

INSIGHTS INTO NON-UNIFORM COPPER AND BRASS CORROSION IN POTABLE WATER SYSTEMS

Emily Allyn Sarver

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Dr. Marc Edwards, Committee Chair

Dr. Sean Corcoran, Member
Dr. Andrea Dietrich, Member
Dr. Gerald Luttrell, Member
Dr. Jeffrey Parks, Member

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ABSTRACT

Non-uniform corrosion of copper and brass in potable water systems poses both economic and environmental problems associated with premature plumbing failures and release of metals. With respect to copper pitting corrosion, it was found that forensic testing (i.e., in pipe-loops) is the only investigative technique that can closely mimic conditions found in real water systems and produce unambiguous results; and, if used in combination with electrochemical techniques, it may also provide some mechanistic insights into the pitting process. Using pipe-loops, it was demonstrated that copper pitting in aggressive water qualities (i.e., chlorinated, high pH and low alkalinity) is deterministic and reproducible. Additionally, the effects of various chemical and physical factors on pitting were investigated. Overall, increased flow velocity and frequency, increased chlorine residual and decreased hardness were found to accelerate pitting; whereas increased phosphate and silica were found to decelerate pitting.

Several mitigation strategies for copper pitting in aggressive water were further investigated, and experimental data were interpreted utilizing electrochemical theory to evaluate specific effects on the initiation and propagation phases of pitting. Surprisingly, it was found that decreased chlorine may delay pit initiation, however, even relatively low levels of chlorine may eventually initiate and propagate pits. Increased alkalinity appears to decelerate pit growth, but does not prevent pit initiation. NOM can delay pit initiation and propagation, although the potential for DBP formation in chlorinated waters makes inhibition by NOM an unfavorable alternative. At sufficient dosages, phosphate and silica corrosion inhibitors may completely stop pitting, consistent with the success of several field trials. At very low dosages, phosphate and silica may actually accelerate pinhole failures, so these inhibitors should not be under-dosed.

While brass alloys exist that can limit dezincification problems, they are not always utilized in potable water applications due to high costs, and so dezincification is a re-emerging issue in some countries, including the US. Little research has been conducted in the past several decades regarding the effects of water chemistry, and almost no work has addressed the roles of physical factors associated with real plumbing systems. Thus, a comprehensive review of these topics was conducted.

To better understand the effects of some factors associated with specific plumbing installations on dezincification and other brass corrosion types, a series of pipe-loop studies was carried out. It was confirmed that increased oxidant delivery rates to cathodic surfaces, either via increased oxidant concentration or increased flow velocity, can increase corrosion rates. Several key differences were observed with respect to corrosion of brass located in copper plumbing tube systems as opposed to plastic. When copper tubes contribute copper ions to water, brass corrosion becomes more selective for zinc; but if galvanic connections are made between the copper tubes and brass, selectivity for zinc is reduced while overall corrosion rates are accelerated. As opposed to copper tubing, plastic maintains oxidant (e.g., free chlorine) levels,

and may thereby increase brass corrosion and build-up of corrosion by-products. Finally, it was found that increased temperature can significantly increase lead leaching from brass.

Following recent outbreaks of brass dezincification failures, NSF/ANSI Standard 14 has been revised to require that all NSF 14-listed brass is dezincification resistant, as certified by satisfactory results from an accelerated test method (ISO 6509). Various brasses were tested using this method as well as a longer-term jar method utilizing real potable water. Results of the two tests were in good agreement with respect to dezincification, specifically; but some inconsistencies were observed with respect to uniform corrosion and lead leaching.

DEDICATION

For Pat and Steve...

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PREFACE

Non-uniform copper and brass corrosion can seriously impact the service life of potable water systems, producing leaks (e.g., copper pinholes) and/or burst failures (i.e., due to build-up dezincification corrosion deposits), and even leaching harmful metals (e.g., lead) to water. On top of the economic burdens associated with repairing and/or replacing failed plumbing components, and the environmental hazards associated with tap water contamination and water damage to infrastructure, outbreaks of non-uniform corrosion failures may lead to loss of confidence in the sustainability and safety of the potable water supply. Although electrochemical theories exist to generally explain non-uniform corrosion of both copper and brass, relatively little is known about the influences of many chemical and physical factors commonly encountered in potable water systems. Moreover, few laboratory studies have successfully reproduced these types of corrosion as they occur in practice, and the meaningfulness of many accelerated test methods is questionable.

The goals of the work presented herein were to better understand the nature of copper pitting and non-uniform brass corrosion in potable water systems. This was achieved by reviewing the literature on both topics, replicating the phenomena under realistic conditions (e.g., Figure P.1), evaluating the effects of various chemical and/or physical factors, and examining investigative techniques. Much of this work was funded by the Water Research Foundation (WRF) on project #4289 and/or the Copper Development Association.

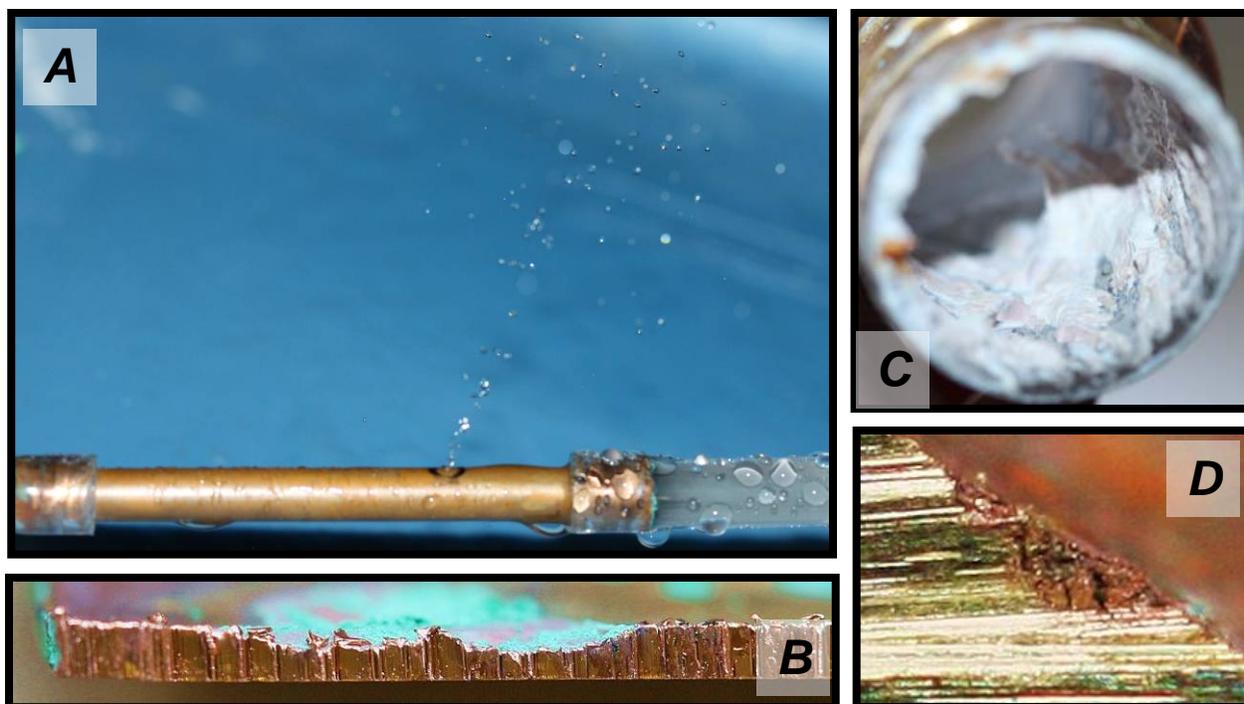


Figure P.1: Replication of copper pitting and brass dezincification phenomena in laboratory pipe-loop studies. *A* shows a fully-penetrating copper pinhole leak, *B* shows deep pits into copper tubing, *C* shows build-up of “meringue” dezincification corrosion deposits inside a brass component, and *D* shows plug-type dezincification penetrating into a brass fitting.

ORGANIZATION OF DISSERTATION AND ATTRIBUTIONS

This dissertation is composed of five manuscripts, each of which has been published, accepted for publication, or recently submitted to a peer-reviewed journal (as noted at the beginning of each chapter). In addition to the collaborative efforts of the author and her advisor, Dr. Marc Edwards, other researchers contributed to several of the manuscripts and are listed as co-authors as appropriate. The manuscripts are formatted according to the requirements of the journals to which they were submitted, and organized as follows:

- Chapter 1, “Copper Pitting in Chlorinated, High pH Potable Waters,” is a three-part paper that 1) highlights results from nearly a decade of studies at Virginia Tech, 2) examines strengths and limitations of various investigative techniques, and 3) presents recent research results which demonstrate that copper pitting is both deterministic and reproducible in certain

aggressive waters. Paolo Scardina, Caroline Nguyen and Rebecca Lattyak-Slabaugh contributed to experimental work, analyses and/or writing included in the first two parts of the paper, and Kara Dodson contributed to the third part.

