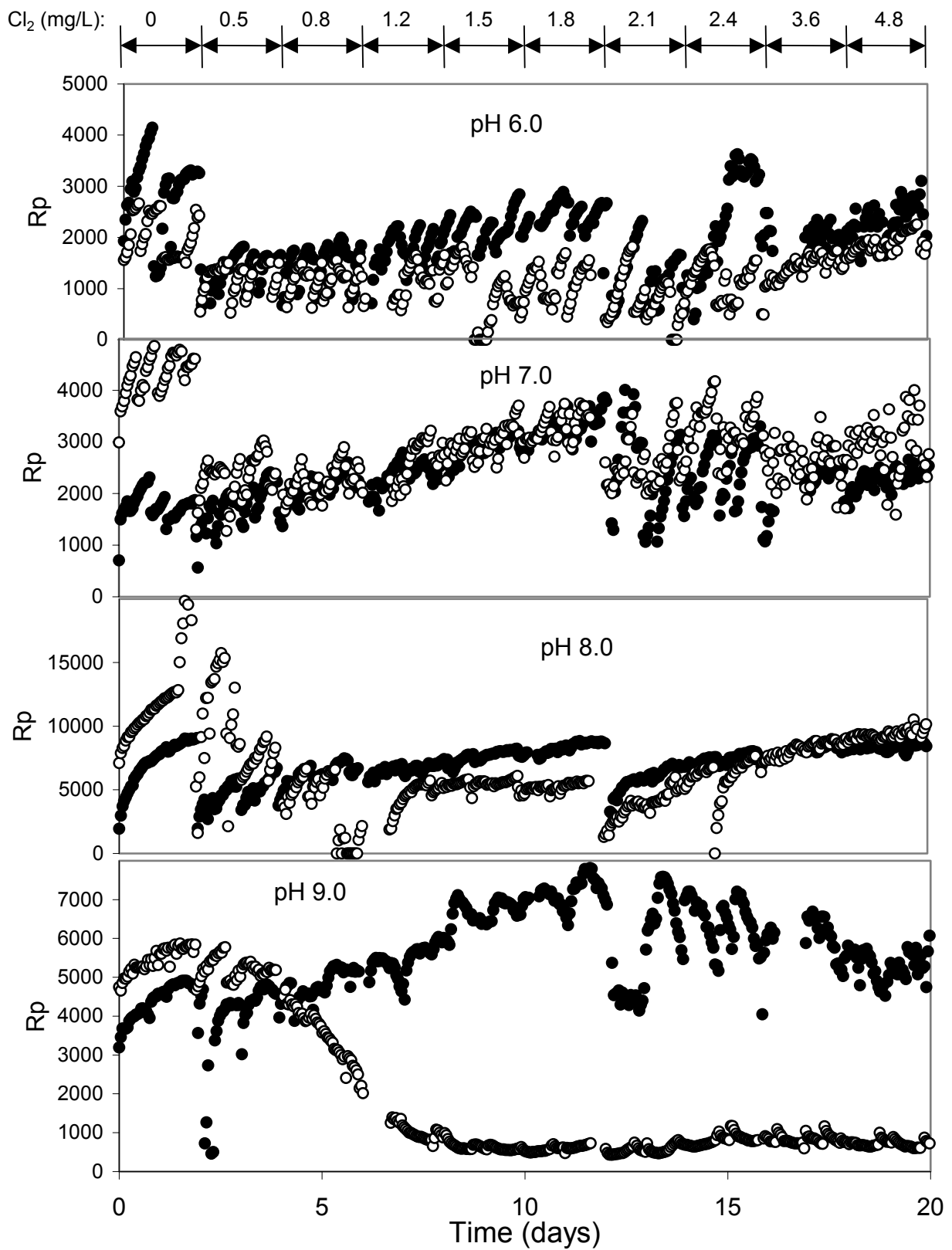


Figure 3-4. Polarization resistance data in Ohms. Open and Closed circles denote with and without aluminum solids, respectively. Complete Water change on Day 12.

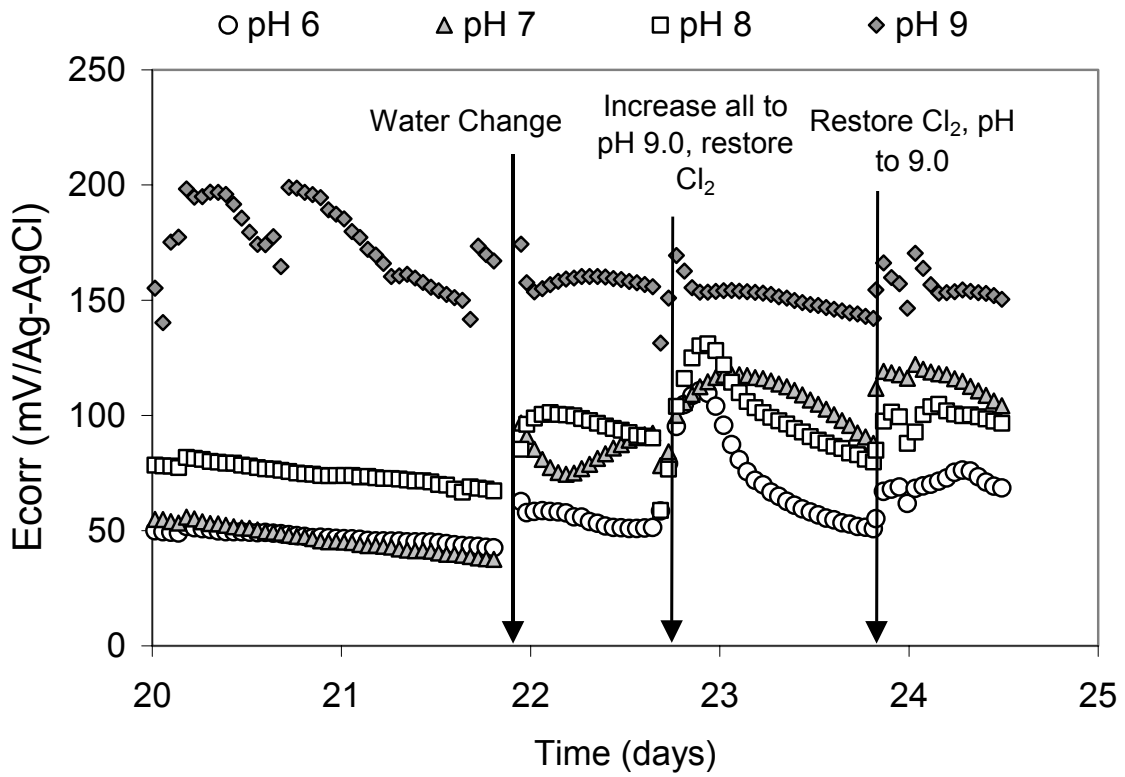


Figure 3-5.  $E_{corr}$  results from experiments with aluminum solids after day 20. Chlorine = 6.0 mg/L as  $Cl_2$ .

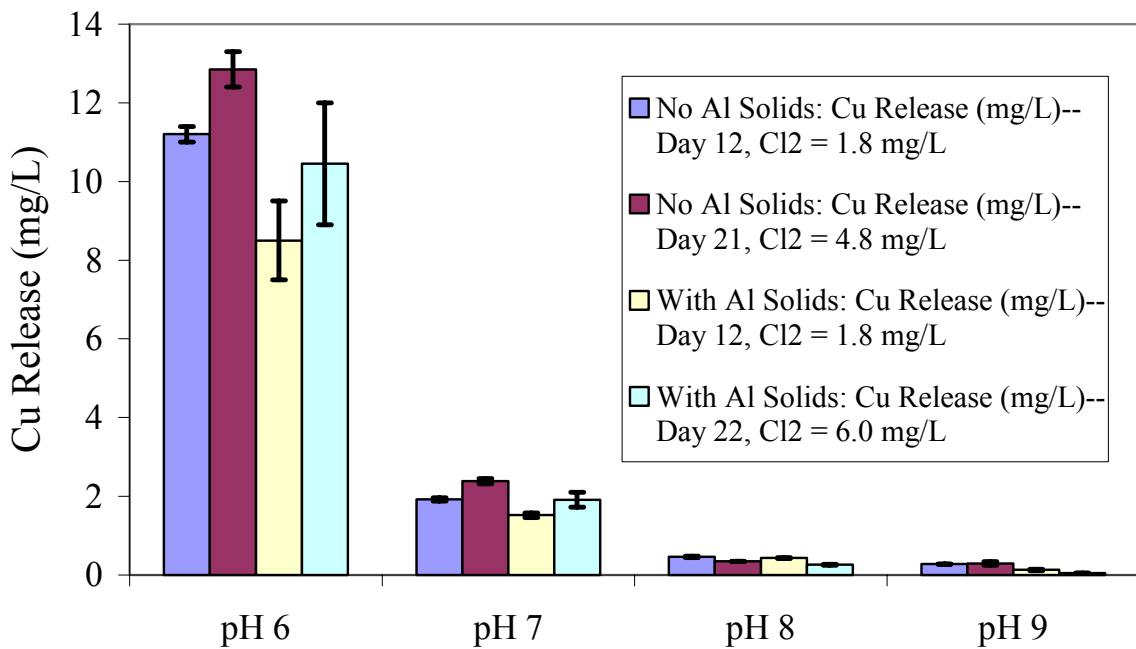


Figure 3-6. Average Copper Release based on duplicates measured before water change on Day 12 and end of experiment. Error bars represent the low and high measurements of the duplicate samples.

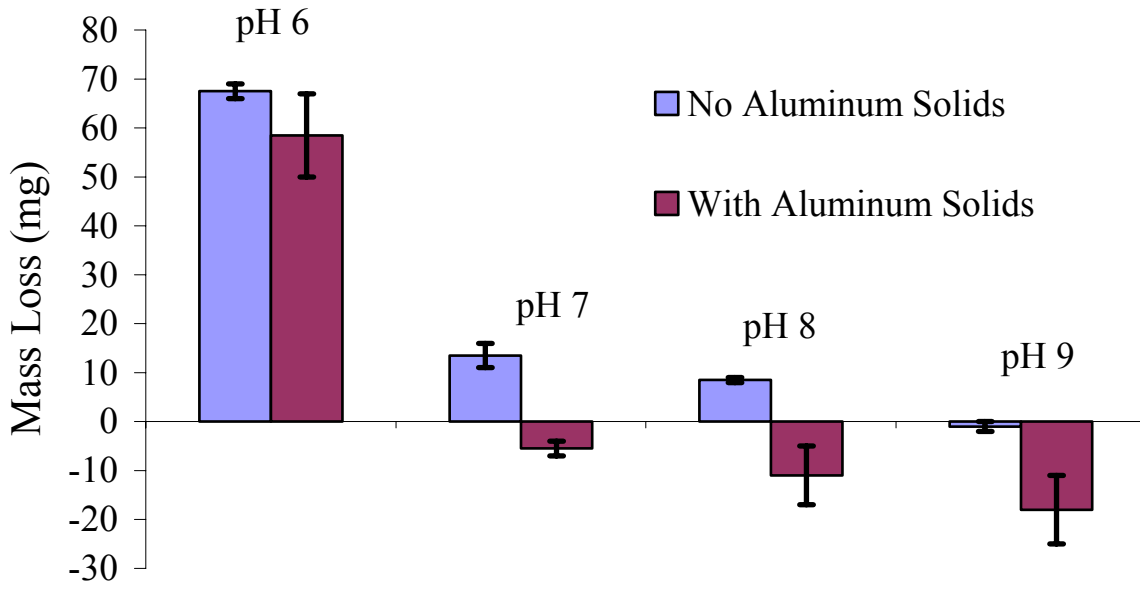


Figure 3-7. Average mass loss from copper samples based on duplicates. Negative values indicate a mass gain. Error bars represent the low and high measurements of the duplicate samples.

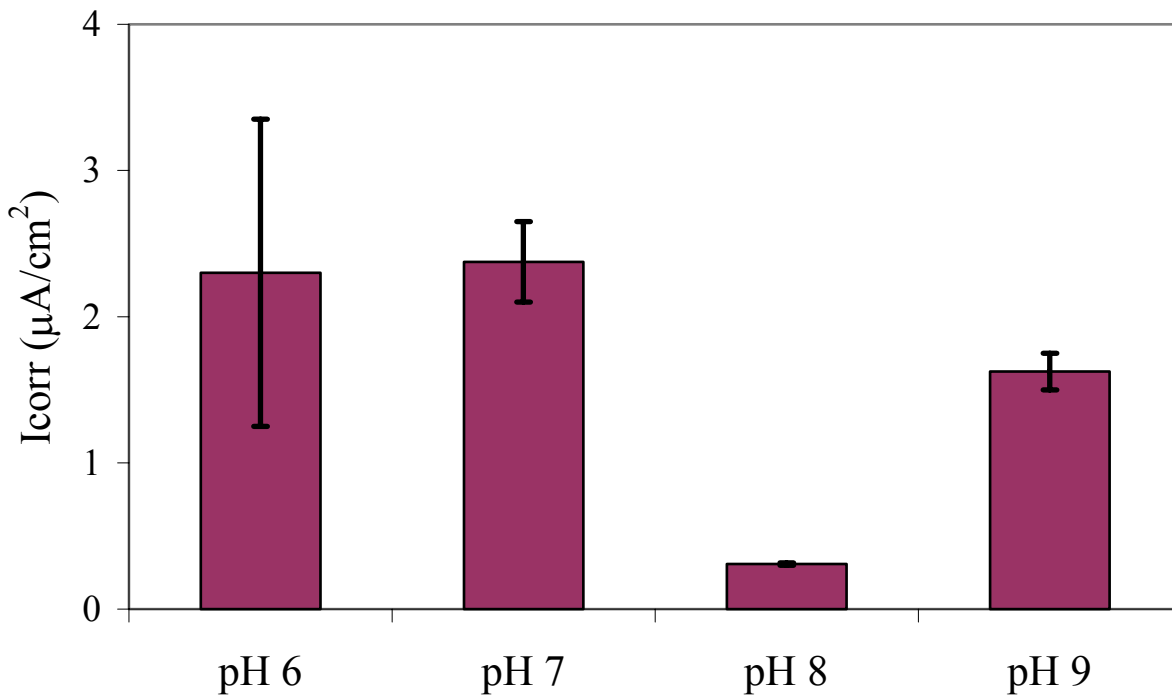


Figure 3-8. Average corrosion rate during day 23 with aluminum solids present. Water changed 18 hours before data was collected. Cl<sub>2</sub> = 6.0 mg/L. Error bars represent the low and high measurements of the duplicate samples.