- Chapter 2 is entitled “Mitigation of Copper Pitting Corrosion in Chlorinated, High pH, Low Alkalinity Potable Waters,” and presents results of small- and large-scale pipe-loop studies aimed at inhibiting pitting in aggressive water.
- Chapter 3 is a “Review of Brass Dezincification Corrosion in Potable Water Systems.” Yaofu Zhang contributed to both the review research efforts and writing of this paper.
- Chapter 4, “Effects of Flow, Galvanic Connections and Temperature on Corrosion of Brass Plumbing Devices,” presents results from three experiments conducted to assess the effects of site-specific conditions on brass dezincification and lead leaching.
- Chapter 5 is entitled “Comparison of Brass Dezincification Test Methods: Exposure to Real Water vs. ISO 6509,” and describes a comparative study between realistic and accelerated testing for dezincification susceptibility of brass alloys. Yaofu Zhang conducted the real-water testing and results analyses.

COMPLEMENTARY WORK

In addition to the manuscripts included in this dissertation, a full research report (for WRF project #4289) and four conference presentations complementary to this work were/will be completed on the topics of copper pitting and brass dezincification:

- Sarver, E.; Zhang, Y.; and Edwards, M. (draft final report submitted October, 2010; final report to be published 2011) Copper Pitting and Brass Dezincification: Chemical and Physical Effects. Water Research Foundation, Denver, CO.

- Sarver, E.; and Edwards, M. (November, 2009) *Understanding Dezincification Failures in Premise Plumbing Systems*. Water Quality and Technology Conference of the American Water Works Association, Seattle, WA.
- Sarver, E.; Dodson, K.; and Edwards, M. (June, 2010) *Effects of Water Chemistry and Some Physical Factors on Copper Pitting Corrosion in Potable Water Systems*. Annual Conference and Exhibit of the American Water Works Association, Chicago, IL.
- Dodson, K; Sarver, E.; and Edwards, M. (June, 2010) *Effects of Free Chlorine Residual and Potential Corrosion Inhibitors on Copper Pitting*. Annual Conference and Exhibit of the American Water Works Association, Chicago, IL.
- Sarver, E.; and Edwards, M. (accepted for November, 2010) *Effects of Flow, Galvanic Connections and Temperature on Brass Dezincification Corrosion in Potable Water Systems*. Water Quality and Technology Conference of the American Water Works Association, Savannah, GA.

CHAPTER 1: COPPER PITTING IN CHLORINATED, HIGH PH POTABLE WATERS

Emily Sarver, Kara Dodson, Paolo Scardina, Rebecca Lattyak-Slabaugh,

Marc Edwards and Caroline Nguyen

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ABSTRACT

Copper pitting corrosion in potable water systems poses economic and environmental problems associated with pinhole leaks. Reproducing precise conditions that create pinholes in the laboratory has proven very difficult; to date, “aggressive” water quality (i.e., chlorinated, high pH and also low alkalinity) is the only cause which has been replicated as it occurs in potable water systems. Pitting in this water type is accelerated with higher chlorine, flow velocities and durations, and is inhibited by high levels of silica and phosphate. While only forensic test (e.g., pipe-loop) results can be interpreted with complete confidence, numerous limitations of such testing might be overcome via complementary studies using sophisticated electrochemical methods once aggressive waters are identified. Under “worst-case” conditions, pipe-loops can reproducibly create pitting in relatively short times and on very short copper tubes.

INTRODUCTION

Pitting corrosion of copper tubing in potable water systems can produce fully-penetrating pinhole leaks and associated expenses for repair and/or replacement of plumbing and water-damaged materials or mold control (Edwards et al., 1994a; Lytle et al., 2008). While pitting failures are relatively rare on average, they may occur in outbreaks that severely impact particular communities or buildings (Edwards et al., 2004), and the total associated cost has been estimated at nearly \$1 billion annually in the U.S. (Scardina et al., 2008).

Development of simple and reliable techniques to study, understand and predict copper pitting problems is highly desirable, but major obstacles exist, not the least of which has been the difficulty in reproducing copper pitting in the laboratory as it occurs in practice. This is partly because pitting is believed to arise from a number of causes (Edwards et al., 1994a) including: “aggressive” water chemistries (Rushing, 2002), microbial activity (Cantor et al., 2006), erosion corrosion or cavitation (Coyne, 2009), surface anomalies in tubing (Smith et al., 1990), or poor installation (Meyers et al., 1994). There is really no way of reproducing and studying all causes in a simple test. To illustrate, aggressive water is the only suspected cause of copper pinholes proven in the laboratory under scientifically reproducible conditions. In 2002, it was first suggested that a combination of free chlorine, aluminum (Rushing et al., 2004) and possibly elevated pH (Rushing, 2002) may have contributed to pitting in a specific potable water in Maryland, (which also had relatively low alkalinity). In 2004, Marshall confirmed high pH as a critical factor for pitting of new copper in this water and produced multiple pinholes on a short length of copper tube during a year-long test (Marshall, 2004). This was the first time that a realistic, synthesized water had reproduced copper pitting as it was thought to occur in practice (Veazey, 2004). Previously, some practical testing had been successful in identifying important

factors contributing to pitting, like the role of chlorine (Fujii et al., 1984) or carbon films (Smith et al., 1990), but only by exposing copper to real waters already associated with pitting in the field. So, these hard-earned prior insights were gained without actually identifying a precise water chemistry that caused pitting.

Since the Rushing et al. (2004) and Marshall (2004) discovery of a chlorinated, high pH water recipe that caused copper pitting, substantive fundamental understanding has been developed by other researchers for this mechanism of pitting. For example, the work of Cong et al. (2009, 2010) has provided in-depth insights regarding pit initiation kinetics and susceptible chemistries. Also, Lytle et al. independently determined that high pH waters, with some chlorine and low alkalinity (but without aluminum) could create significant non-uniform corrosion and substantive pits (up to 20% wall penetration within 99 days) on Type M copper tubing. In the process, they better defined the range of what may be considered aggressive water chemistries (Lytle et al., 2008). Thus, much more is now understood about mechanisms and required levels of aluminum, alkalinity, chloride, sulfate and pH relative to copper pitting in potable waters.

The usefulness of various investigative techniques for future research and engineering analyses of pitting deserve careful consideration. Practicality of test methods (i.e., how closely they can represent real systems) and meaningfulness of experimental and/or in-situ data (i.e., how effectively they indicate pitting) are important issues that have largely gone undefined. Although no standard test exists to diagnose pitting across a wide range of water types, once an aggressive water is identified, it may be possible to narrow-in on influential factors, screen for effective inhibitors, and pinpoint constituents that accelerate pit initiation and propagation such that pitting could be avoided or mitigated. Upon identification of “worst-case” conditions, it may

even be possible to reproduce pitting on relatively short copper tubes – which would indicate that water chemistry-induced pitting is highly deterministic, as opposed to a statistical fluke.

Indeed, a variety of short-term tests have been proposed and utilized over the years which rely on electrochemical data to purportedly provide such insights (e.g., Duranceau et al. 2004, Nguyen 2005). While such tests were always of uncertain accuracy (i.e., results were never verified practically), they were justified given the high economic stakes involved, a general electrochemical basis or at least a theory for interpreting results, and the fact that better approaches were simply not available. Test methods capable of producing unambiguous, forensic evidence in the form of observable pits or pinhole leaks on copper are obviously useful, and pipe-loops may provide this capability while mimicking many conditions present in real systems (e.g., water chemistry and flow). But such methods require long test times and are cost intensive, and reproducibility is rarely assessed. Successful pipe-loop testing also often requires significant prior knowledge of conditions that induce pitting. For example, exhaustive attempts in the early 1990's to reproduce "blue water" pitting using water at treatment plant invariably failed; success was only achieved after moving the pipe-loop to remote parts of the distribution system without chlorine and using low flow frequency (Edwards et al., 2000). Conversely, initial attempts by Rushing (2002) and Marshall (2004) to reproduce serious copper pitting experienced in another situation, were completely unsuccessful with low chlorine and/or low flow frequency; and success was only achieved using higher chlorine residual and high flow frequency (Marshall, 2004). Another limitation of pipe-loops is that they do not independently provide mechanistic understanding that can be gained from an array of electrochemical techniques (e.g., Cong, 2009).

The specific objectives of this paper are: first, to briefly synthesize nearly a decade of practical pipe-loop research aimed at identifying chemical and physical factors that contribute to

aggressive copper pitting in high pH waters with relatively high chlorine and low alkalinity (Part 1); second, to review investigative techniques and discuss the limitations of each in studying copper pitting in this aggressive water type (Part 2); and, finally, to demonstrate that, once contributing factors and effective investigative techniques have been identified, copper pitting test work can be conducted reproducibly and provide definitive insights (Part 3).

MATERIALS AND METHODS

Part 1: A Decade of Pipe-loop Studies in Chlorinated, High pH Waters

Following published or publicized work by Rushing et al. and Marshall et al. (full results in Rushing, 2002; Marshall, 2004), a series of studies was conducted to identify chemical and physical factors contributing to rapid pitting of new copper in chlorinated, high pH, low alkalinity waters. Each study used variations on Marshall's (2004) synthesized water recipe (termed Marshall pitting water or MPW herein) that produced pinholes. Brief descriptions of materials and methods are below; complete details are in publicly available theses (Murray-Ramos, 2006; Lattyak, 2007; Custalow 2009).

Study by Murray-Ramos

Murray-Ramos (2006) conducted a 15-month pipe-loop study in the MPW to investigate the influence of common potable water constituents, including iron (as opposed to aluminum) solids, chloramine (as opposed to chlorine) disinfectant, natural organic matter (NOM), phosphate, chloride and sulfate. Loops were constructed identically, and included multiple plumbing materials (i.e., copper, brass, stainless steel and plastics).

Studies by Lattyak

Lattyak (2007) conducted two studies of copper pitting to investigate the roles of chemical inhibitors and flow velocity. In the former, Lattyak used the MPW with varying

amounts of phosphate, zinc phosphate and NOM – which were predicted to inhibit pitting. Pipe-loops had constant, relatively low flow velocities between 1.2-2.5 ft/s (0.4-0.7 m/s), and tests lasted 15 weeks. In the latter study, Lattyak again used the MPW in pipe-loops that each had a different velocity between 0.9-6.6 ft/s (0.3-2.0 m/s), and tests lasted four months.

Studies by Custalow

Custalow (2009) also utilized pipe-loops in two studies. One investigated impacts of several water constituents/parameters on copper pitting during a four week experiment. In individual loops with moderate velocity of 3 ft/s (0.9 m/s), six variations of the MPW were tested: 1) the exact MPW 2) without aluminum, 3) without aluminum and diluted 1:10 with deionized water, 4) without hardness, 5) with silica, and 6) with chloramine (instead of chlorine). The other study investigated the roles of flow velocity and tube wall thickness. In this eight-week study, the MPW was used in a matrix of pipe-loops with varying flow velocities between 0.7-11.2 ft/s (0.2-3.4 m/s) and nominal copper tube diameters (i.e., ¼”, ½” and ¾”).

Part 2: Examination of Various Investigative Techniques

In an extensive project to study monitoring techniques for non-uniform corrosion of copper piping, numerous electrochemical indicators and test methods that have been used to characterize copper pitting propensity were examined. Full details on materials and methods are included in the final project report (see Edwards et al., 2008b) and are not given here, but an overview is provided in the results section.

Part 3: Demonstration of Reproducibility and Deterministic Nature of Pitting

Testing in Part 3 of this work was carried out in small- and large-scale pipe-loops to demonstrate the reproducibility and deterministic nature of experimental results in several variations of MPW.

Small- and Large-scale Pipe-Loops

Small-scale testing was conducted in 30 L pipe-loops (Figure 1.1). Each contained one 3” (7.6 cm) length of ¼” (0.63 cm) diameter, thin-walled (0.014” in or 0.036 cm) copper tubing. Clear vinyl tubing was used to connect copper pipe sections to submersible, magnet-drive centrifugal pumps (polypropylene and stainless steel construction), which re-circulated water at a constant velocity of approximately 5.0 ft/s (1.5 m/s).

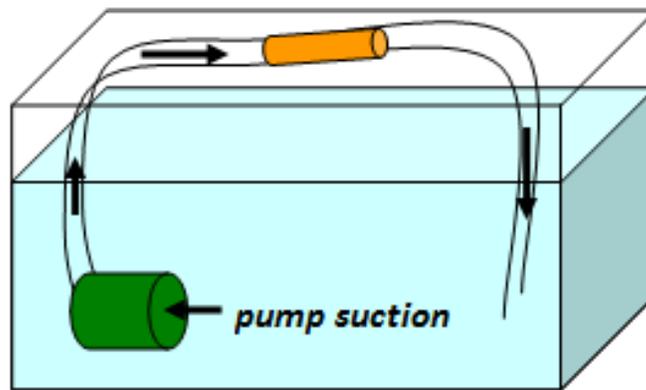


Figure 1.1: Experimental apparatus for small-scale triplicate testing; the flow velocity was about 5.0 ft/s (1.5 m/s) and direction is indicated by arrows.

Large-scale testing was conducted in 94 L pipe-loops (Figure 1.2), which were designed to more realistically represent a premise plumbing system and used off-the-shelf copper tube. All four copper sections (designated *T*, *1*, *2* and *3* in Figure 1.2) were physically separated with vinyl tubing, but were electrically connected via external copper wires. This allowed for electrochemical measurements by temporarily replacing the wires with a multi-meter. Vinyl tubing was used to connect copper to magnet-drive centrifugal recirculation pumps (polypropylene construction), which re-circulated water at a constant velocity of approximately 4.5 ft/s (1.3 m/s). Each pipe-loop included three 1’ (30.5 cm) lengths of ¾” (1.9 cm) diameter, Type M copper, which were oriented in-flow; and one 2” (5.1 cm) length of the same tubing located out-of-flow (i.e., dead-end “*T*” in Figure 1.2). This “differential flow” configuration practically represents a

plumbing system wherein one copper tube is removed from flow, while another experiences constant or frequent flow. Differential flow was expected to heighten corrosion activity in these tests via development of a concentration cell (i.e., lowered pH and chlorine levels, and build-up of high salt content in the stagnant *T* water as compared to the flowing bulk water).

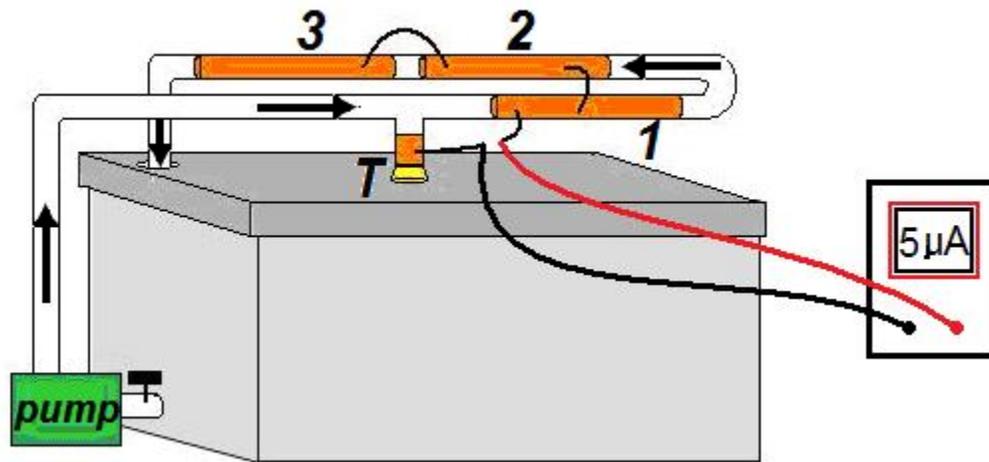


Figure 1.2: Experimental apparatus for large-scale duplicate testing; the flow velocity was about 4.5 ft/s (1.3 m/s) and direction is indicated by arrows.

All tests used C12200 copper and polypropylene plastic reservoirs that were closed to limit atmospheric influences on water quality (e.g., changes in alkalinity, temperature). Copper tubes were de-burred, rinsed, allowed to dry and weighed prior to assembling pipe-loops.

Water Quality

Four water qualities (Table 1.1) were tested in both small- and large-scale pipe-loops. The control water was identical to the MPW, except that it did not include aluminum solids. Based on other results from Part 1, the control and no hardness waters were expected to support pitting corrosion, and the waters with added phosphate or silica were expected to inhibit pitting. Triplicate testing was conducted in the small-scale pipe-loops for all conditions (12 tests total); duplicate tests were conducted in large-scale loops for the control and no hardness conditions, and single tests were conducted for the phosphate and silica conditions (6 tests total).

Table 1.1: Water quality conditions for small- and large-scale tests.

No.	Name	Description of Water Quality	Number of Tests	
			Small-scale	Large-scale
1	Control	pH 9.2, 4 mg/L free chlorine, 20 mg/L Cl ⁻ , 17 mg/L SO ₄ ²⁻ , 34 mg/L alkalinity as CaCO ₃	3	2
2	No hardness	all Ca replaced with Na	3	2
3	Phosphate	control water + 1.0 mg/L (as P) ortho-phosphate	3	1
4	Silica	control water + 5.0 mg/L (as Si) silica	3	1

Bulk water was changed weekly in small-scale pipe-loops for all conditions for the entire test period. It was changed weekly in large-scale loops during the first eight weeks of testing, and every other week (control and no hardness condition) or every third week (phosphate and silica conditions) thereafter. Due to relatively high chlorine decay rates in the aggressive control and no hardness waters, water was changed more frequently to maintain consistent chloride levels.