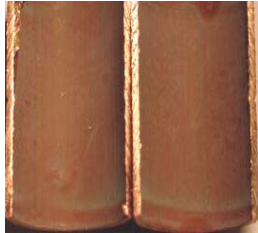



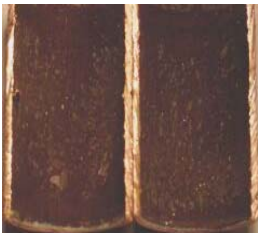
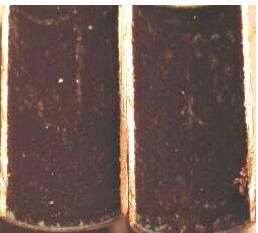


	pH 6	pH 7	pH 8	pH 9
No Al Solids				
With Al Solids				

Figure 3-9. Copper samples cut in half after end of experiment.

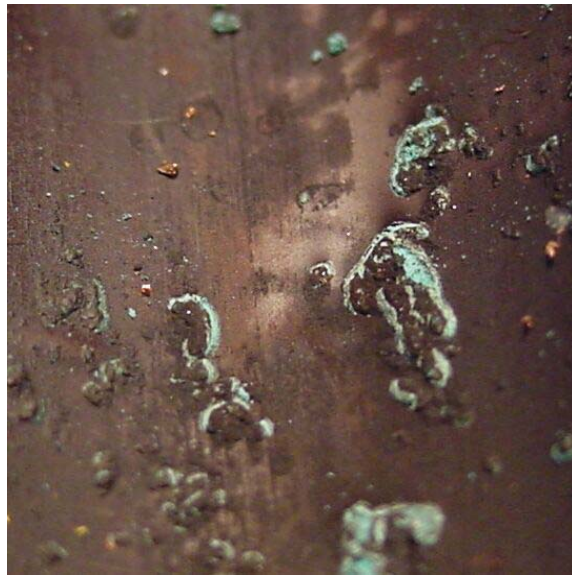


Figure 3-10. Close up of corrosion byproducts formed on pH 9 sample exposed to aluminum solids and chlorine.

## **CHAPTER 4: THE ROLE OF TEMPERATURE GRADIENTS IN RESIDENTIAL COPPER PIPE CORROSION**

Jason C. Rushing and Marc Edwards

### **ABSTRACT**

Experiments were conducted to determine the effect of sustained temperature gradients of  $\approx 20$  °C on copper pipe corrosion under stagnant conditions in simulated potable water. An apparatus was constructed to 1) apply realistic temperature gradients to the pipes, 2) monitor copper release to the water, and 3) measure thermogalvanic currents between the warm and cold sections of pipe. The orientation of the pipe in relation to the temperature gradients determined whether convection currents developed that promoted mixing during stagnation, and this influenced the magnitude of the temperature gradient in the pipe. The temperature gradient led to significant sustained thermogalvanic currents. Mixing of the water within the pipe also influenced copper leaching and scale buildup.

**KEYWORDS:** copper, temperature gradients, thermogalvanic corrosion

### **INTRODUCTION**

When a water consumer turns on a tap and passes water through a copper pipe, the highly conductive plumbing quickly comes into thermal equilibrium with the water flowing through it. In the case of hot water piping, water temperatures are commonly about 40 °C, whereas in wintertime water temperatures near 1 °C are common. Similarly, as water sits stagnant in the pipe when it is not in use, the pipe will gradually either warm up or cool down in response to the temperature of its local environment. If a copper tube is buried in a cold soil (i.e., service lateral in the winter), temperatures could drop to 1 °C, while temperatures in an interior wall of a home would be 15 to 25 °C higher.

It is relatively well known that temperature affects the rate of corrosion, the solubility of solids on the interior pipe wall, and the susceptibility of copper tube to erosion corrosion. However, a recent review also suggests that serious mechanical stresses could arise within pipes due to temperature changes, mainly because the protective scale on pipes has a different coefficient of thermal expansion than the metal itself [1]. This might cause the scale to “spall” from the pipe with loss of protection and introduction of copper to drinking water. Such changes in temperature might be responsible for 1) the high release of copper to water observed in some cases during winter months [2], and 2) why plumbers sometimes see a relationship between copper pinhole failures and a change in temperature [3].

These problems might also be caused by sustained temperature gradients applied to pipes. There are many reasons why such temperature gradients would be present on copper pipe in practice. For instance, copper pipe sitting in an underground service line would tend to take on the temperature of the soil, whereas the other end of the same tube within an exterior/interior wall of a home might be 20 °C colder or warmer. Likewise, adjacent/connected hot and cold water lines naturally lead to sustained temperature gradients. Anecdotal evidence is that pipes with large temperature gradients are more likely to fail, and perhaps introduce more copper to the drinking water.

Thermogalvanic corrosion may cause the early failure of pipes exposed to a sustained temperature gradient. Most of the work that has been done on this subject demonstrates that large temperature differences between sections of copper metal can cause serious corrosion problems under acidic, deaerated, and constant flow conditions [4, 5]. Other work has examined the effect of aerated NaCl solutions flowing over a small area with temperatures up to 100 °C higher than the rest of the copper tube [6]. However, we are unaware of any attempts to assess the effect of temperature differences on internal corrosion under conditions realistic to domestic potable water tubing. In this work, an apparatus was developed to impose temperature gradients on copper pipes and to monitor their effect on copper corrosion in such an environment. Both the thermogalvanic current and the corrosion by-product release to the water were monitored as part of this evaluation.

## MATERIALS AND METHODS

Two 6 meter sections of 2.5 cm diameter type L copper pipe were obtained from a local hardware store and were cut into 0.3 and 0.6 meter sections. A 2.5 cm threaded PVC ball valve (dielectric) and silicon glue were used to join the 0.3 meter copper pipe sections together (Figure 4-1). Copper wire with an alligator clip was secured to each 0.3 meter section using electrical tape.

Temperature gradients were imposed on the copper pipe using an insulated 1 cubic meter plywood box stored in a 5 °C constant temperature room. A fan and 100 watt light bulb with a dimmer knob were used to keep the temperature inside the box constant at  $25 \pm 1$  °C. To impose temperature gradients, selected pipes were set halfway through the top, bottom, and sidewalls of the box (Figure 4-2). Additional pipes were set horizontally and vertically and kept at constant temperatures of 5 and 25 °C. Each condition was tested using a 0.6 meter continuous section of pipe as well as a pipe sample with two 0.3 meter sections joined with the PVC ball joint.

A synthetic water containing 300 mg/L as CaCO<sub>3</sub> alkalinity, 14 mg/L chloride, 500 mg/L sulfate, and 15 mg/L silica as SiO<sub>2</sub> (added as reagent grade sodium salts) was used to fill the pipes after the pH of the water was lowered to 6.3 using CO<sub>2</sub> gas and stored at 5 °C for at least 24 hours. The ends of the pipe were capped with no. 5 ½ rubber stoppers. During the 4 month experiment, the water in the pipes was changed three times per week (M,W,F) at approximately the same time of day. Samples for total copper were collected once a week. Each sampling occurred after 48 hours of contact between the water and the pipe. Water samples from the 0.6 meter continuous section of pipe were obtained by removing one rubber stopper and emptying the entire contents of the pipe into a clean container. Samples from pipes on each side of the PVC valve were obtained after closing the ball valve between the two sections. The rubber stoppers were subsequently removed and each half was then emptied into a different clean container. Collected samples were periodically filtered through a 0.45 µm nylon syringe filter. The amount of copper found in these samples is defined as soluble for this work, although it is recognized that small copper particles or colloids could pass through a 0.45 µm pore size filter.

All samples were preserved with 2% nitric acid and then analyzed for copper using Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) per standard method 3120 B [7].

Current measurements were obtained by inserting a digital ammeter with 0.1  $\mu\text{A}$  precision between the two alligator clips bridging the PVC valve (Figure 4-1). For the pipes with a temperature gradient, the positive terminal on the ammeter was always connected to the section of pipe that was exposed to 25 °C. The resistance of the ammeter and cable was 0.1 ohm. Surface temperature measurements on the pipes were obtained with a type T thermocouple, and water temperatures were measured with a digital thermometer.

## **RESULTS AND DISCUSSION**

The discussion of the experimental results is presented in four sections: 1) the role of pipe orientation on temperature gradients, and then the corresponding effects on 2) copper release, 3) copper scale formation, and 4) thermogalvanic corrosion currents.

### **Pipe Orientation and Temperature Gradients**

The orientation of the pipe exposed to a temperature gradient is predicted to be very important in determining the temperature stratification and the behavior of the water within the pipe (Figure 4-3) during periods of stagnation. Because the density of water decreases as temperature increases above 5 °C, the water in a vertically aligned pipe that is warm on top and cold on the bottom will become stratified, much like a lake in the summer, because less dense water is on top of more dense water. This thermally “stable” condition will naturally act to prevent mixing of water in the pipe during periods of stagnation, and will therefore maintain larger temperature differences within the pipe. If the temperatures were reversed on this same pipe, cold on top and warm on the bottom, mixing will naturally take place. Under this thermally “unstable” condition, water will rise from the bottom as it warms and will sink from the top as it cools.

In spite of the fact that copper is such a good thermal conductor, significant copper pipe surface and water temperature gradients developed in pipes that were exposed to the temperature

gradient. For pipes joined with a PVC ball valve, the thermally stable vertical pipe exposed to 25 °C on the top had a maximum external pipe wall surface temperature difference of about 19 °C. The ends of the pipes arranged in the thermally unstable vertical and horizontal positions differed in temperature by only 9-11 °C (Figure 4-4). Because the pipes were exposed to the same external air temperature gradient, the smaller temperature difference on the surfaces of the thermally unstable pipes can only be attributed to the water mixing within the pipe and resulting transport of heat. The maximum temperature difference along the external surface of the 0.6 meter continuous pipe sections were 1-3 °C less than the corresponding pipes with the PVC ball joints, but were still significant (data not shown).

The water temperature within the pipe is very important because it can affect copper solubility and the rate of corrosion. The magnitude of difference in the water temperatures in pipes separated by the PVC ball valve was consistent with the external surface temperature gradients on the copper pipe. The thermally stable vertical pipe had an average water temperature difference of 17 °C between the top and bottom section, while the thermally unstable vertical and horizontal pipes had average water temperature differences of only 3 and 5 °C respectively. Because only an average water temperature measurement could be obtained from each section or pipe on either side of the ball valve, the maximum water temperature difference between the two ends of the pipe was probably greater. In summary, even though the pipes were exposed to the same extremes in external air temperature, pipe orientation had a large effect on mean water temperature along the length of the pipe.

### **Copper Corrosion Byproduct Release**

From day 42 through the end of the experiment, the control pipes exposed to a constant temperature of 5 °C released around 5 mg/L copper while the pipes exposed to 25 °C released about 1 mg/L of total copper to the water after 48 hours of stagnation (Figure 4-5). Because > 80% of the copper was soluble, the amount of copper released into the water should be predicted by  $K_{sp}$  values for known copper solids. When the chemical equilibrium program Mineql<sup>+</sup> [8] was used to predict copper solubility in the model water, soluble copper was predicted to range from 1 mg/L at 25 °C to 2 mg/L at 5 °C. Malachite [  $Cu_2(OH)_2CO_3$  ] is predicted to form and control solubility of copper in the pipe (Figure 4-6). However, regardless of which solid forms,

the model predicts greater solubility and therefore more copper release to the water at lower temperatures.

Batch experiments in beakers and without copper pipe tested the accuracy of the copper solubility model. 30 mg/L of copper was added as copper nitrate [  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  ] to the experimental water at 5 and 20 °C, and soluble copper concentrations were tracked over time. After 72 hours, there was no detectable drop in soluble copper levels. The experiment was repeated, but with the addition of 30 mg/L of copper scale that was removed from a corroded copper pipe that had been exposed to a constant 25°C. After 72 hours, soluble copper levels were 5.1 and 1.4 mg/L at 5 and 20 °C respectively, which is roughly the same level of soluble copper found in the constant temperature pipe experiments. It is clear from these two simple experiments, that copper precipitation is controlled by reactions occurring on the surfaces of solids. Without a “seed” on which copper can react to form a solid, solubility remains much higher than predicted by thermodynamics. It is also known that temperature, aqueous silica, and sulfate in the water can affect the formation of specific cupric solids [9]. However, the data from the batch solubility tests, pipe experiment, and model prediction support the general idea that more copper is released to cold water.

Because of mixing and water temperature stratification of only a few degrees, soluble copper in the pipes exposed to an unstable temperature gradient was around 2.5 mg/L in both the cold and warm sections (Figure 4-5). Although there was some variability from week to week, soluble copper levels from the cold and warm ends of the vertical pipe in the unstable orientation were always within 0.1 mg/L of each other. Interestingly, particulate copper was consistently found in the warm, bottom section of the pipe at levels ranging from 0.9 to 3.4 mg/L, while the copper in the top section of the pipe was always completely soluble. This result suggests an interesting effect on copper solubility and transport in pipe exposed to an “unstable” temperature gradient (Figure 4-7). Conceptually, as copper is released into the cold, top section of the pipe, it is soluble up to approximately 5 mg/L. However, as this water drops in the pipe and is warmed due to the convection currents, copper becomes less soluble, can precipitate, and then settle. When this copper-depleted water returns upward to contact the colder section of pipe, it can re-dissolve additional copper. This mechanism could occur indefinitely, causing very high levels of particulate copper to be released when the water is flushed from the pipe. This mechanism may

explain why stagnation sometime results in elevated levels of particulate copper in the water, at least in localized areas, especially during winter months when sustained temperature gradients are most likely to form [2].

The vertical pipe exposed to the stable temperature configuration had soluble copper levels of 6 mg/L in the bottom, cold section, and 3 mg/L in the warm, top section (Figure 4-5). These levels are slightly higher than what one would expect based on the water temperature alone and the results from the constant temperature pipes. There was also consistently some particulate copper found in the bottom, cold section of the pipe. Furthermore, the average copper release from both sections of pipe in this orientation is approximately 5 mg/L, while the average release from the pipes exposed to the unstable orientations was only 3 mg/L. This same trend was seen in the 0.6 meter continuous sections of pipe that were exposed to temperature gradients. It is uncertain at this time why the thermally stable pipe had higher levels of copper release, but as is discussed later, it could be related to the thermogalvanic current that developed between the two pipe sections in this orientation.

### **Temperature effect on Copper Scale**

The effect of temperature on cupric solid formation is apparent in the scale that formed on the pipe walls (Figure 4-8). Although the surface generally had a dull brown color, the pipes exposed to only 25 °C (no temperature gradient) had a vivid blue green scale that covered approximately 50% of the inside wall, while the pipes exposed to only 5 °C water had virtually no blue or green scale at all. Not surprisingly, the vertical pipes exposed to the stable temperature gradient developed both of these types of scale, consistent with the temperature of each section. The pipes exposed to the unstable temperature gradient also developed some noteworthy scale patterns. The 25 °C ends had a significant covering of light blue scale, while the 5 °C ends had none, consistent with the fact that copper is less soluble at higher temperatures. There was also some evidence of scale deposition patterns consistent with formation along lines of circulation within the pipe.

### **Thermogalvanic Currents**

A simple ammeter was used to measure electrical currents between the pipe sections connected with the PVC ball valve. The currents between different connected sections of pipes exposed to constant temperatures were consistently  $0 \pm 1 \mu\text{A}$ . These small currents can be attributed to variations between the sections of pipe that were joined together and represent a detection limit for the experimental method.

Currents between the pipes exposed to the stable temperature gradient (warm on top, cold on bottom) were much larger and consistently positive (Figure 4-9). During the first week, current measurements reached  $14 \mu\text{A}$ . After four weeks, the current had fallen off slightly to a peak of around  $8 \mu\text{A}$ , and maintained this level for the rest of the experiment. Positive currents indicate that the cold section of pipe is anodic to the warm section of pipe. When the ball valve was closed, currents dropped to 0 as expected.

For a pipe of this dimension, a current of  $10 \mu\text{A}$  is equivalent to a current density of  $0.04 \mu\text{A}/\text{cm}^2$ . Compared to a pipe mass of 270 g, this current density would produce a relatively insignificant 0.21 g of additional pipe mass loss per year. Moreover, considering that a high current density for copper corrosion during flow would be  $1.0 \mu\text{A}/\text{cm}^2$ , the thermogalvanic current density is not considered excessive in the context of uniform corrosion. However, if the extra corrosion rate were somehow concentrated on a small area of pipe equal to 1% of the total pipe area, half the wall thickness would be gone in 5 years, compared to 100 years without it. Furthermore, if the amount of extra copper corroded were completely released to the water during stagnation, an additional 4 mg/L of copper would be released to the water each day. This would be of concern given an EPA Action Limit for copper of 1.3 mg/L. Although it is rarely the case that corrosion translates directly to water contamination, the excess corrosion caused by this thermogalvanic effect might be responsible for why more copper was released into the pipes in the stable temperature orientation (Figure 4-5) and is certainly not beneficial under any circumstances.

During week five of the experiment, water was not changed within the thermally stable pipe for 1 week, during which time the current between the warm and cold sections of pipe for both the thermally stable and unstable orientations fell to  $0\text{-}2 \mu\text{A}$ . This gradual decrease in the

thermoelectromotive current is thought to be due to development of a concentration gradient of  $\text{Cu}^{2+}$ , dissolved oxygen, or pH within the pipe to counteract the effect of temperature.

The electrical currents traveling between the pipes exposed to the thermally unstable positions were initially positive but not as large as those seen in the thermally stable position. Furthermore, after 14 weeks, there was very little current measured in the horizontal pipe, and the current in the vertical pipe had actually become slightly negative (Figure 4-9). The reason for the gradual decrease in current and change in direction is not yet understood, but is undoubtedly related to changes in the controlling redox reactions at the surface within the tube.

In order to determine if the thermoelectromotive currents would cease in the absence of oxygen, a simple experiment was conducted at the end of the experiment. Experimental water was deaerated by bubbling a mixture of nitrogen gas and  $\text{CO}_2$  in order to remove oxygen and keep pH at 6.3. The deaerated water was then poured into an old pipe that had been previously exposed to a constant  $5^\circ\text{C}$  during the course of the experiment. The pipe was then placed in the temperature exposure rig in the thermally stable position (warm on top, cold on bottom), and electrical currents between the cold and warm sections were tracked for three days. The current between the two sections started at about  $14\ \mu\text{A}$  and dropped to around  $5\ \mu\text{A}$  after three days exposure (Figure 4-10). This same trend was seen when the experiment was repeated with the same pipe, but excess sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) was added to insure complete removal of dissolved oxygen per standard method 4500-O G [7]. These results indicate that something besides (or in addition to) the reduction of oxygen is driving the thermoelectromotive couple in this system. Since reduction of water can be ruled out because it is thermodynamically unfavorable, the reduction reaction driving the thermoelectromotive current may involve an oxidized copper compound already present on the pipe wall or within the water. More work is needed to better understand the reactions involved in this system.

## CONCLUSIONS

The orientation and differential heating of a pipe can have an effect on how much copper is released into the water due to temperature related changes in solubility and induced mixing or

stability. Furthermore, when a temperature gradient is imposed on a pipe, corrosion accelerating thermogalvanic currents can develop. Although not as practically significant as changes observed in copper solubility or mixing, these currents may explain some instances of increased copper release or decreased tube lifetimes. Temperature gradients and pipe orientation are important factors in understanding the process of copper corrosion in domestic plumbing, and may be key to explaining specific problems such as excessive copper corrosion or copper release in some systems.

It is expected that the same mechanisms explored here will contribute to corrosion of other common plumbing materials, including lead and iron. Considering the suspected health risks associated with excessive metal consumption and the costs associated with the failure of plumbing materials, more study of the fundamental mechanisms associated with this type of corrosion is needed.

## **ACKNOWLEDGEMENTS**

This work was supported by the National Science Foundation (NSF) under grant BES-9729008. Opinions and findings expressed herein are those of the authors and do not necessarily reflect the views of NSF.

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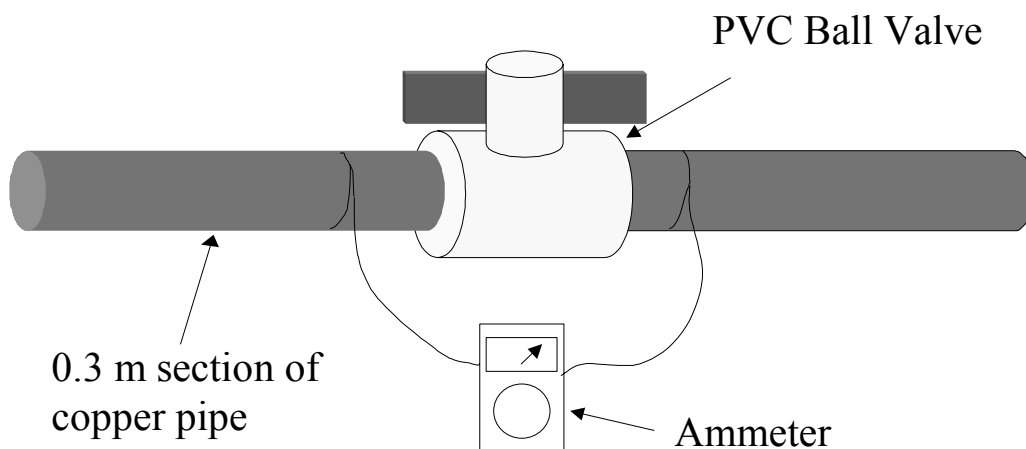


Figure 4-1. Pipe setup and current measurement technique for pipe sample with PVC ball valve dielectric

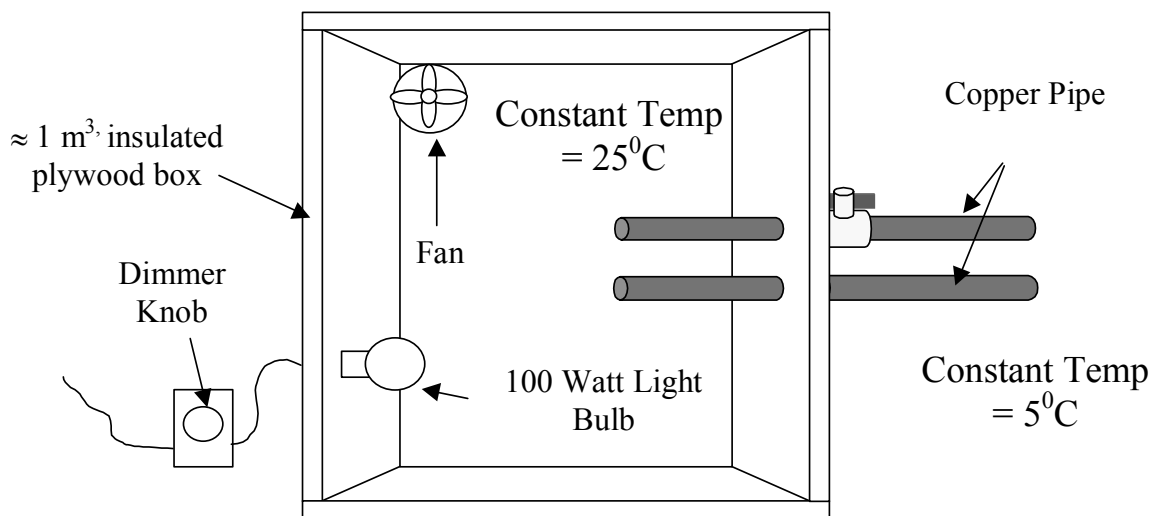


Figure 4-2. Experimental rig set up. Copper pipe setup in picture was replicated in ceiling and floor of insulated box. Pipe samples also placed inside and outside to expose samples to a constant 5 or 25 °C.

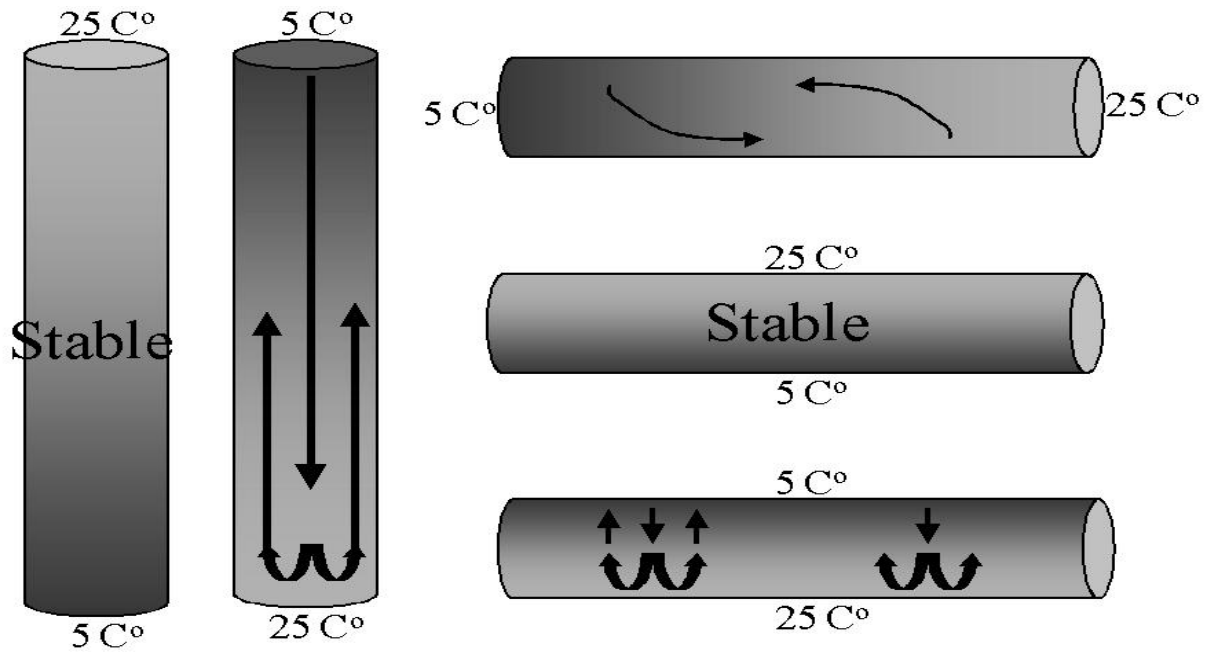


Figure 4-3. Schematic illustrating how temperature differences on different ends of a copper pipe would set up convection currents that enhance or act to prevent mixing during stagnation.

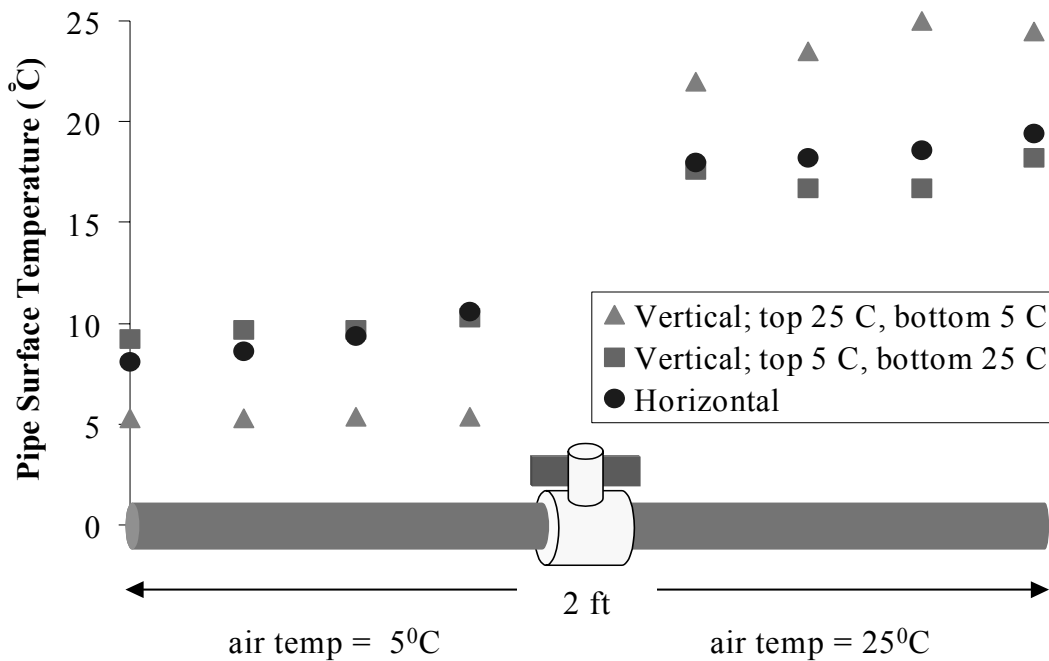


Figure 4-4. External surface temperatures for copper pipes joined by PVC ball valve.