Test waters were made-up using deionized water and reagent-grade chemical salts, and were analyzed via ICP-MS for quality assurance. Free chlorine was added as NaOCl from a concentrated (6%) bleach stock. pH was adjusted using NaOH and HNO₃ stock solutions. Automatic feed systems were utilized in conjunction with manual adjustment (at least four times per week) to maintain targeted pH and chlorine residual. pH was measured using a double-junction Ag-AgCl electrode, and was generally maintained within 0.3 units of the target (i.e., 9.2 ± 0.3). Free chlorine residual was measured using a Hach Chlorine Pocket Colorimeter II, and was generally maintained within 0.5 mg/L of the target (i.e., 4.0 ± 0.5 mg/L).

Other Measurements

Changes in electrochemistry and chemistry were monitored in-situ during testing, and copper tubes were subject to forensic evaluation at the end of tests. Corrosion potential (E_{corr}) and “chlorine demand” of copper in each test were measured once per water change cycle. E_{corr} measurements were made using a Fluke 87 Series multi-meter (internal resistance <100 Ω) against a Beckman Coulter double-junction Ag-AgCl reference. One lead of the multimeter (i.e.,

ground) was in contact with the reference electrode (submerged in the bulk water), and the other was in contact with a copper tube. Chlorine demand (mg/day/cm²) is operationally defined as the mass addition rate of free chlorine required to maintain the target level in the bulk water, normalized for copper surface area exposed to water. Chlorine demand was calculated by Equation 1, and should theoretically be positively correlated with pitting.

$$\text{chlorine demand} = \frac{V_B(C_{Bi} - C_{Bf}) + V_F C_F + V_S C_S}{t(A)} \quad (\text{Eq. 1})$$

where t is elapsed time (days), A is copper surface area exposed to water (cm²), V_B is bulk water volume (L), C_{Bi} and C_{Bf} are initial and final bulk chlorine concentrations (mg/L), V_F and C_F are volume (L) and chlorine concentration (mg/L) of feed solution automatically added, and V_S and C_S are volume (L) and chlorine concentration (mg/L) of stock solution manually added.

Forensic examination of copper included quantitative characterization of pit depths and growth rates, and qualitative characterization of corrosion scales. At the conclusion of tests, tubes were removed from pipe-loops, allowed to dry, cut lengthwise and cleaned. Corrosion scales were removed chemically using Twinkle brand household copper cleaner in small-scale tests, and mechanically using a Dremel tool with a fine steel brush in large-scale tests. Tube wall thicknesses were measured with a digital, fine-tip Mitutoyo micrometer (0.001 mm resolution).

RESULTS AND DISCUSSION

Part 1: A Decade of Pipe-loop Studies in Chlorinated, High pH Waters

A decade of research helped elucidate the influence of some chemical and physical factors on rapid copper pitting in chlorinated, high pH, low alkalinity potable waters (Table 1.2).

This work began after an outbreak of pitting in homes served by a Maryland water utility (Edwards et al., 2004; Rushing et al., 2004). Pipe-loop tests were conducted wherein copper was exposed to synthesized water, representative of the problematic water as distributed from the

treatment plant (i.e., pH 8, 4 mg/L chlorine, 50 mg/L CaCO₃, 1 mg/L Al-Al(OH)₃). Initial tests used very infrequent flow at low velocity (1.1-2.2 ft/s) which, based on earlier work (Edwards et al., 1994a) was expected to maximize pitting. After eight months, no pits or pinhole leaks formed. But, non-uniform corrosion scales were observed, as was a characteristic rise in E_{corr} , which has been purported to indicate the onset of pitting (e.g., Pourbaix, 1972) (see *Part 2*). Further work suggested the tendency towards pitting could be dramatically increased at higher pH (Rushing, 2002).

Marshall (2004) then conducted pipe-loop tests in a similar water (i.e., the MPW), but at a higher pH (9.2 instead of 8.0). Although the problematic Maryland water was at pH 8.0 leaving the treatment plant, the pH rose in some areas affected by pitting due to contact with fresh cement in newly-lined water mains. Within a one-year test, Marshall produced twelve pinhole leaks on new copper tubes exposed to constant flow, but no pits at all occurred in situations with infrequent flow. Based on this work, it was suspected that in this water, the supply of chlorine to the copper surface was a key factor in initiating or propagating pits. Marshall (2004) also produced limited results demonstrating that new, polished copper (i.e., to remove any surface deposits or defects that may have been present from manufacturing) behaved similarly to new, un-polished copper. Thus, all further tests were conducted with the latter.

More pipe-loop studies in similar waters were then conducted. One long-term study using the MPW did not produce pinholes, but did produce very deep pits (i.e., greater than 25% wall penetration of Type M tube) in numerous test conditions, including one in which iron solids were substituted for aluminum solids (Murray-Ramos, 2006). Pitting was inhibited if chloramine was used in place of chlorine, or if phosphate or relatively high levels of NOM were added (Edwards et al., 2008a). Retrospective evaluation of the Murray-Ramos' study suggested that, amongst

other possibilities (e.g., presence of other piping materials), the reduced rate of pitting attack versus that observed by Marshall (2004) was due to a failure to maintain the chlorine residual at the target value of 4 mg/L throughout testing. Typically, chlorine was only adjusted to the target twice per week, and average chlorine levels were only about 0.75 mg/L.

Later work (Lattyak, 2007) used pipe-loops to examine the effects of potential pitting inhibitors in the MPW while maintaining chlorine at 4 mg/L via a chemical feed pump arrangement. This confirmed that phosphate and NOM could inhibit pitting corrosion of copper tubing, even when chlorine was maintained at very high levels. When phosphate inhibitor dosing was interrupted, pits formed rapidly, indicating that inhibitors must be dosed continuously to limit pitting in this water type. Furthermore, in Lattyak's control condition (without any inhibitor), pits penetrating about 50% of the (Type L) copper tube wall were observed after only 15 weeks of testing, reproducing the very high rate of attack observed by Marshall (2004) when chlorine was maintained at high levels.

In another study (Custalow, 2009) the influence of several chemical constituents was investigated. It confirmed the previous finding that chloramine (instead of chlorine) did not create pits, and demonstrated that high levels of silica could serve as a natural pitting inhibitor. This work also confirmed a hypothesis of Marshall (2004) and results of Lytle et al. (2008) that the presence of aluminum solids is not necessary to catalyze pitting if pH is above about 8.5.

Table 1.2: Summary of pipe-loop studies of copper pitting corrosion in high pH, high chlorine potable waters.

Author(s)	Test Conditions			Time to Pitting/ Pinholes	Major Findings/Comments
	Water Quality	Materials	Flow		
Rushing (2004)	pH 8; 4 mg/L Cl ₂ [†] ; 1 mg/L Al [‡]	1' lengths, ¾" diam., Type L	low velocity (1.1-2.2 ft/s); primarily infrequent and intermittent	<ul style="list-style-type: none"> No pitting or pinholes. Non-uniform scale formation and variable E_{corr} suggested pitting was activated. 	<ul style="list-style-type: none"> E_{corr} rise induced during intermittent flow (vs. quiescence) may be due to increased Cl₂[†] at copper surface. Relatively low pH and/or intermittent flow may have prevented pit initiation.
Marshall (2004)	pH 9.2; 4 mg/L Cl ₂ [†] ; 2 mg/L Al [‡]	1' lengths, ¾" diam., Type M	low velocity (0.9-1.9 ft/s); varying flow frequency between tests	<ul style="list-style-type: none"> Within 1 year, 12 pinholes formed under constant flow. Pits penetrating 80% of pipe formed under frequent flow. 	<ul style="list-style-type: none"> High pH, high chlorine water with Al can unambiguously cause pitting of copper pipes. Constant flow led to higher pitting propensity and E_{corr} than constant stagnation or infrequent flow.
Murray-Ramos (2006)	pH 9.2; <1 mg/L Cl ₂ [†] ; 2 mg/L Al [‡] ; varied other constituents	3' lengths; ½" diam., Types K, L, M; also other materials	high then low velocity (8 ft/s for first 2 months, 2 ft/s after); constant	<ul style="list-style-type: none"> After 15 months, significant pitting occurred in control and other conditions with 4 mg/L Cl₂[†] and no inhibitors. 	<ul style="list-style-type: none"> Maintenance of high pH and Cl₂[†] may be necessary to pit propagation. Fe solids appeared to render water more aggressive than Al.
Lattyak (2007) – Exp. 1	pH 9.2; 4 mg/L Cl ₂ [†] ; 2 mg/L Al [‡]	1' lengths, ¾" diam., Type L	velocity varied between tests (0.9-6.6 ft/s); constant	<ul style="list-style-type: none"> After 4 months, pits penetrating 43% of pipe (2.8 ft/s) and 72% of pipe (6.6 ft/s). 	<ul style="list-style-type: none"> Pitting propensity increased with flow velocity. “Flow electrification” phenomenon observed; Electrification most intense at moderate velocity.
Lattyak (2007) – Exp. 2	pH 9.2; 4 mg/L Cl ₂ [†] ; 2 mg/L Al [‡] ; varied inhibitors dosages	2" lengths, ¾" and ½" diam., Type L	low velocity (1.2-2.5 ft/s, depending on pipe size); constant	<ul style="list-style-type: none"> After 3.5 months, pits penetrating 50% of pipe produced in control (no inhibitor). 	<ul style="list-style-type: none"> Pitting propensity dramatically reduced by PO₄ and Zn-PO₄ inhibitors. Upon stopping inhibitor dosing, shallow pits formed on pipes previously subjected to inhibitors.
Custalow (2009) – Exp. 1	pH 9.2; 4 mg/L Cl ₂ [†] ; 2 mg/L Al [‡]	1' lengths, ¾", ½", and ¼" diam., Type L	low to high velocity (0.7-11.2 ft/s) ^{‡‡} ; constant	<ul style="list-style-type: none"> Within 8 weeks, 2 pinhole leaks formed on ¼" tubing subjected to highest flow. 	<ul style="list-style-type: none"> Pitting propensity increased with flow velocity.
Custalow (2009) – Exp. 2	pH 9.2; 4 mg/L Cl ₂ [†] ; 2 mg/L Al [‡] ; varied other constituents	2" lengths, ½" diam., Type K	moderate velocity (3.0 ft/s); constant	<ul style="list-style-type: none"> After 4 weeks, significant pitting in conditions without Al. 	<ul style="list-style-type: none"> Al not necessary to initiate pitting at pH 9.2 with high Cl₂. Si and chloramine inhibited electrochemical activity and pitting of copper.