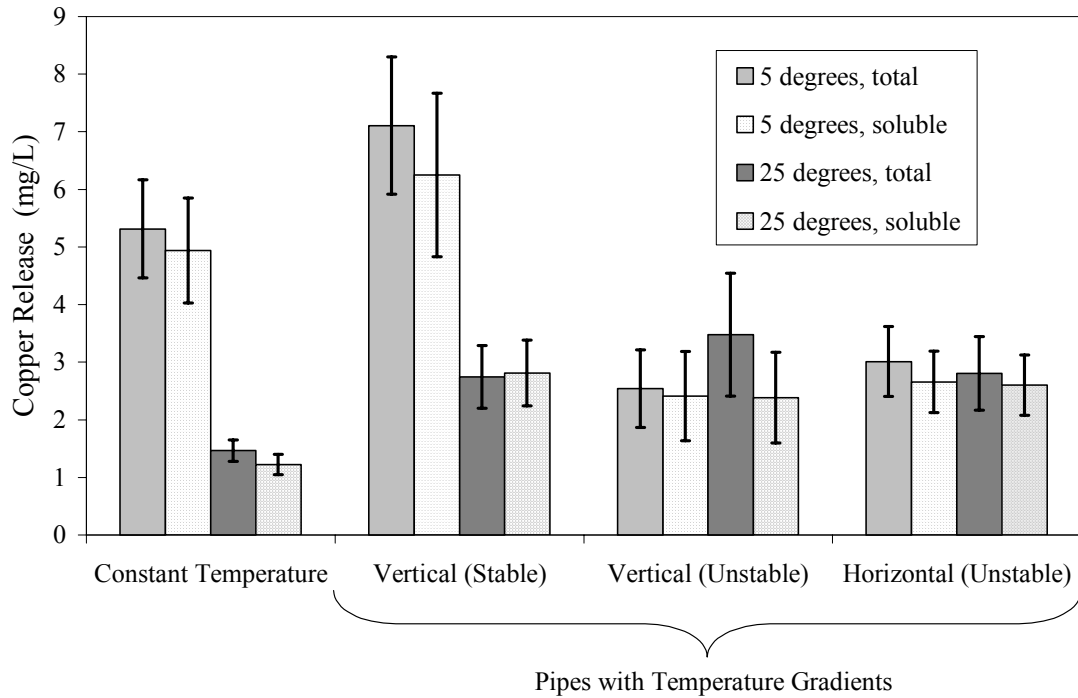


Figure 4-5. Average copper release for days 42-98. Data derived from 6 samplings during this period. Error bars represent 95% confidence intervals.

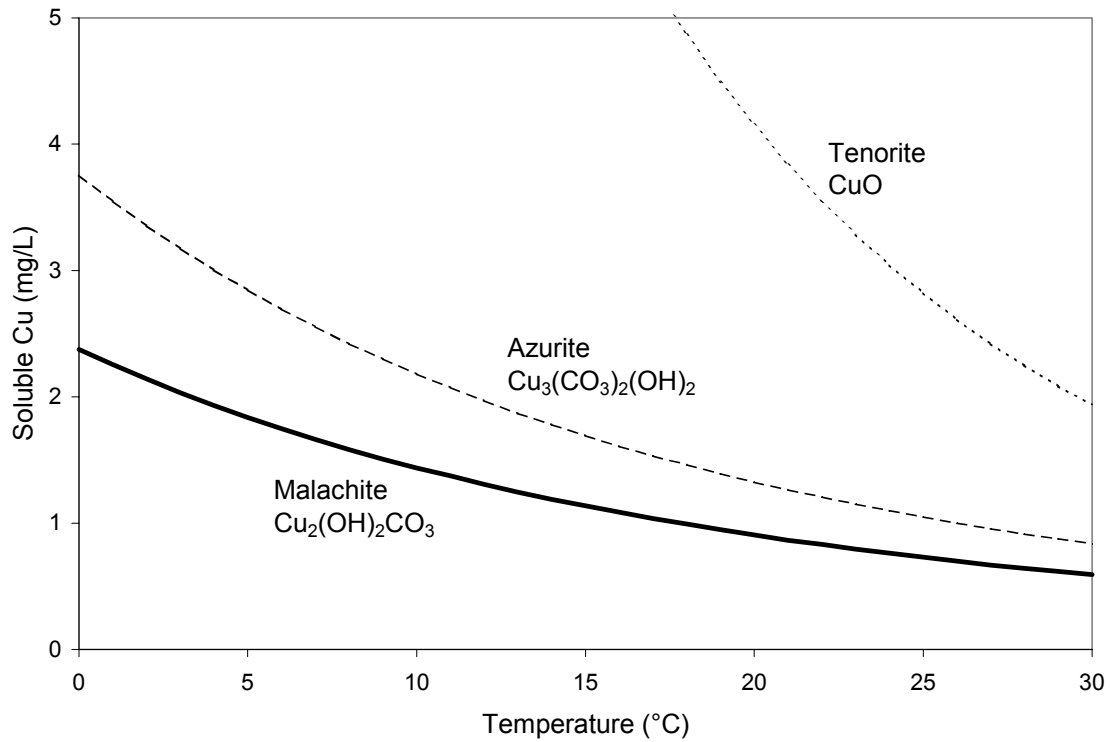


Figure 4-6. Predicted cupric solid formation as function of temperature for the water chemistry used in this experiment

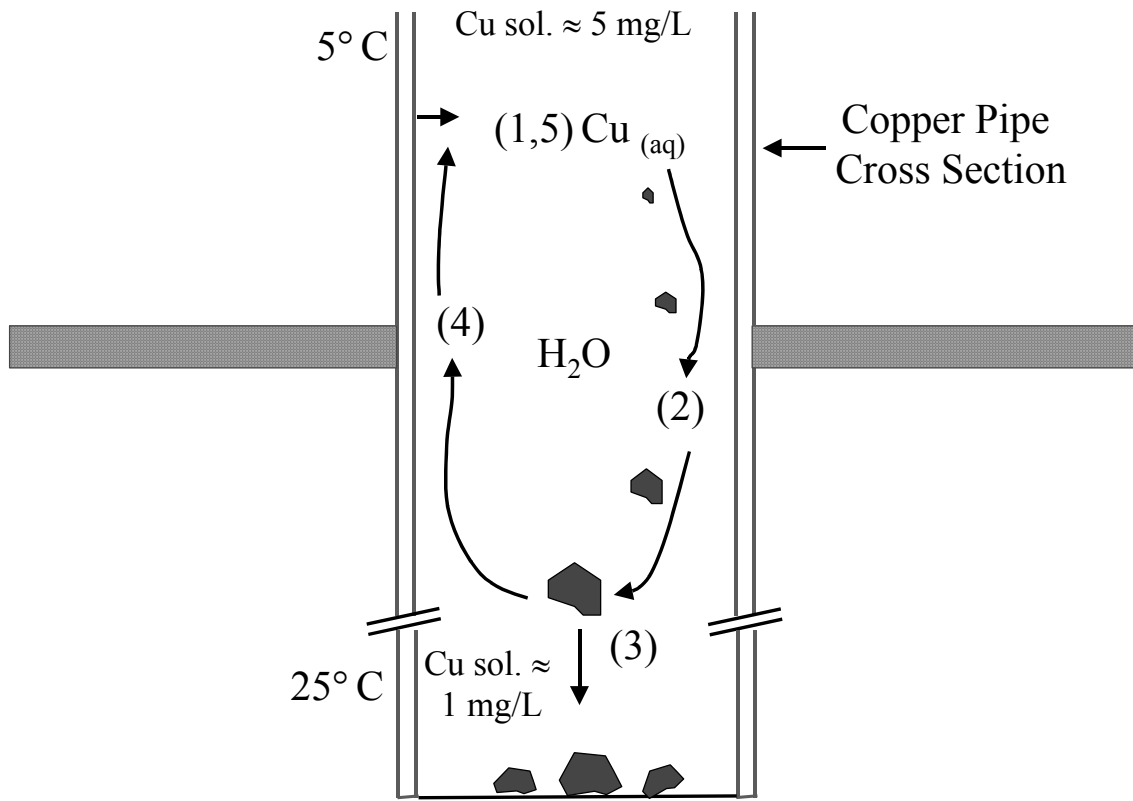


Figure 4-7. Mechanism causing elevated particulate copper levels in pipe exposed to temperature gradients after stagnation: (1) soluble copper release, (2) soluble copper transport to warm section due to convection currents, (3) copper solid precipitation and settling due to decreased solubility, (4) water return to cold section without soluble copper, (5) more soluble copper release.

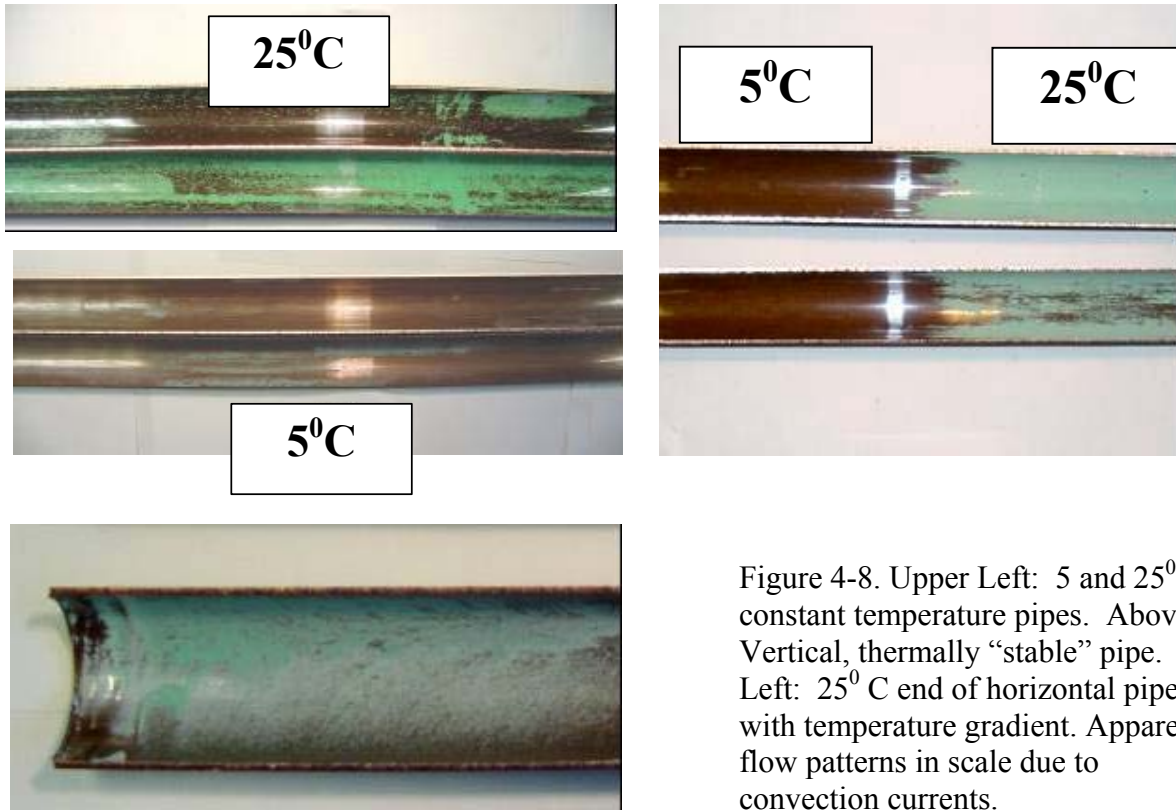


Figure 4-8. Upper Left: 5 and 25<sup>0</sup> C constant temperature pipes. Above: Vertical, thermally “stable” pipe. Left: 25<sup>0</sup> C end of horizontal pipe with temperature gradient. Apparent flow patterns in scale due to convection currents.

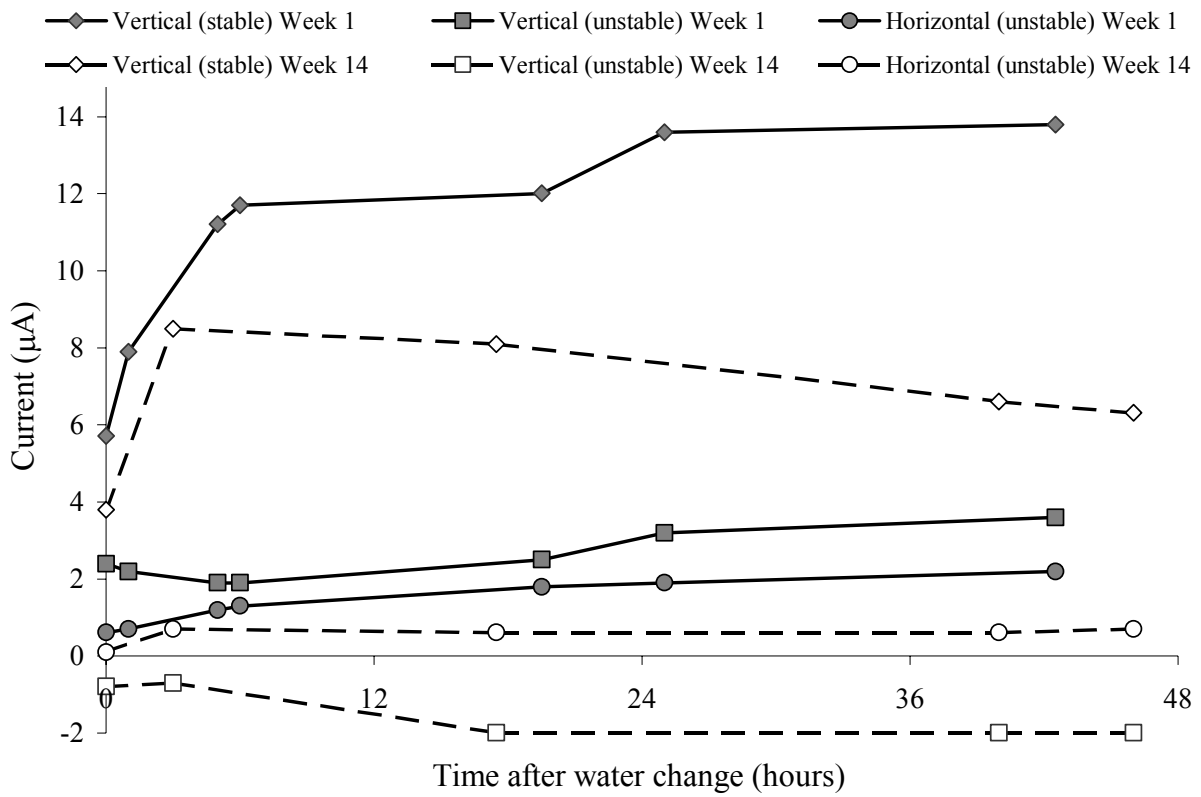


Figure 4-9. Thermogalvanic currents over two 48 hour periods, 14 weeks apart.