[†]Cl₂ = free chlorine residual; [‡]Al = aluminum solids as Al(OH)₃; ^{††}refrigerator tube; ^{‡‡}each loop had unique velocity/pipe diameter combination

Custalow (2009) and Lattyak (2007) additionally showed that pitting propensity increased with water flow velocity in the MPW. After just four months of testing, Lattyak observed pits penetrating 72% of the pipe wall at 6.6 ft/s (2.0 m/s), whereas pits penetrated 43% of the wall at 2.8 ft/s (0.9 m/s); no pits at all were observed when velocity was at or below 1.6 ft/s (0.5 m/s). Custalow found that maximum pit depth increased with flow velocity for a given tube diameter, but conclusions could not be drawn regarding the influence of tube wall thickness on pitting rate.

The above results represent substantive advances in understanding how rapid pitting can occur in chlorinated, high pH, low alkalinity waters.

Part 2: Examination of Various Investigative Techniques

Investigative techniques that have been used to study or monitor copper pitting corrosion include collection of electrochemical, chemical and physical data believed to correlate with the onset and/or progress of pitting. The basis for each technique is discussed below, as are advantages and disadvantages (Table 1.3). In this paper, techniques are classified as either *electrochemical* or *forensic*, but in practice there is frequently overlap between data types and experimental set-ups depending on research goals. Additional details related to this research are provided elsewhere (Edwards et al., 2008b).

Table 1.3: Summary of investigative techniques commonly used to characterize copper pitting propensity.

Description	Advantages	Disadvantages
Electrochemical Techniques		
<p>Corrosion Potential (E_{corr}), Corrosion Current (I), Electrochemical Noise (ECN) Measure electrochemical activity/fluctuations in activity of copper surface and attempt to interpret type and extent of corrosion.</p>	<ul style="list-style-type: none"> • Inexpensive, non-destructive and easy to use. Provides in-situ data that can be tracked over time. • Can be used in conjunction with most any test apparatus. 	<ul style="list-style-type: none"> • Trends may be misinterpreted without forensic data for verification. • May be influenced by oxidant levels and/or fluid flow. • Data may vary between samples exposed to identical conditions. • Noise in E_{corr} and I may be conflicting.
<p>Electrolytic and Galvanic Macro-Cells Three electrode apparatuses with copper anodes; external power source initiates/drives pitting in most cases.</p>	<ul style="list-style-type: none"> • Inexpensive and easy to use. • May provide short-term results. • If external power source not used, capable of better representing cathodic half-reaction of pitting. 	<ul style="list-style-type: none"> • If external power source is used, only provides insight into anodic half-reaction of pitting. • Pits may differ mechanistically from those formed under practical conditions. • Apparatuses not representative of geometry/physio-chemical conditions in real systems.
<p>Coupled Multi-Electrode Arrays (CMEA) and Pit Wires Macro-cell apparatuses in which copper wire tips are used to simulate pits; external power source may or may not be used.</p>	<ul style="list-style-type: none"> • Inexpensive and easy to use, depending on analytical methods. • May provide short-term results. • Can interrogate suspected pit sites. 	<ul style="list-style-type: none"> • Large variations may exist in performance between wires manufactured/stored/maintained identically. • May be difficult to detect small corrosion currents. • May not provide adequate representation of geometry/physio-chemical conditions in real systems.
Forensic Techniques		
<p>Forensic Analyses Measure physical and/or chemical changes in copper samples, and sometimes water.</p>	<ul style="list-style-type: none"> • Only analysis proven capable of confirming copper pitting corrosion in potable water. 	<ul style="list-style-type: none"> • Cannot often be done in-situ (with exception of bulk water analysis). • Analysis may be destructive to samples, time intensive.
<p>Coupons and Pipe-loops Variable apparatus configurations with small copper samples and/or pipes exposed to water(s) of interest.</p>	<ul style="list-style-type: none"> • Capable of most closely representing real potable water systems. • May provide forensic evidence. • Flexibility in experimental design. 	<ul style="list-style-type: none"> • May require long test durations to produce pitting/pinholes • Experimental maintenance may be time/labor intensive. • Reproducibility of results unconfirmed to date.

Electrochemical Techniques

Electrochemical techniques have been widely applied to investigate pitting propensity, including a range of test methods that rely on measurement of electrochemical activity of copper exposed to a water supply of interest. Depending on the experimental apparatus, corrosion current (I) data between paired copper samples may be obtained via use of a zero-resistance ammeter (ZRA), and E_{corr} can be determined by measuring the voltage between the exposed copper and a reference electrode (e.g., Ag-AgCl or calomel). E_{corr} reflects the balance of oxidation-reduction reactions at the copper surface. In theory, if the cathodic reaction rate is accelerated (or the anodic reaction rate is slowed), E_{corr} will rise to reflect a new steady state condition. This is expected in cases where pitting occurs via large cathode to anode surface area ratios. Conversely, if the anodic reaction rate is accelerated (or the cathodic reaction rate is slowed), corrosion may tend to be more uniform and E_{corr} should fall or remain relatively stable.

E_{corr} rise. Pourbaix (1972) first noted that, for certain waters, if new copper was placed in water that did not result in pitting, E_{corr} would typically rise to less than 100 mV after a few days and then stabilize. However, in waters that supported pitting in practice, E_{corr} would rise over a period of months to a much higher critical value (often termed E_{pit}) in experiments, at which point pits were thought to initiate on the copper samples. Subsequent authors have noted similar trends in copper pitting research (Edwards et al., 1993; Rushing, 2002), and have confirmed that E_{corr} rise does indicate onset of pitting in chlorinated high pH, low alkalinity waters (Cong, 2009). However, the relationship between rising E_{corr} and pitting corrosion is largely unproven for other types of pitting. For example, studies of E_{corr} in a sulfide-containing water suspected to cause pitting strongly suggested that falling (not rising) E_{corr} might be a better indicator of pitting activity (Edwards et al., 2008b). Testing may also require long durations before meaningful

insights are obtained under realistic conditions. Also, normal flow variations have been observed to influence E_{corr} rise data (Rushing, 2002). Despite these limitations, E_{corr} data collection is relatively inexpensive, simple, and non-destructive, and may provide useful information in combination with other methods or if prior knowledge exists about pitting in a given water.

Electrochemical Noise. Electrochemical noise (ECN) has also been used to gather insights into copper pitting (e.g., Smith et al., 1990) – though its general usefulness is somewhat speculative (Edwards et al., 2008b). ECN refers to the intensity of variations from the statistical mean value of E_{corr} on a copper surface or measurements of current (I) flowing between two coupled sections of copper. The general idea is that a greater variation in I and/or E_{corr} data for a given water, the greater the likelihood of non-uniform corrosion (ASTM G199-09).

ECN data collection shares many of the advantages of E_{corr} (e.g., inexpensive, non-destructive) and has been utilized to track corrosion processes since the late 1960's (Iverson, 1968). It has recently gained popularity for assessing pitting corrosion (e.g., Smith et al., 1990; Legat et al., 1995), and was most convincingly demonstrated for this purpose by Smith et al. (1990) during an investigation of carbon residues on copper pitting propensity. But, in a follow-up study, Sandenbergh et al. (1996) reported that the ECN technique could give faulty insights into pitting depending on physical exposure conditions. Specifically, flowing conditions resulted in increased noise and spurious conclusions. This problem was later confirmed by Rushing et al. (2004), who suggested that large variations in E_{corr} were directly attributable to varying concentrations of chlorine at the copper surface during intermittent flow events. The net result of this and other analysis raised concerns as to whether ECN actually reflects pitting reactions indirectly, or whether it simply reflects changes in surface potential due to changing solution chemistry (e.g., chlorine levels in the pipe) or other physiochemical conditions triggered by flow.