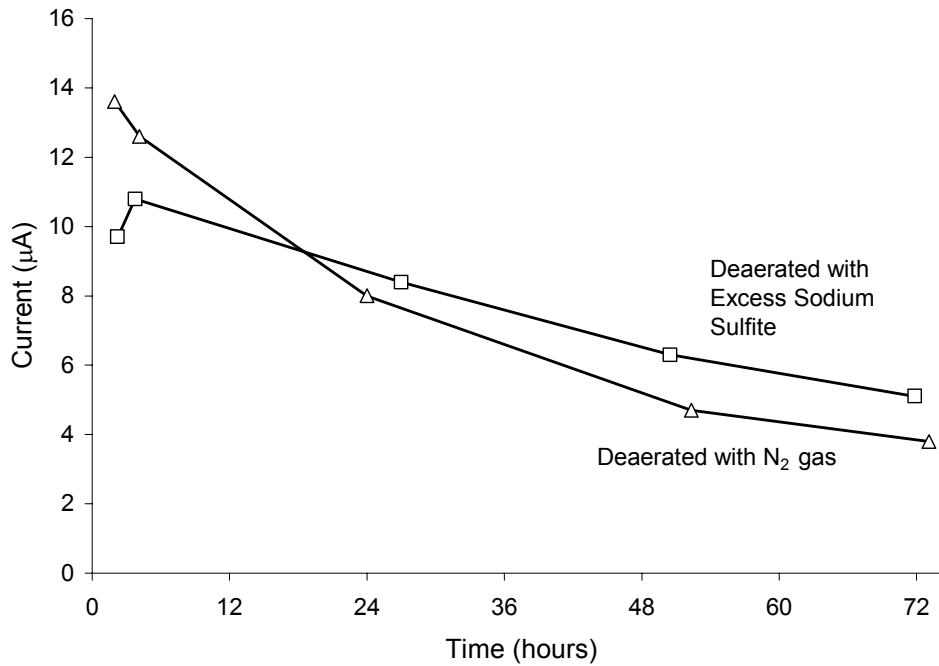


Figure 4-10. Thermogalvanic currents after oxygen removal with N<sub>2</sub> gas stripping or addition of excess sodium sulfite to scavenge all O<sub>2</sub> from the water

## **CHAPTER 5: SOME EFFECTS OF AQUEOUS SILICA ON THE CORROSION OF IRON**

Jason C. Rushing, Laurie S. McNeill, and Marc Edwards

### **ABSTRACT**

Silica is an important natural component of ground and surface waters, and is sometimes added as an inhibitor to control “red water” problems caused by corroding iron pipes. However, the effect of silicates on many aspects of iron corrosion has never been assessed. Experiments with water containing 0.5, 10, 25, or 50 mg/L as SiO<sub>2</sub> demonstrated a significant interplay between aqueous silica and iron corrosion. During this four month experiment, higher levels of silica caused more iron release to the water and decreased the size of suspended iron particles. The process of iron corrosion also changed aqueous silica concentrations; silica was released into the water from the cast iron during corrosion and removed from the water by incorporation into the scale layer. Silica also affected the type of scale that formed on the iron coupons. Scale at the lower silica concentrations was fairly uniform and easy to remove from the coupons, while the scale from the high silica reactors was more dense, and was more difficult to remove. Scale from the highest silica reactor also developed tall tubercles. Hydrogen gas-containing bubbles were evolved from some tubercles and this source of reduction was significant under all experimental conditions.

### **INTRODUCTION**

Water utilities will spend hundreds of billions of dollars repairing and replacing corroded iron pipes over the next 20 years and must attempt to develop strategies to deal with “red water” associated with rusting drinking water pipes (AWWARF, 1996; AWWA, 1999). Among the factors that influence red water and iron corrosion, the most frequently investigated are microbes, pH, buffering intensity, calcite saturation, dissolved inorganic carbon, phosphate, dissolved oxygen, chlorine, temperature, chloride and sulfate (Baylis, 1926; AWWARF, 1996; McNeill and Edwards, 2001a). However, existing theories are not sufficient to explain severe

outbreaks of red water and excessive iron corrosion problems when they occur, and as a result, corrosion control measures are based on trial and error approaches.

The presence of dissolved silica in water may have a significant influence on both iron corrosion and iron release to waters. Although silicates are typically only considered in the context of their addition as a corrosion inhibitor, silica is also naturally present at 1–20 mg/L as SiO<sub>2</sub> in surface water and 7–45 mg/L as SiO<sub>2</sub> in groundwater (Davis, 2000). Polymeric silicates first found use as a drinking water additive to aid coagulation through interparticle bridging and other unspecified mechanisms (Baylis, 1937; Stumm, et al., 1967). They were later applied to the sequestration or dispersion of naturally occurring iron in groundwaters, as well as iron particles in distribution systems (Hazel, et al., 1949; Schenk and Weber Jr., 1968; Dart and Foley, 1970; Dart and Foley, 1972; Browman, et al., 1989; Robinson, et al., 1992; Schock, et al., 1998). Addition of silicate-based inhibitors has also been reported to decrease (Williams, 1990; Raad, et al., 1998), or have mixed effects (Williams, 1990), on iron corrosion rates. One study found that natural silica present in the water was concentrated in a relatively protective iron scale (Riddick, 1944).

Silica can also strongly impact the chemistry of iron hydroxides. For example, the presence of silica can affect the crystallinity and size of iron oxide formed (Anderson and Benjamin, 1985; Mayer and Jarrell, 1995). Davis et al. also recently demonstrated that silica sorption to iron hydroxides produced a highly negative surface charge, which in turn led to the creation of smaller iron particles from larger particles (Davis, 2000; Davis, et al., 2001). Based on this fundamental work, it would be anticipated that dissolved silica in water might also increase detachment of particles from rust on the surface of a corroding iron pipe. This work investigates the influence of dissolved silica on iron corrosion rates and red water using a well-controlled batch reactor under aerated conditions.

## **MATERIALS AND METHODS**

Iron release to water was assessed by exposing cast iron coupons in a continuously mixed batch reactor. The iron samples were cylindrical sections of cast iron bar, 2.15 cm in diameter

and 1.9 cm long. The samples were coated with epoxy, leaving only the top flat surface exposed. The one liter volume of synthetic water contained 215 mg/L as CaCO<sub>3</sub> alkalinity, 100 mg/L chloride, and 100 mg/L sulfate added as reagent grade sodium salts, and was selected based on its similarity to the water chemistry used in previous iron corrosion studies (Smith, et al., 1998; McNeill, et al., 2000). Filter sterilized deionized water was used to create the synthetic waters, but no attempts were made to prevent or measure microbiological activity within the reactors. Four reactors were used, each with a different level of silica: 0.5, 10, 25, or 50 mg/L as SiO<sub>2</sub>. A predetermined amount of hydrochloric acid was added to each water concurrent with silica dosing to hold pH constant. As much as 50 mg/L additional chloride was added from this source. The reactors were kept in a 20°C constant temperature room. The set-up was also replicated in a 5°C constant temperature room in order to assess the effect of temperature on corrosion rates and iron release, yielding a total of eight experiments (4 silica levels x 2 temperatures).

Each reactor consisted of a 14 cm tall Nalgene 1-L polycarbonate container with a screw cap and nine iron samples placed on a 2.5 cm wide doughnut shaped shelf approximately 4 cm below the surface of the water. When the containers were filled, 3 cm of head space existed between the surface of the water and the screw on cap. The reactors were washed in 10% nitric acid and rinsed with deionized water prior to use. The water was continually stirred with a 2.5 cm magnetic stir bar rotating at 350 rpm. Periodic dissolved oxygen measurements, obtained with a Horiba multi-probe, showed that the reactors were well aerated and near saturation for dissolved oxygen at all times. A constant pOH of 6.0 was used for both temperatures, which translates into a pH of 8.09 and 8.66 at 20°C and 5°C respectively. pH values were monitored regularly and adjusted to the original value with a saturated CO<sub>2</sub> solution or 1 N sodium hydroxide as necessary, although observed variations were minor (+/- 0.2 units).

Three times a week, a total sample and a sample filtered through a 0.45- $\mu$ m pore size nylon membrane filter (totaling 10 ml) were collected from each reactor, and that volume of solution was replaced with fresh water of the original water chemistry and silica content. The water in each reactor was also completely changed with water of the original water chemistry and silica content two times over the four-month duration of the experiment in order to determine if observed trends would be repeated. Total iron release was assessed with each water

change (and at the end of the experiment) by removing the iron coupons from the reactors and digesting the water remaining in the reactors with 5% nitric acid. This was done to quantify total iron release, including any iron that had sorbed to the apparatus or settled to the bottom of the reactor and was therefore not measured during routine sample collection.

All samples were digested with 5% nitric acid and analyzed for iron and silicon using Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) according to Standard Method 3120 B (AWWA, et al., 1998). Ferrous iron ( $\text{Fe}^{+2}$ ) was measured using the 1,10 phenanthroline spectrophotometric technique on a Hach DR2010 spectrophotometer. Hydrogen gas in the headspace was measured by RGA5 Process Gas Analyzer after sampling with a gas syringe.

After four months, weight loss, scale build-up, and scale composition and morphology were assessed by removing three representative iron coupons from each reactor. Samples were dried for 1 week in a dessicator. A Teflon coated scraping tool was used to remove most of the scale from the samples, followed by a buffing tool to remove the remaining scale dust. In order to determine the scale composition, 100 mg of scale from the three iron coupons in each reactor was placed in 125-mL polycarbonate bottles and digested in 5% nitric acid. Undigested particles were captured on a 0.45- $\mu\text{m}$  filter and were further digested in a 10% hydroxylamine-HCl solution according to Standard Method 3500-Fe (AWWA, et al., 1998). Each digested solution was filtered again through a 0.45- $\mu\text{m}$  filter. The total iron and silica content of the scale was determined by analyzing the filtrate from both digestion methods using ICP-ES.

## **RESULTS AND DISCUSSION**

When examining corrosion problems, it is essential to differentiate between the corrosion rate of the iron pipe (i.e. oxidation of  $\text{Fe}^0$  to  $\text{Fe}^{+2}$ ) and actual release of iron into the water as a red, yellow, brown, or orange particle. In fact, the rate of corrosion typically has little correlation to the amount of iron that actually goes into the water, primarily due to the deposition of oxidized iron or other compounds into a scale which serves as a large reservoir of corrosion by-products. Experimental results are presented in three sections describing the influence of silica on iron release, corrosion rates, and scale morphology. Thereafter, some fundamental

aspects of silica effects on particle size and iron oxidation are explored. Unless otherwise stated, all silica concentrations discussed subsequently refer to aqueous silica and are expressed in mg/L as SiO<sub>2</sub>.

### **Iron and Silica Release to Water**

The regularly collected samples showed some interesting trends in iron and silica levels over time. In most of the reactors, the amount of total iron suspended in the water would initially increase at a rapid rate and then become almost constant after several days (Figure 5-1). This plateau effect was observed after each of the two water changes during the course of the experiment. It is unlikely that corrosion actually stopped when iron release rates leveled off; the observed plateau behavior is probably due to the formation and settling of larger iron particles as iron concentration increased, or a previously undefined equilibrium between particles on the sample surface and particles in solution. Whatever the exact mechanism, the reactors with more silica had greater initial iron release rates and reached a higher iron concentration plateau, which in turn produced more colored water (Figure 5-2). It is important to also note that soluble and particulate ferrous iron was not detected in any of the reactors, suggesting that most of the iron present in the water was in the ferric form.

Interestingly, silica concentrations also varied during the experiments—they increased or decreased over time depending on the initial level of silica in the water (Figure 5-1). The waters with 50 or 25 mg/L initial silica experienced a decrease in silica concentrations with time, with levels dropping as much as 50% within two to three weeks after the water change. Eventually, the rate of silica concentration decline began to slow; this tended to occur in conjunction with slower rate of iron release. In contrast, silica levels in the reactors with 0.5 mg/L initial silica increased steadily and then leveled off between 6 and 9 mg/L as SiO<sub>2</sub>. Silica levels remained approximately constant in the waters with an initial silica concentration of 10 mg/L. The aqueous silica in all the reactors was on average 96% soluble.

Where was the silica coming from in the reactors with low initial silica, and where was it going in the reactors with high initial silica? Control experiments demonstrated that the experimental apparatus itself was not releasing silica, and digestion of the contents of the reactor after water changes showed that silica was not sorbing to the apparatus. Furthermore, aqueous

silica concentrations remained constant in the absence of corroding iron coupons. It is therefore clear that the iron samples were acting as both a source and a sink for silica in the various experiments.

Cast iron contains approximately 2.5% silica by weight, so corroding iron can release silica to the water, which could explain the increase in silica with time. A few different processes may be responsible for silica removal from the water. First, silica could have been incorporated into the scale by simply sorbing to the iron surface. Secondly, the relationship that appears to exist between the rates of iron release and silica removal implies the formation of an iron-silica solid on the surface of the iron scale. Finally, some other factor in the system with the corroding cast iron could have catalyzed the formation of a crystalline form of silica, as per the results from Harder and Flehmig (Harder and Flehmig, 1967). Although the exact mechanism is unknown, silica levels in all of the reactors trended toward ~10 mg/L, suggesting that the rate of silica release and silica removal from solution are balanced at this level for these experimental conditions.