Electrochemical Cells. A variety of set-ups may be used to collect electrochemical data to investigate copper pitting. Electrolytic cells are simple, three-electrode systems (working copper electrode, counter electrode and reference electrode) immersed in a test solution. In a “fixed anodic potential” test, the voltage of the copper is held constant, and a rising current over time is believed to indicate that a water will support pitting corrosion (e.g., Edwards et al., 1994b). In a “cyclic voltammetry” test, the voltage is systematically varied – applied first in one direction, and then in the reverse direction – and a current response which traces a clockwise loop when plotted against applied voltage is believed to indicate pitting (Singh et al., 1992). Both test types are potentially useful in classifying waters that might form protective pit caps (or tubercles), which are thought to be essential to pit propagation; but, used in isolation, neither provides insights to the cathodic reaction(s), which may control the pitting rate. To study both anodic and cathodic reactions, a combination of electrochemical methods is required.

Galvanic macro-cells differ from electrolytic cells in that both the working and counter electrodes are copper (as in a copper plumbing system). They are electrically connected but physically separated, allowing for measurement of I between the electrodes (in addition to E_{corr}). Differential anodic and cathodic environments can also be simulated by subjecting the anode and cathode to waters representative of the pit and bulk water, respectively (e.g., Mattsson et al., 1968; Singh et al., 1992). It is thought that, in waters which support pitting, I should increase or remain stable; but in waters which “kill” pits, I should decrease rapidly. Mattsson et al. (1968) suggested a physiochemical explanation for this: in the former condition, tubercles are porous, allowing ion transport, and thus formation and propagation of a concentration cell to drive pitting. But, in the latter, tubercles are highly resistant and of low porosity, limiting pit propagation.

Although external voltage application is not inherently necessary for galvanic macro-cell tests, it – or other means of artificial pit initiation – has typically been used (e.g., Singh et al., 1992). This, again, reflects the fact that until very recently (i.e., until the Marshall, 2004 work) it was not understood how to reproduce pitting in the laboratory as it could occur in the field. Since artificial pit initiation may be mechanistically different than natural formation, it was always understood that the the macro-cell testing might not be realistic.

Coupled multi-electrode arrays (CMEA) and pit wire apparatuses present two more test methods for investigating copper pitting. They represent more realistic modifications of galvanic macro-cells, in which one or more wire tips may represent a pit site. CMEA's are designed to represent a planar surface, like a pipe wall, and consist of multiple (i.e., tens to hundreds) coupled copper wires – of which only the tips are exposed. Electrochemical activity between temporarily disconnected wires can be monitored using a ZRA. Theoretically, in waters which support pitting, only a small number of wire tips should become anodic (i.e., the pits), while all others become cathodic (i.e., the large cathodic surfaces). The pitting propensity is interpreted based on the magnitude of I between the anodes and cathodes; higher I should indicate higher propensity. In waters which do not support non-uniform corrosion, about the same number of wire tips are expected to become anodic as those that become cathodic. Artificial voltages may be applied to CMEA's to initiate or drive corrosion, as was the case in their early use for copper pitting studies (e.g., Ansuini, 1991). However, Cong et al. (2010) recently conducted a matrix of copper pitting studies using much more sophisticated CMEA's which were allowed to corrode naturally in the MPW. In addition to surveying the dependence of pitting propensity of potable waters on pH and other chemical parameters, this work also highlights several advantages of the CMEA method, including the ability to interrogate individual electrodes (i.e., wires).

Pit wire apparatuses are a hybrid between a CMEA and galvanic macro-cell. They consist of one or more copper wires electrically connected to a larger copper cathode (e.g., a tube or plate). The surface area ratio between the pit wire(s) and large cathode is designed to better represent the geometry of a real system, and tests allow simulation of differential environments (see above). While an external power source could be utilized to initiate corrosion on the pit wire, the apparatus was designed and tested by Nguyen (2005) to allow for natural corrosion. A major advantage of this method is that if a pit could be grown on the wire tip, tracking I could provide a direct measurement of copper pitting under conditions realistic conditions, thus pinpointing the time and circumstances surrounding pit initiation. However, this approach was not effective when tested in a range of pitting and non-pitting waters (Edwards et al., 2008b).

Forensic Techniques

Forensic techniques rely on direct evidence of pitting corrosion: specifically, the formation of pits or pinholes on copper samples or "coupons" exposed to a water supply of interest (ASTM G46 and ASTM D2688-83). Compared to electrochemical techniques in isolation, results can be unambiguous, but a major drawback is that long term exposures may be required to obtain meaningful results. Various equipment (e.g., fine-tip micrometer, SEM) can be used after exposure to quantify corrosion characteristics including pit depths, pit density and/or location on the copper sample, pit geometry, total weight change of the sample, scale mineralization and/or characterization of uniformity, and tubercle mineralization and geometry. Lytle et al. (2008, 2010) have recently illustrated the usefulness of this approach in characterizing pitting in both laboratory and field testing.

Coupon test methods provide flexibility in the exact type of copper sample to be used (e.g., flat "plate" samples or short lengths of tubing), and exposure conditions. Both simple jar

tests (e.g., Rushing et al., 2004) as well as pipe-loop apparatuses (e.g., Marshall, 2004; Lytle et al., 2008) can be used, and the latter has the advantage of reproducing hydraulics in actual pipes. The oxidation and reduction reactions are allowed to proceed naturally on the copper samples, and coupon and pipe-loop tests are typically conducive to in-situ collection of electrochemical data (e.g., I or E_{corr}) or incorporation of CMEA's, which might provide additional insights.

To perform coupon or pipe-loop tests, bulk water is generally changed via a dump-and-fill protocol on a pre-determined schedule in order to maintain targeted water quality (e.g., Lytle et al., 2008), and various monitoring techniques can also be utilized to this end (e.g., automatic pH and chlorine adjustment via chemical feeds). Chemical analyses of bulk water can aid in mass balances on various constituents including copper, oxidants (i.e., chlorine or dissolved oxygen), and common scale constituents (e.g., calcium, chloride, sulfate), and in monitoring microbiological activity. Furthermore, pit water analysis can provide information on the local environment (e.g., pH, salt concentrations) developed beneath a tubercle, which may govern the rate of pit propagation (Pourbaix et al., 1972; Lytle et al., 2010).

The Case for Pipe-Loops

Considering all of the above approaches in a multi-year comparative study, it has been concluded that, at present, indicators relying solely on electrochemical data cannot be used with confidence over a wide range of practical conditions (Edwards et al. 2008b). Moreover, coupon and/or pipe-loop tests appear to be the only reliable means of obtaining clear and confident insights to pitting trends, since they have the capability to produce tangible evidence of the corrosion. Thus, conventional electrochemical measurements (e.g., E_{corr} rise, ECN) can only be interpreted with confidence in conjunction with complementary forensic data. While they did

not demonstrate problems with electrochemical measures, Lytle et al. (2008) also concluded that pipe-loop tests are effective in evaluating pitting corrosion in aggressive waters.

Despite clear advantages over electrochemical methods in isolation, it should be noted that pipe-loops have significant limitations. They do not provide mechanistic understanding of initiation and propagation pitting steps, as do more sophisticated CMEA's when pitting occurs (e.g., Cong, 2009). Also, to realistically reproduce pitting, exposure must include both flow and chemical conditions that cause pitting in the field. Meeting this requirement has not been straightforward, as demonstrated by numerous historical pipe-loop test failures; so copper pitting in some situations has been described as a *random* process (Farooqi, 2006) that perhaps requires extraordinary lengths of tubing to replicate. To illustrate, in one distribution system plagued by copper pinholes, it was estimated that about 0.04 leaks occurred per 100 m of copper tubing (1 leak per 2.5 km) (Edwards et al., 2004). If this directly translated to a statistical likelihood of reproducing pits in a pipe-loop, there would be virtually no chance of recreating pitting on a few feet of tubing. Conversely, if copper pitting was actually *deterministic*, caused by specific combinations of water chemistry and flow patterns present in just a sub-set of premises in a distribution system, identifying and testing these conditions may sometimes be possible using just a few inches of tubing (provided that the tube length is not so short as to limit cathodic current). The next section explores the hypotheses that pitting is deterministic in certain chlorinated, high pH, low alkalinity waters, and that operating a pipe-loop under worst-case conditions can create rapid and reproducible pitting.

Part 3: Demonstration of Reproducibility and Deterministic Nature of Pitting

Results of small- and large-scale pipe-loop testing in the four test waters (Table 1.1) indicate that forensic, electrochemical and chemical data can be highly reproducible (Table 1.4). Small-scale triplicate tests were run simultaneously, whereas large-scale duplicate tests (control and no hardness only) were run in two sets (i.e., LX-1 followed by LX-2 tests). During the second run, a building power outage was scheduled, which would have significantly affected test operation and maintenance, so these tests were concluded several weeks prematurely. While differential flow in the large-scale tests did produce some differential concentration cells as indicated by water chemistry (e.g., locally lower pH and chlorine concentrations within the stagnant *T* water) and electrochemistry (i.e., anodic corrosion currents on the *T* vs. in-flow copper), significant pitting only occurred on sections of copper exposed to flow. Hence, subsequent results and discussion are limited to copper exposed to flow.

The control and no hardness waters produced severe pitting and fully-penetrating pinhole leaks (i.e., 100% wall penetration) on copper in both small- and large-scale tests. In contrast, waters with added phosphate or silica largely inhibited pitting corrosion. More specifically, the time-to-first leak (i.e., number of days a test was run until a pinhole failure occurred) was shortest for the control and no hardness conditions, and pinhole leaks were not observed for the phosphate or silica conditions during testing. Inhibition of copper pitting in similar waters by phosphate was also reported by others (e.g., Marshall et al., 2006; Lytle et al., 2008).

Table 1.4: Summary of results from small- and large-scale tests; individual tests are labeled by their respective apparatus, water quality condition, and number (e.g., L2-1 refers to the first large-scale test in the water with no hardness).

Test		Duration	Time-to-First Leak	Max. Pit Penetration	Avg. [†] Pit Growth Rate		Avg. [†] E _{corr} ^{††} (vs. Ag-AgCl)		Avg. [‡] Chlorine Demand	
		days	days	%	μm/day	95% CI ^{‡‡}	mV	95% CI ^{‡‡}	mg/day/cm ²	95% CI ^{‡‡}
1 (Control)	S1-1	67	62	100	2.9	±0.3	500	±34	1.20	±0.66
	S1-2	67	60	100	2.4	±0.4	494	±34	1.58	±0.47
	S1-3	67	60	100	2.7	±0.3	487	±25	1.18	±0.58
	L1-1	210	205	100	2.2	±0.2	458	±34	0.46	±0.05
	L1-2	161	-	90	2.8	±0.2	455	±53	0.51	±0.12
2 (No Hardness)	S2-1	67	43	100	2.5	±0.5	550	±53	1.63	±0.81
	S2-2	67	32	100	2.3	±0.4	679	±40	1.66	±0.50
	S2-3	67	53	100	2.4	±0.4	588	±53	1.41	±0.71
	L2-1	189	150	100	1.5	±0.2	575	±56	0.37	±0.07
	L2-2	182	-	72	1.9	±0.1	599	±90	0.32	±0.12
3 (1 mg/L P)	S3-1	87	-	6	0.1	±0.0	124	±7	0.30	±0.33
	S3-2	87	-	3	0.0	±0.0	124	±6	0.40	±0.29
	S3-3	87	-	6	0.1	±0.0	116	±9	0.56	±0.35
	L3-1	490	-	12	0.1	±0.0	88	±5	0.04	±0.03
4 (5 mg/L Si)	S4-1	87	-	7	0.1	±0.0	114	±8	0.48	±0.38
	S4-2	87	-	6	0.1	±0.0	120	±6	0.50	±0.28
	S4-3	87	-	6	0.0	±0.0	98	±9	0.52	±0.27
	L4-1	490	-	18	0.2	±0.0	139	±16	0.04	±0.03

[†]average of 24 (small-scale) or 48 (large-scale) deepest pits; if fewer pits formed, wall thickness measurements on un-pitted portions of the pipe are included

[‡]average after third week of testing to account for initial rise in E_{corr} data

^{††} E_{corr} represents the mixed potential of all copper in apparatus

^{‡‡}confidence interval

Copper tubing in large-scale loops had a wall thickness roughly 2.5 times greater than that in small-scale loops. For small-scale triplicates, control tests leaked within just three days of each other (i.e., 60 -62 days), and tests with no hardness leaked within three weeks of each other (i.e., 32-53 days) (Figure 1.3). At large-scale, both of these conditions also produced leaks (at 205 and 150 days, respectively) in the first (L1-1 and L2-1, respectively) of two tests. Comparing

time-to-first leak between small- and large-scale tests, small-scale tests leaked about 3.5 times faster than large-scale in both cases (Figure 1.3), indicating that scale-up from fairly simple to more complex systems was relatively reproducible after accounting for differences in tube wall thickness. Other parameters that might account for the slight differences include flow conditions (e.g., velocity, uniformity) and tube lengths.

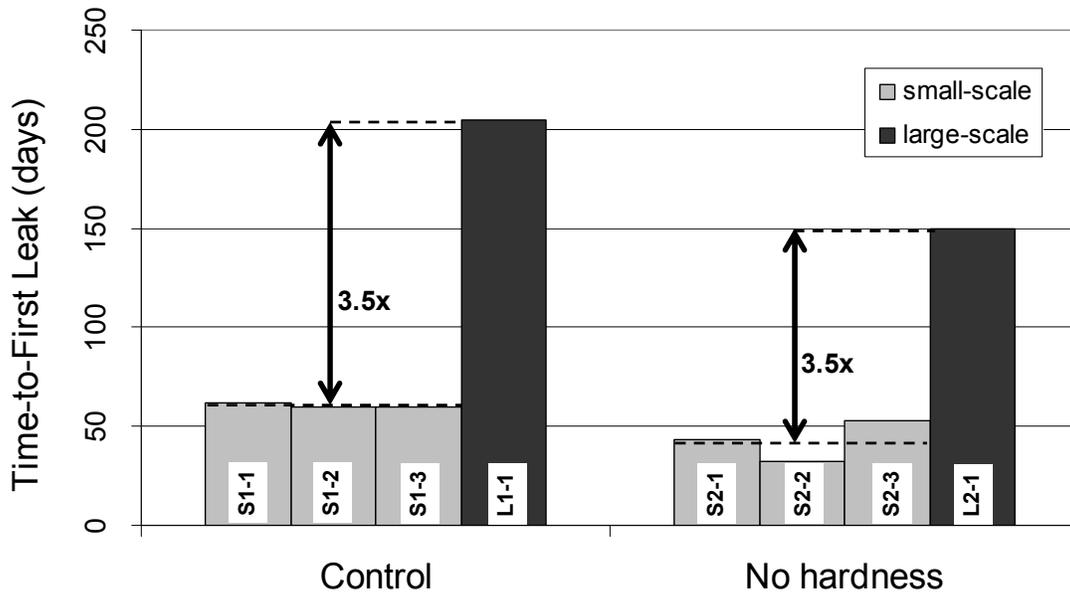


Figure 1.3: Time-to-first leak for control and no hardness conditions; in both conditions, small-scale tests leaked about 3.5 times faster on average than large-scale tests. Copper in large-scale tests had a wall thickness about 2.5 greater than that in small-scale tests.

For large-scale duplicate control and no hardness tests (L1-2 and L2-2) run at a different time of year than originals, severe pitting was observed but pinholes did not form. This may be due to several factors, including the power outage that resulted in test L2-1 running for a shorter time than was required to produce a leak in L1-1 (i.e., 161 vs. 205 days). Changes to uncontrolled parameters such as temperature may have also played a role. Despite discrepancies in maximum pit growth rates, average pit growth rates were in excellent agreement (Figure 1.4).

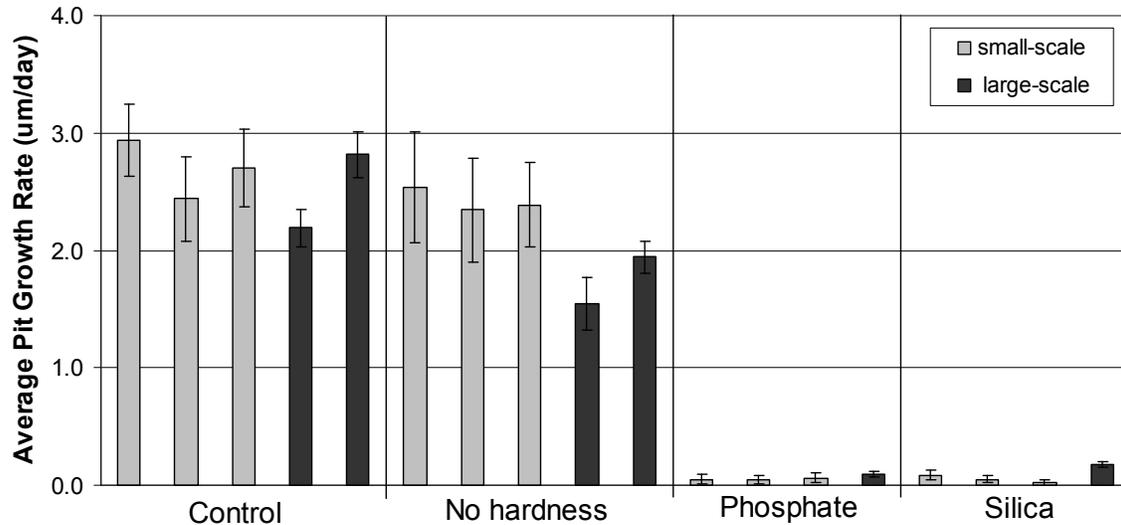


Figure 1.4: Average pit growth rates; error bars represent 95% confidence intervals.