There was some evidence to suggest that temperature played a role in total iron release over the course of the experiment. For example, iron coupons in the 0.5 mg/L silica containers released 54% more iron to the water at 5°C compared to 20°C (Figure 5-3). Likewise, the coupons in the 10 and 25 mg/L silica containers at 5°C released 67% and 64% more iron than their counterparts at 20°C. Total iron release in the 50 mg/L silica containers was nearly the same for both temperatures. It is unclear whether or not temperature is directly or indirectly responsible for these observed results. Recent work has explored the importance of temperature on iron corrosion, and has found that low temperatures can result in more iron release to the water (Smith, et al., 1998; McNeill, et al., 2000). Temperature can influence many water chemistry parameters including dissolved oxygen solubility, oxidation rates, activity coefficients, and microbial activity. Each of these factors can affect the rate of iron corrosion, the properties of the iron scale, and by-product release into the water (McNeill and Edwards, 2002). Consequently, no simple explanation can be provided that can explain why lower temperatures caused more iron release except at 50 mg/L silica.

The initial silica level in the reactors had a significant effect on the total amount of iron released to the water, with more iron released to the water with higher levels of silica (Figure 5-3). However, the difference in iron release was greatest at the beginning of the experiment. After the first 27 days of the experiment at 20°C, 12 times more iron was released to the water with 50 mg/L silica than to the water with 0.5 mg/L silica (35 mg compared to 3 mg). After the final water change (days 74–127), only 1.6 times more iron was released to the water with 50 mg/L silica compared to the water with 0.5 mg/L silica (18 mg compared to 11 mg). Thus, as the iron samples aged, the total iron release decreased in the reactors with the highest levels of silica, while the total iron release increased in the reactors with lower levels of silica. During the relatively short timeframe of this experiment, silica consistently caused more iron release for all conditions and increased the occurrence of red water. However, if the rate of iron release to water continued to decrease in the reactors with high levels of silica, the long-term effects of silica might be beneficial and less iron may ultimately be released by these iron samples compared to samples in low silica waters.

### **Iron Corrosion Rates**

Based on the observed trends in iron release, it might be expected that high silica increased corrosion rates. However, the overall weight loss (a measurement of corrosion rate) for the iron samples either stayed the same or slightly decreased with increasing levels of silica (Figure 5-4). In addition, the difference between the samples at 5°C and 20°C was not significant at the 95% confidence level. The overall weight loss of the coupons includes two components: the iron released to solution plus the iron attached to sample as scale. However, the amount of iron released to solution was a small fraction of the overall weight loss compared to the amount deposited in the scale. As a result, the mass of iron incorporated into the scale was closely related to the overall mass loss for all experimental conditions (Figure 5-4).

Previous studies have found that silica has mixed effects on corrosion rates (Williams, 1990; Raad, et al., 1998). Williams found varying weight loss for cast iron coupons exposed for 150 days to natural waters from different sources under different silica dosing and flow conditions. Unfortunately no water quality data were given, making it impossible to correlate

those results with water quality factors. Raad et al. used a linear polarization method with carbon steel electrodes in a water low in alkalinity and hardness, initially saturated with DO, and with 2 – 3 mg/L SiO<sub>2</sub> naturally occurring. Ten mg/L SiO<sub>2</sub> was added at pH 7.7 and 9.0 and the corrosion rate was monitored for 14 days; reactors with added silica showed about 25% lower corrosion rate and weight loss compared to the control. The short-term nature of the experiment, the use of carbon steel rather than cast iron, and the use of natural water instead of synthetic might explain the observed beneficial effect of silica. It is very likely that water chemistry influences the nature of the action of added silica on the corrosion rates of iron, and more research is needed to fully understand these effects.

### **Scale Composition and Morphology**

The physical and chemical properties of the iron scale formed during corrosion are very important. The scale formed on a pipe may provide protection from further corrosion, or it might slough off into the water causing outbreaks of red water. Furthermore, formation of scale as large tubercles can increase head loss through pipe systems and certain scales might encourage heavy localized corrosion known as pitting. In this study, silica not only affected iron release, it also had an important effect on scale properties.

*Si Content of Scale.* Scale on samples from the 50 mg/L silica reactors had almost three times higher average silica content than the 0.5 mg/L silica reactor (6.92% vs. 2.46% by weight as SiO<sub>2</sub>), and in the 50 mg/L silica reactor, nearly three times more Si was associated with the iron scale than was released from the iron during corrosion (Figure 5-5). In contrast, in the 0.5 mg/L silica containers, the mass of Si in the scale was about equal to the amount of Si released during iron corrosion. A mass balance of Si in the system confirmed that aqueous silica lost from solution was incorporated into the iron scale and was responsible for the observed drop in silica levels in the containers with high levels of initial silica. In the reactor with the lowest silica, although significant increase of silica concentration in solution was observed, the majority of Si from the corroding cast iron remained in the scale.

*Scale Morphology.* Silica also had obvious visual impacts on the scale morphology (Figure 5-6). The samples from the 0.5 mg/L silica rig developed scale that was mostly uniform in structure and color. In contrast, samples with higher silica had scale with irregular formations and black spots. Although no quantitative measurements were made, the scale formed at higher silica concentrations appeared denser and was more difficult to remove from the coupons compared to the other reactors. The samples from the reactor with the highest level of silica (50 mg/L SiO<sub>2</sub>) also developed tall tubercles, a characteristic not found in the other samples (Figure 5-7). Differences in scale formations are most likely due to the effect of incorporated silica within the scale and not the amount of iron released into the water. As mentioned earlier, most of the corroded iron mass remained attached to the iron coupons, and only a small fraction was released into the water for all conditions.

The durability of the scale formed might also be very important. Scale that is easily flaked off might be more likely to cause red water problems, while scale that is tougher and denser could potentially protect the iron from further corrosion. Although the iron exposed to high levels of silica consistently released more iron to the water during the duration of the experiment, the decreasing rate of iron release in these reactors could be attributed to the development of a more protective scale layer. However, widespread formation of tall tubercles (such as in the 50 mg/L silica reactors) on a pipe wall could lead to unacceptably high head loss in a water distribution system.

*Hydrogen Evolution.* A small bubble was observed to “erupt” from the mouth of some of the tubercles in the 50 mg/L SiO<sub>2</sub> container approximately every 15 minutes (Figure 5-7). A submerged, inverted test tube was placed over the tubercle to collect some bubbles for analysis using gas chromatography (GC), and the bubbles were determined to be predominantly hydrogen. The source of the hydrogen is presumably the reduction of water by iron corrosion:



To approximate the rate of hydrogen evolution, each container was sealed with a screw-on cap and gas was allowed to accumulate in the headspace for 24 hours. After 24 hours, H<sub>2</sub> levels ranged from 14 to 240 ppm (atmospheric H<sub>2</sub> ≈ 0.5 ppm), which means an estimated 0.1 –1.5 % of the total corrosion rate was associated with hydrogen evolution at that time. This result is

surprising because hydrogen evolution is not expected to be significant in a well-mixed, aerobic environment. Moreover, this is clearly an absolute lower bound to the actual amount of corrosion related to hydrogen evolution, because of potential leaking of hydrogen from the system and possible recombination of hydrogen with oxygen.

Conventional wisdom holds that all iron oxidation in aerated systems is related to the reduction of O<sub>2</sub>, and it is thought that accurate corrosion rates can be determined by tracking the disappearance of oxygen in a closed system (AWWARF, 1996). This work raises some doubts about this assumption, because it appears that the coupling of iron metal oxidation to the reduction of H<sup>+</sup> is a significant component of iron corrosion, even in well-aerated environments.

### **Si Effects on Particle Size and Iron Oxidation Rates**

It has been demonstrated that silica can cause iron hydroxide particles to have highly negative surface charges, which leads to the formation of smaller particles that are more likely to remain suspended in solution (Dart and Foley, 1970; Dart and Foley, 1972; Robinson, et al., 1992; Davis, 2000). Phosphorous, which is also used to control red water problems, has also been shown to similarly affect iron particle size (Lytle and Snoeyink, 2000). The scale layer on the iron coupon can be viewed as one large particle, and if silica causes this “particle” to develop a highly negative surface charge, it follows that smaller particles would form and be released into the water at a higher rate in the presence of silica. Other work has shown that high levels of silica alter the mineralogy of ferrous oxidation products in natural systems, causing smaller and more stable solids to form (Mayer and Jarrell, 1995). Either of these two mechanisms, the formation of negatively charge particles and alteration of the mineralogy of ferrous oxidation products, can potentially explain why there was more iron release to the water in the reactors with high levels of silica.

To gain some fundamental insight into possible mechanistic causes for the observed silica effects on iron release and scale formation, two types of experiments were conducted. First, samples were collected from the reactors and passed through nylon 0.45- $\mu\text{m}$  and cellulose acetate/nitrate 0.02- $\mu\text{m}$  pore size membrane filters to operationally characterize the size distribution of the iron particles formed from corrosion of the cast iron samples. For comparison, a similar experiment was conducted with aerated synthetic water containing 1 mg/L

$\text{Fe}^{+2}$  which was oxidized in the presence of various amounts of silica (a system without the confounding influence of corrosion). Second, experiments were conducted to determine the effect of silica on the oxidation rate of ferrous iron.

*Particle Size.* Consistent with previous results, silica had a dramatic influence on the particle size distribution in both the samples from the reactors and in the samples dosed with  $\text{Fe}^{+2}$  (Figure 5-8). In both systems, increasing the silica concentration reduced the size of iron particles formed. For the low silica conditions, nearly all of the iron was greater than 0.45- $\mu\text{m}$  in size (72% in the 0.5 mg/L  $\text{SiO}_2$  reactor and > 95% in the 0 mg/L  $\text{SiO}_2$   $\text{Fe}^{+2}$  experiment). At 25 mg/L  $\text{SiO}_2$ , 84% of the particles from the reactor and 71% from the  $\text{Fe}^{+2}$  experiment were between 0.02- $\mu\text{m}$  and 0.45- $\mu\text{m}$ . At 50 mg/L  $\text{SiO}_2$ , 47% of the iron from the reactor and about 76% from the  $\text{Fe}^{+2}$  experiment passed through the 0.02- $\mu\text{m}$  pore size filter.

*Ferrous Oxidation.* The composition of the scale formed on corroded samples will depend partly on whether the precipitated iron was in ferrous ( $\text{Fe}^{+2}$ ) or ferric ( $\text{Fe}^{+3}$ ) form. To determine if silica had any effect on the oxidation of iron from  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$ , several tests were performed by adding 30 mg/L of ferrous iron to aerated water of the same chemistry in the batch reactors with different amounts of silica. In the first set of tests, the pH was allowed to change after the addition of ferrous sulfate. For all silica conditions, the initial pH was 8.2, and the final pH was  $6.5 \pm 0.1$ . The rate of pH change was the same for all conditions. In the water with no silica, more than 95% of the ferrous iron was oxidized after 30 minutes. However, in the presence of 25 or 50 mg/L  $\text{SiO}_2$ , only 66% and 60% of the ferrous, respectively, was oxidized after 30 minutes (Figure 5-9). A second set of identical experiments was run, except pH was held constant at 8.1 with the addition of a predetermined dose of 1M NaOH. After 5 minutes, the waters with 0, 25, and 50 mg/L  $\text{SiO}_2$ , had 0.1, 0.9, and 1.1 mg/L  $\text{Fe}^{+2}$  left, respectively (data not shown). As expected, oxidation was much more rapid when the pH was held at 8.1, but the same trend was again observed: silica significantly slowed  $\text{Fe}^{+2}$  oxidation.

Slower oxidation of  $\text{Fe}^{+2}$  may also explain why more iron was released into the water with higher levels of silica. Baylis first recognized the importance of  $\text{Fe}^{+2}$  diffusion through the scale layer, where, given dissolved oxygen and high enough pH, it should oxidize to  $\text{Fe}^{+3}$  and precipitate before it enters the water (Baylis, 1926). Other researchers have also suggested a

relationship between  $\text{Fe}^{2+}$  in the iron scale and iron release to the water (Sarin, et al., 2000). Because of its high solubility, if  $\text{Fe}^{2+}$  reaches the surface of the scale layer, it is likely to be released into the water where it will then oxidize and precipitate and form “red water”. The amount of ferrous iron that reaches the surface of the scale layer is a complex function of the rate of corrosion at the metal surface, the rate of diffusion through the scale, the precipitation of ferrous species such as  $\text{Fe}(\text{OH})_2$  and  $\text{FeCO}_3$ , and the rate of oxidation to  $\text{Fe}^{3+}$  within the scale (Figure 5-10). Thus, since silica is decreasing the rate of oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , thereby allowing more  $\text{Fe}^{2+}$  to go into solution, an explanation is apparent for the relationship between higher silica and more iron release. Additional work is needed to determine if silica impacts the rate of  $\text{Fe}^{2+}$  precipitation or  $\text{Fe}^{2+}$  diffusion.

## CONCLUSIONS

- Silica impacted iron corrosion by
  - increasing the concentration of particulate iron released to water
  - increasing the extent of tuberculation
  - decreasing long term corrosion rates
- Silica decreases the rate of ferrous oxidation in water and interferes with precipitation, factors that combine to increase the concentration of ferrous iron at the water-solution interface.
- Silica decreases particle size, and increases the likelihood of maintaining suspended iron in solution.
- Corrosion of iron via hydrogen evolution is significant even in well-mixed aerobic solutions.

## ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (NSF) under grant no. BES-9729008. The opinions, findings, and conclusions or recommendations are those of the authors and do not necessarily reflect the views of the NSF.

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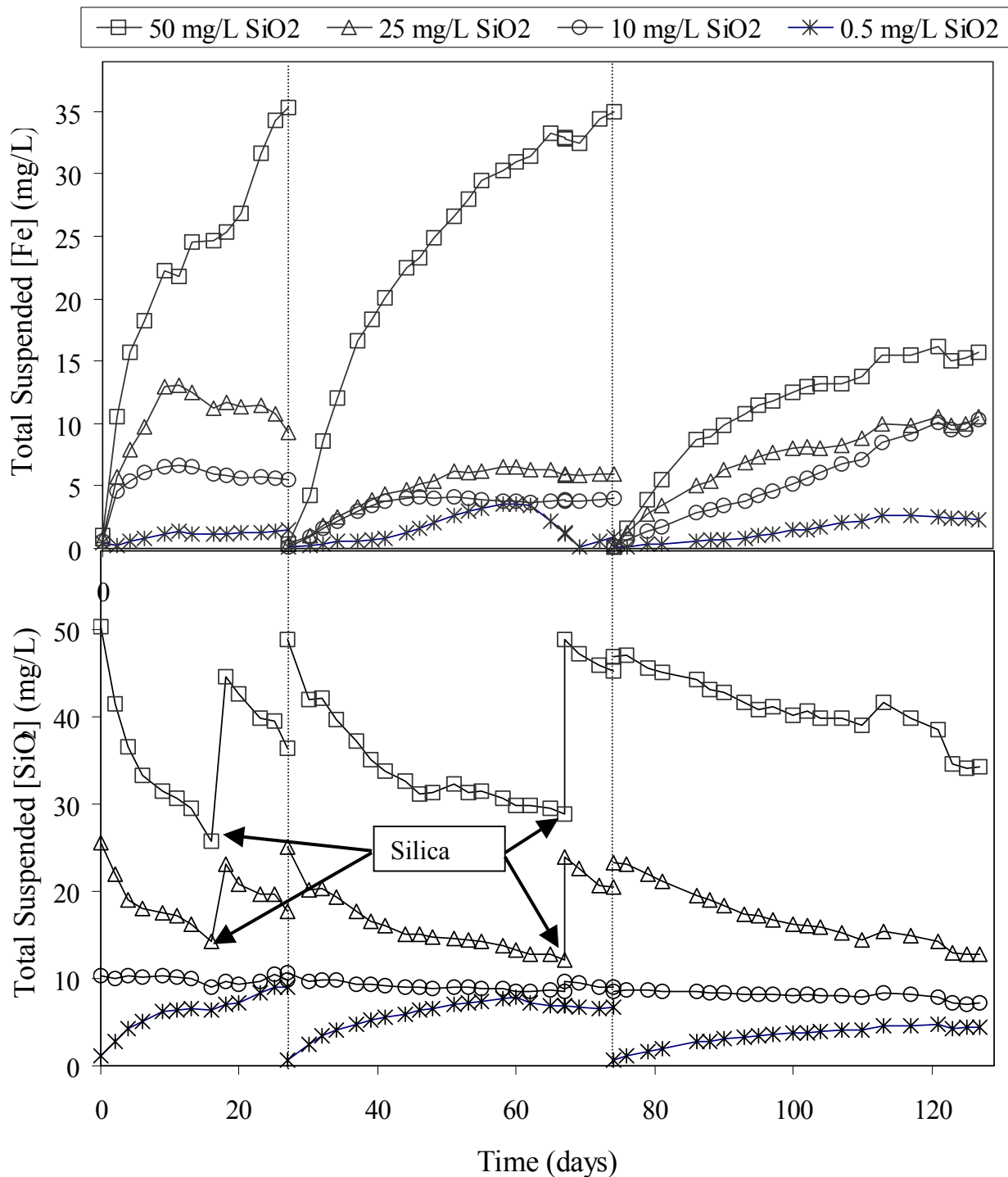


Figure 5-1: Iron (top) and silica (bottom) concentrations in 20<sup>0</sup> C reactors. Water changes occurred at days 27 and 74 and are indicated by vertical dashed lines. Silica was manually dosed to the 50 and 25 mg/L SiO<sub>2</sub> reactors on days 16 and 67 (indicated by arrows) to restore silica to initial concentrations. Same trends seen at 5<sup>0</sup> C.



Figure 5-2: Color difference in water from 0.5 mg/L silica container (left) and 50 mg/L silica container (right) at 20<sup>0</sup> C.

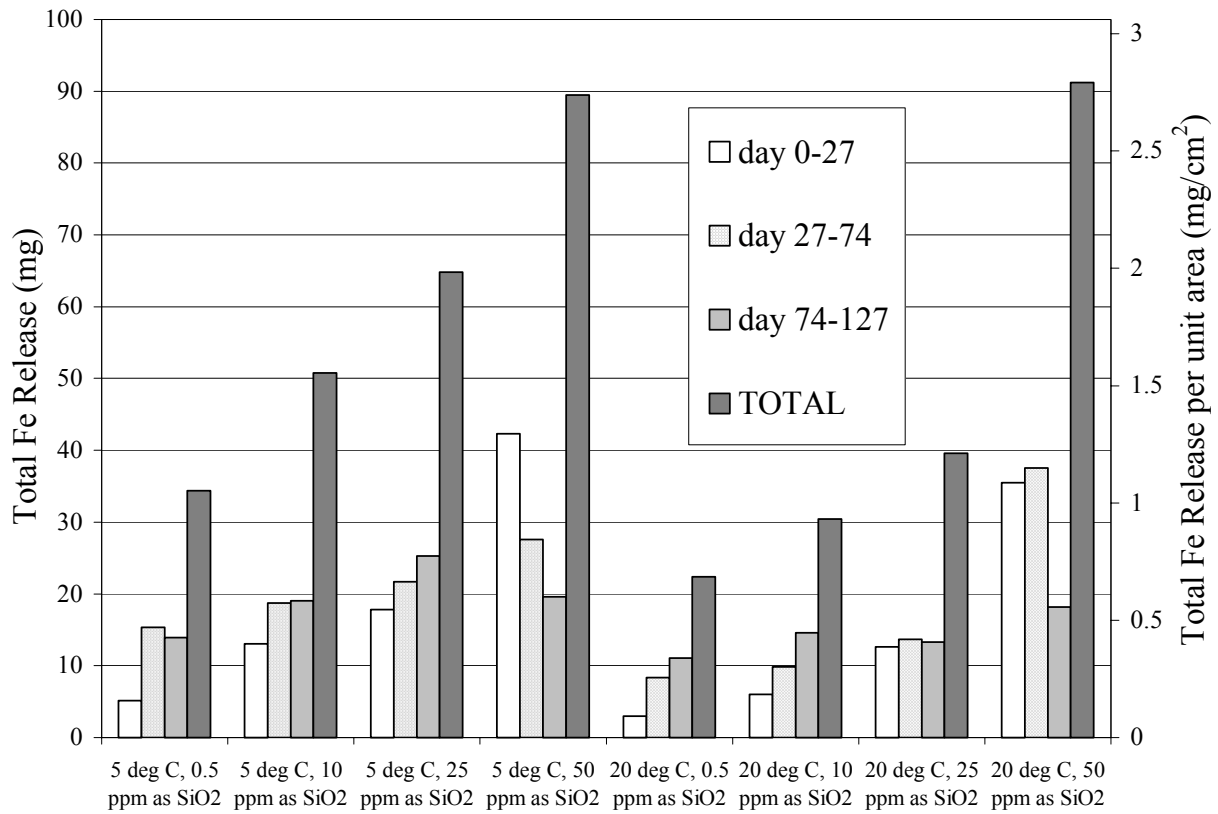


Figure 5-3: Total iron release in reactors at 5 and 20<sup>0</sup> C. Measured after water changes and at end of experiment.

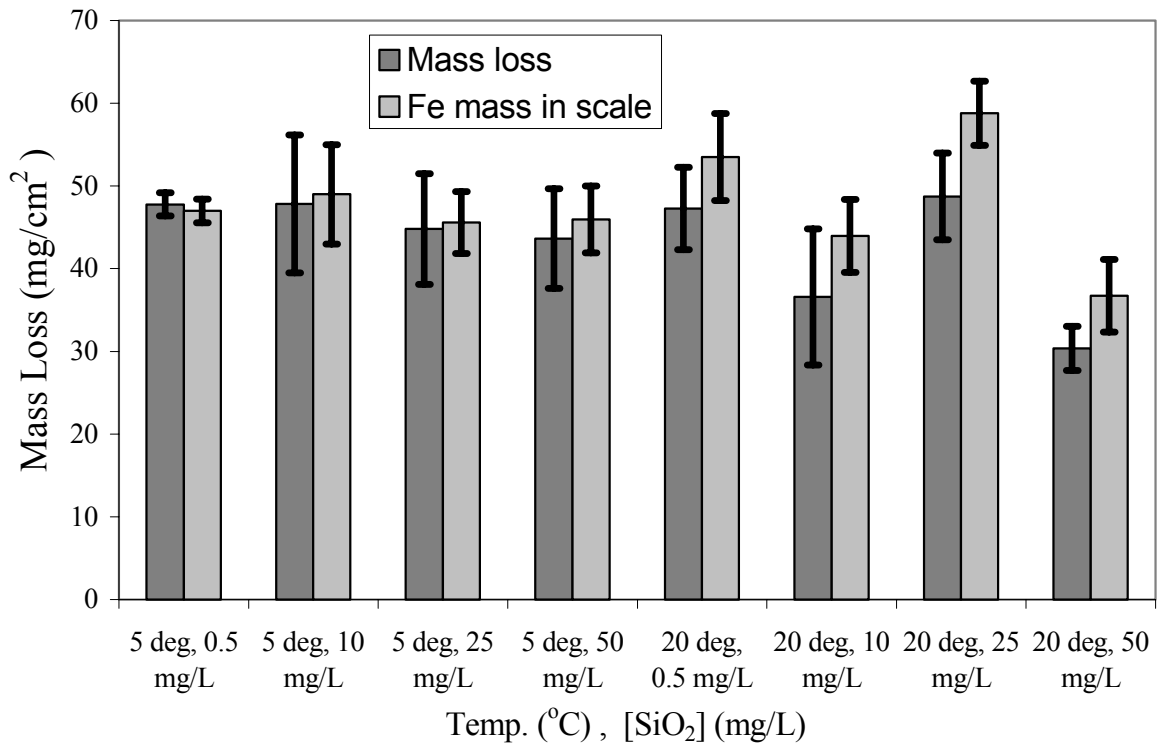


Figure 5-4: Iron coupon mass loss after 4 months. Error bars represent 95% confidence intervals.

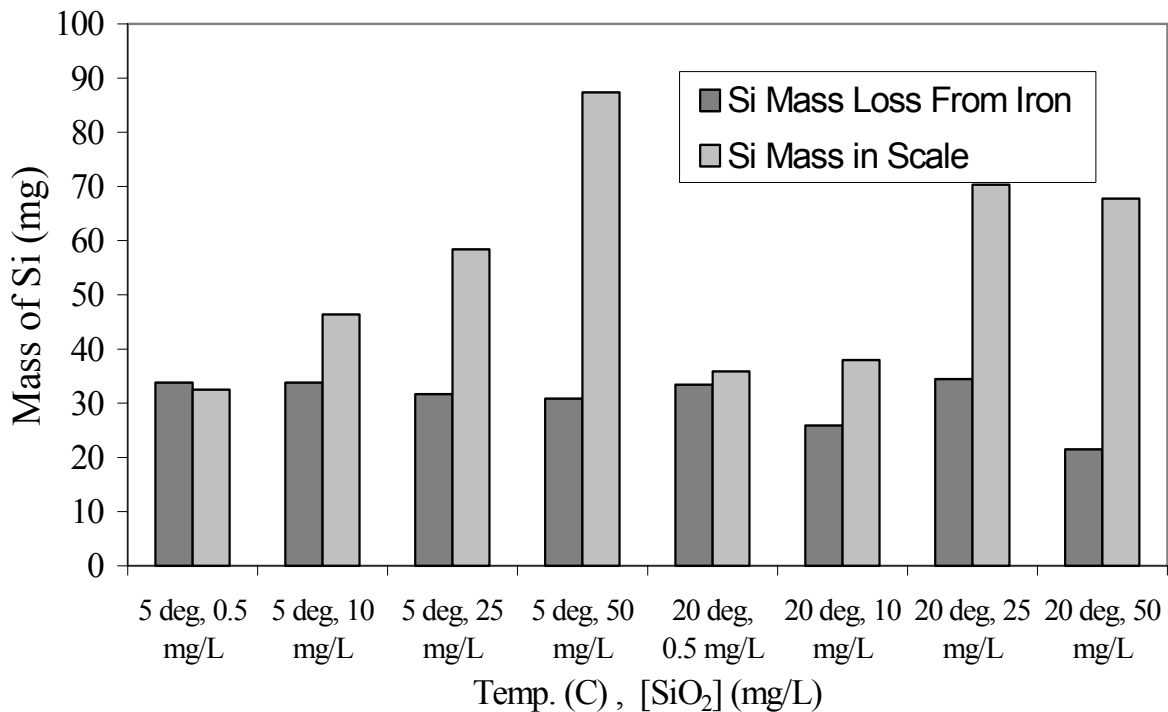


Figure 5-5: Silica loss from and incorporation in iron scale. Silica loss to the water assumed to be 2.5% of the total mass loss of the cast iron coupons.

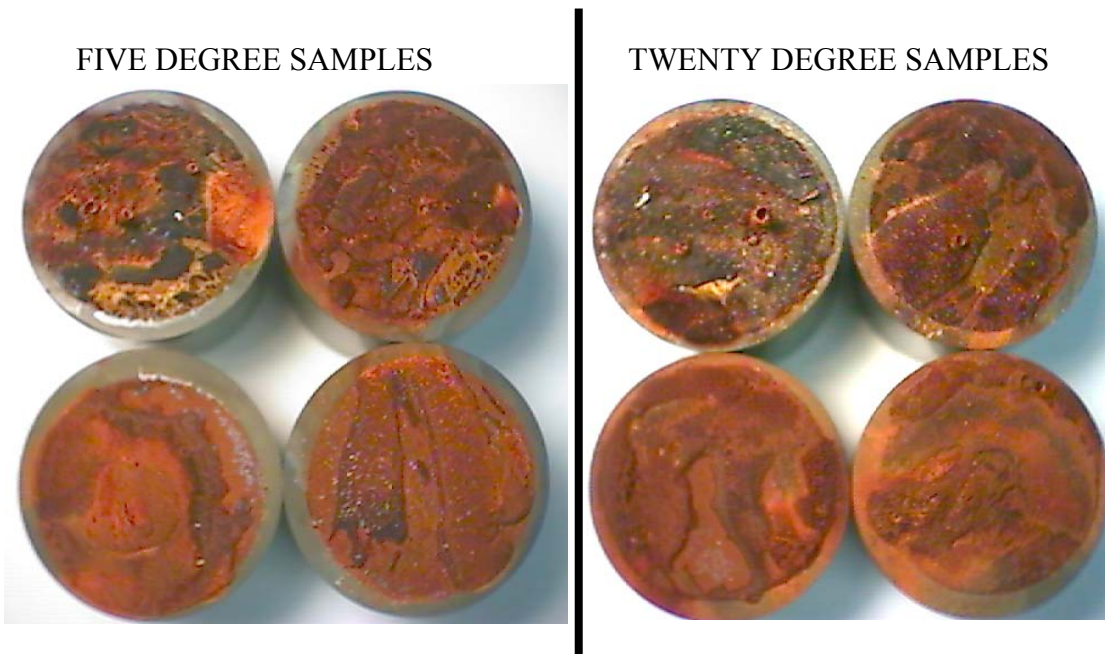


Figure 5-6: Representative corroded iron coupons after end of experiment. For both left and right pictures, from upper left and going clockwise: sample from 50, 25, 10, 0.5 mg/L silica reactor.

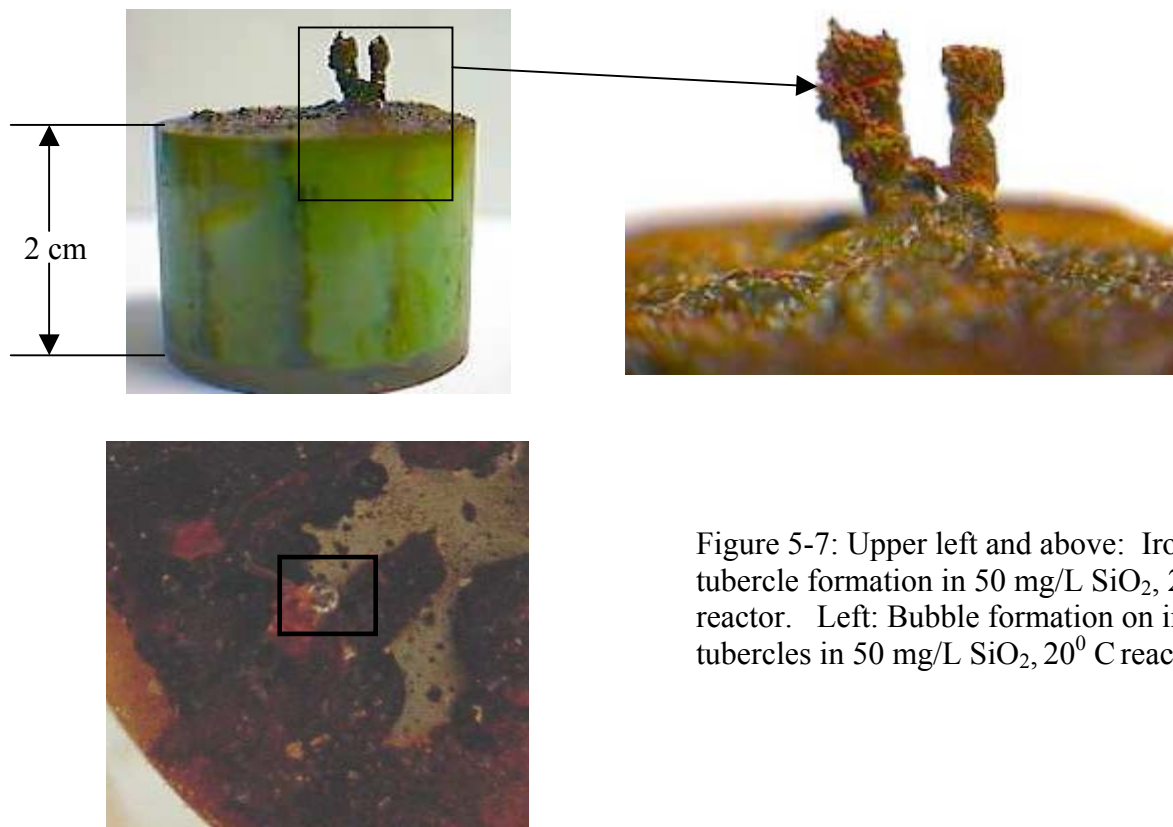


Figure 5-7: Upper left and above: Iron scale tubercle formation in 50 mg/L  $\text{SiO}_2$ ,  $20^\circ\text{C}$  reactor. Left: Bubble formation on iron tubercles in 50 mg/L  $\text{SiO}_2$ ,  $20^\circ\text{C}$  reactor.

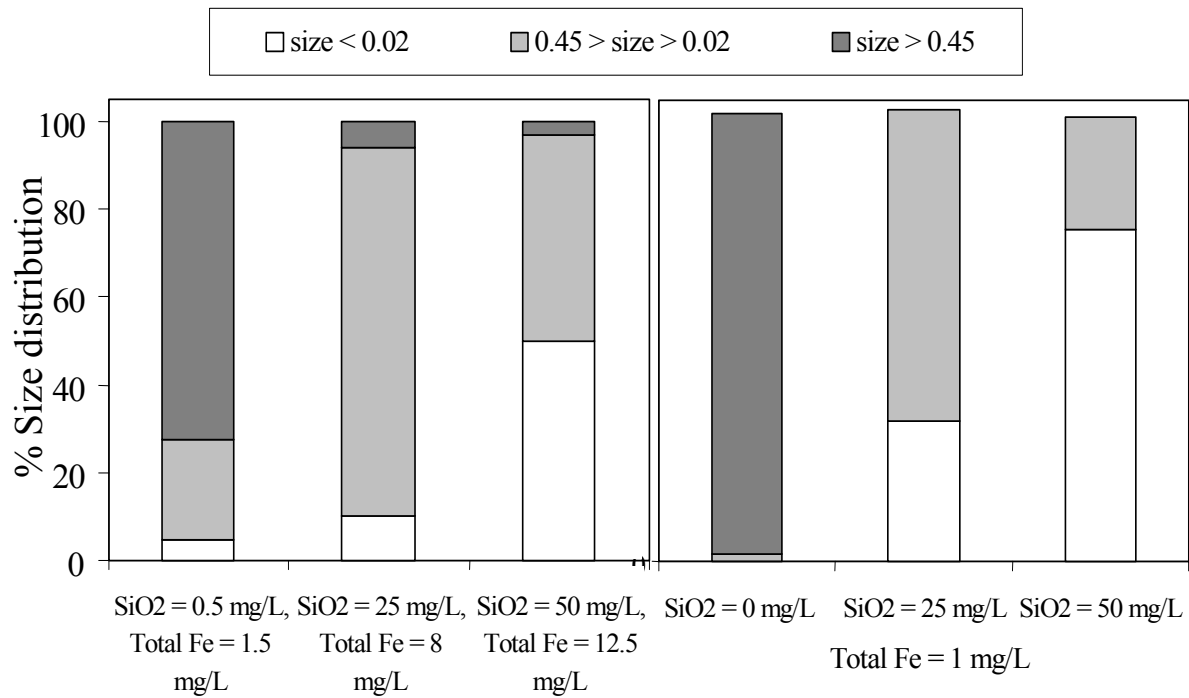


Figure 5-8: Particle size distribution. Sizes in micrometers. On left: Particles from 20<sup>0</sup> C reactors. On right: Particles formed after addition of 1 mg/L Fe<sup>+2</sup> to aerated water.

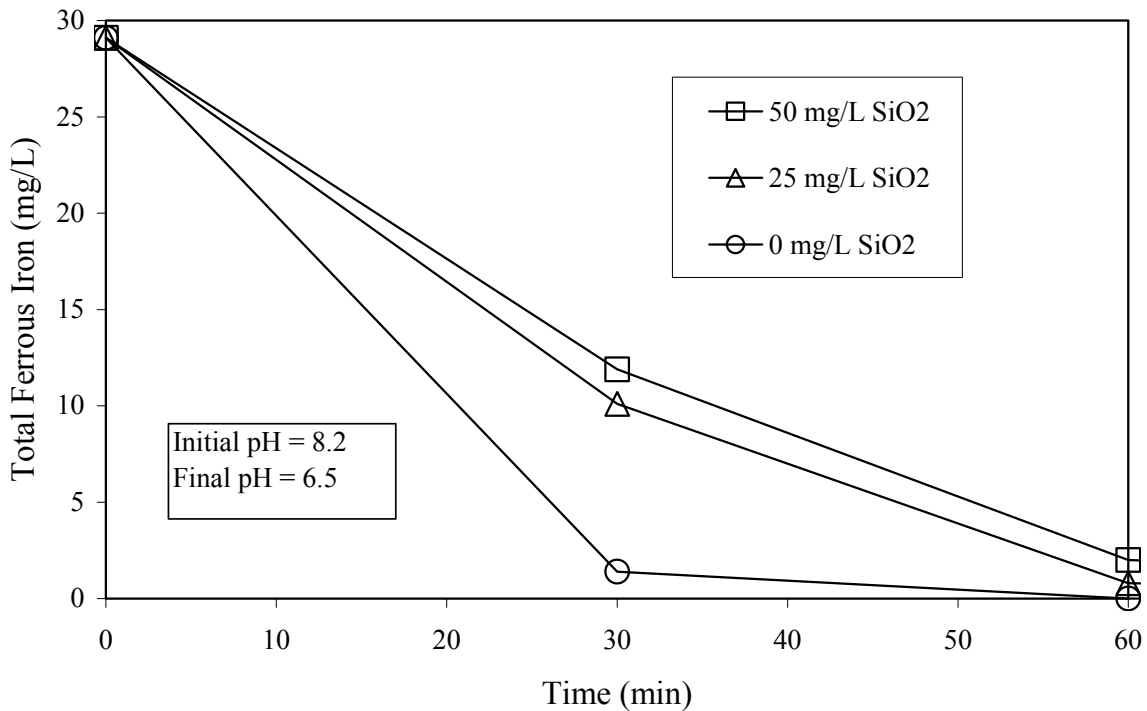


Figure 5-9: Ferrous oxidation under aerobic conditions in the presence of varying amounts of silica.

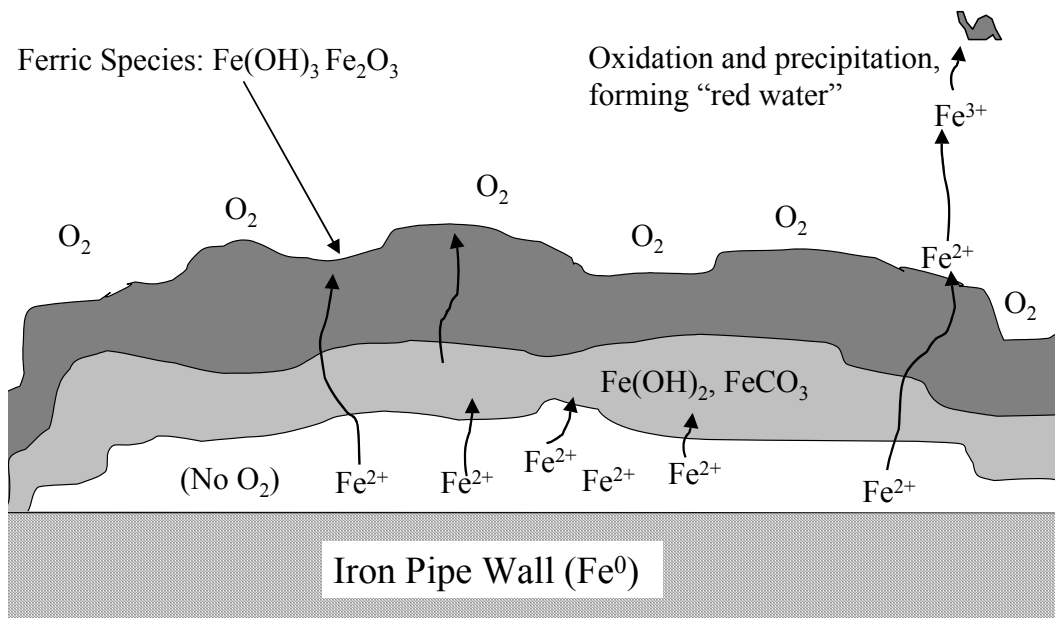


Figure 5-10. Diagram showing possible mechanism of iron release and "red water" formation. The rate of iron released to the water is a function of the amount of  $\text{Fe}^{2+}$  that is at the scale/water interface of an iron pipe.

## CHAPTER 6: SUMMARY OF KEY CONCLUSIONS

- There are no proven causes for pinhole leaks in residential plumbing, only hypotheses that are supported to varying degrees by scientific data, and some that are outright speculation. Pinhole leaks have never been produced in the laboratory under conditions that are scientifically reproducible.
- It is 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.
- An array of chemical, biological and electrochemical tests can shed light on the problem and assist efforts to find a solution. However, these tests require expertise and sometimes provide faulty guidance. Desktop studies of pinhole leak frequency and practices at nearby utilities can also serve as a valuable guide.
- Dosing of orthophosphate might solve the problem in at least some circumstances.
- Chlorine and aluminum solids together can enhance non-uniform corrosion of copper under both stagnant and flow conditions compared to either constituent alone.
- The concentration of chlorine is important in determining its effect on copper; lower doses appear to be beneficial compared to either no chlorine or higher chlorine when aluminum solids are present.
- Flow has an important impact on the corrosion potential of copper exposed to chlorine, or chlorine and aluminum solids at pH 8. Large jumps in potential ( $\approx 100$  mV) are observed when flow starts.
- The gradual increase in corrosion potential as copper is exposed to chlorine under alternating flow and stagnation experiments are likely indicative of a copper surface activating towards pitting.
- The effect of aluminum solids and chlorine in terms of copper pitting under constant flow conditions is most severe at pH 9 compared to lower values. Onset of pitting corrosion at pH

9 was evidenced by high corrosion rates, trends in corrosion potential indicative of pitting, and formation of mounds of corrosion byproducts on the copper surface after just 3 weeks.

- Utility practices in terms of coagulant selection, aluminum carryover, concrete lining, pH control and disinfectant dose needs to be reconsidered in light of the findings of this work. In particular, for copper corrosion, high pH values that reduce copper leaching to water can be expected to increase the likelihood of pitting, especially if aluminum deposits and  $\text{Cl}_2$  are also present.
- The orientation and differential heating of a copper pipe can have an effect on how much metal is released into the water due to temperature related changes in solubility and induced mixing or stability.
- Sustained temperature gradients lead to corrosion accelerating thermogalvanic currents, and may explain problems of excessive copper corrosion and copper release in some systems.
- It is anticipated that all metallic plumbing materials such as lead and iron would be affected similarly by temperature gradients.
- Silica impacts iron corrosion by increasing the concentration of particulate iron released to the water, increasing the extent of tuberculation, and decreasing long-term corrosion rates.
- Silica decreases the rate of ferrous oxidation in water and interferes with precipitation, factors that combine to increase the concentration of ferrous iron at the water-solution interface.
- Silica decreases particle size, and increases the likelihood of maintaining suspended iron in solution.
- Corrosion of iron via hydrogen evolution is significant even in well-mixed aerobic solutions. As utilities attempt to control iron corrosion, the assumption that the only cathodic reaction is oxygen reduction should be re-examined.

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