Trends in in-situ electrochemical and chemical data (Table 1.4) further point to the reproducibility of pipe-loop test methods utilized here for the high pH and high chlorine water. There was good overlap of average E_{corr} 95% confidence intervals for all tests in any water quality condition. Also, chlorine demand data was in reasonable agreement between replicate tests in a given water quality at either small- or large-scale (e.g., L1-1 and L1-2). It was observed that small-scale tests had higher (normalized) chlorine demand than did large-scale for all water conditions. Testing ruled out differences in auto-decomposition rates and the same materials were used in both apparatuses. It is possible that the difference in velocity (i.e., 5.0 vs. 4.5 ft/s, respectively) or chlorine demand of oxide deposits on the reservoirs could have played a role.

Cross-sectioned tubes from the control and no hardness tests (Figure 1.5) revealed that a thick black scale formed with many tubercles, which were blue/green and porous, and had deep pits or pinholes underneath. Pit density appeared higher in the control and pits tended to overlap, whereas they were more isolated in the no hardness condition.

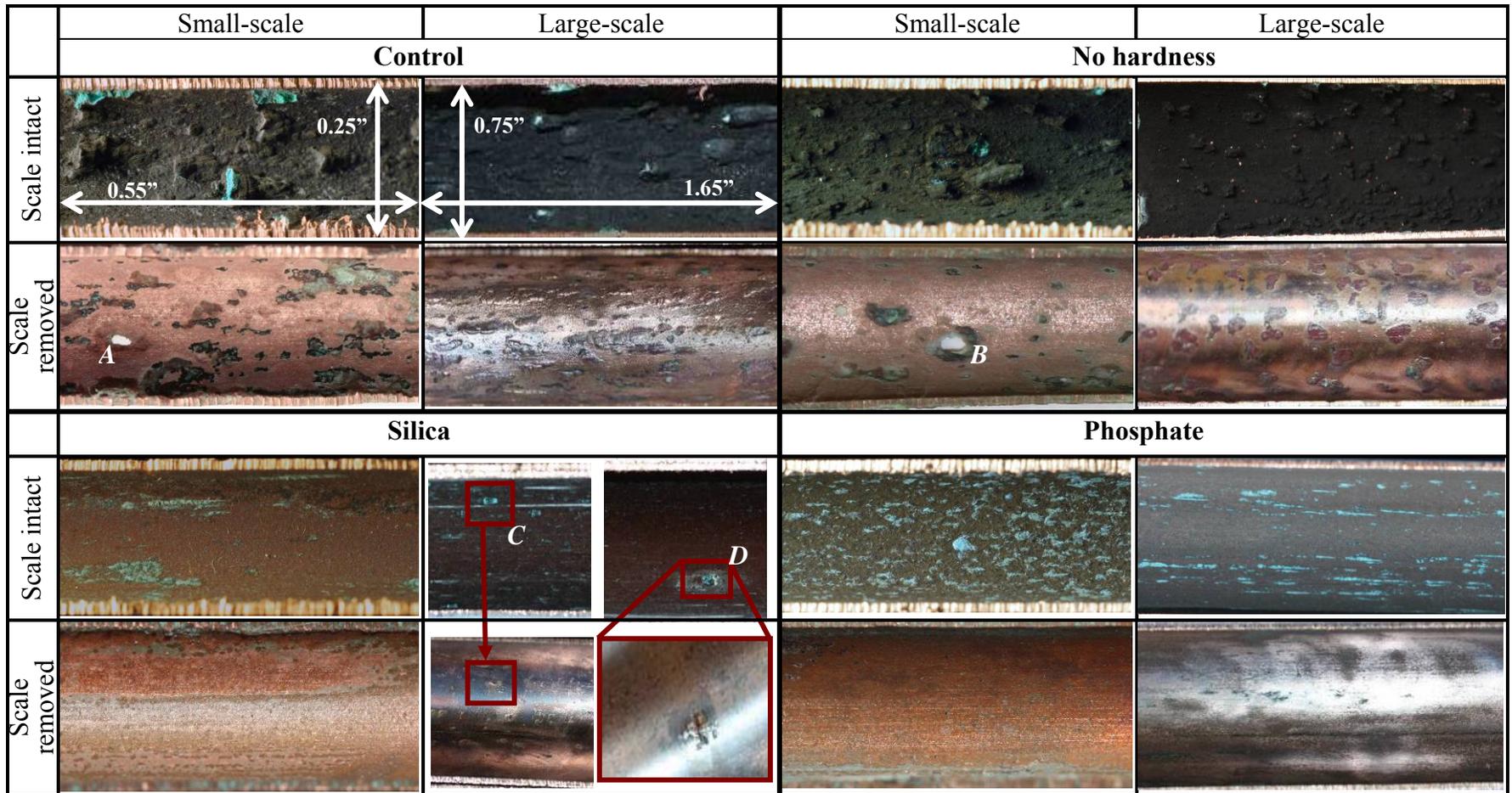


Figure 1.5: Representative photographs of copper tube interiors following testing; relative tube dimensions shown for each apparatus. A and B indicate pinholes that formed during testing, and C and D indicate pits that formed in the high silica condition.

Dosing of high phosphate tended to produce scale that was thin and dark grey, with no signs of tubercles or pitting in either large- or small-scale tests, although there was some uniform corrosion (Table 1.4). Dosing of silica tended to produce scale that was a deep red color, with some tubercles and pits, which was somewhat unexpected given the relatively low, stable E_{corr} observed during testing. In the large-scale test (L4-1), multiple small tubercles with shallow pits underneath (*C* in Figure 1.5) formed. Also, a relatively large tubercle formed in this test, with a corresponding pit that penetrated nearly 20% of the pipe wall (*D* in Figure 1.5). In the small-scale silica tests, a single, relatively large tubercle with a shallow pit underneath was found in test S4-1 (not shown).

Although pipe-loop testing has been an accepted ASTM method for studying pitting corrosion for decades (ASTM 2688-83), it has not always been successful in investigating copper pitting in potable water, presumably due to long exposure requirements, difficulties in replicating nuances that cause pitting corrosion in real systems, and uncertainties regarding reproducibility of results. But, results presented herein support conclusions of Lytle et al. (2008) about the usefulness of such testing in some situations. Once worst-case conditions causing rapid pitting have been identified, as is now the case for the MPW and similar waters, definitive results may be obtained quickly and with high certainty, and even using relatively small lengths of copper. In such cases, effects of dosing inhibitors such as phosphate or silica may also be easily illustrated. Furthermore, use of sophisticated electrochemical methods, like CMEA's (as per Cong et al., 2010) may provide detailed mechanistic understanding, followed by practical verification of key predictions with longer time pipe loops if high confidence is desired.

Extensive research experience has shown that electrochemical data in isolation should be viewed with considerable skepticism. It is not currently possible to use electrochemical noise,

E_{corr} rise, or other simple tests or probes to draw unambiguous conclusions regarding pitting propensity of different waters in short time periods. For that matter, unless precise conditions that cause pitting are known in advance, or researchers are fortunate enough to stumble upon them during testing, pipe-loops alone will not always provide clear insights either.

The greatest barrier to future progress is identification of scientifically reproducible conditions that initiate pitting in the laboratory. For the type of pitting that occurs in relatively high pH water with low alkalinity and free chlorine residual, sound progress has recently been made in a relatively short time using a combination of electrochemical and pipe-loop methods. Similar success can be expected for other pitting types if worst-case conditions are elucidated.

CONCLUSIONS

Aggressive potable water qualities, which in recent laboratory studies have been exemplified by chlorinated waters of high pH and low alkalinity, can cause rapid copper pitting. In this water type, increased flow velocity and frequency also contribute to pitting and pinhole leaks. Currently, only forensic investigative techniques can provide unambiguous evidence of pitting – although complementary electrochemical insights are needed to develop mechanistic understanding. The aggressive conditions cited herein led to highly reproducible, deterministic pitting of new copper in large- and small-scale pipe-loops. Pitting was greatly reduced, if not eliminated, by dosing high levels of orthophosphate or silicates.

ACKNOWLEDGMENTS

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CHAPTER 2: MITIGATION OF COPPER CORROSION PITTING IN CHLORINATED HIGH PH, LOW ALKALINITY POTABLE WATERS

Emily Sarver and Marc Edwards

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ABSTRACT

Copper pitting corrosion in potable water systems can cause premature plumbing failures, leading to economic and environmental concerns. Chlorinated waters with high pH and relatively low alkalinity are known to be particularly aggressive with respect to pitting. The current work demonstrates that, in waters of this type under conditions of continuous flow, phosphate, silica or natural organic matter (NOM) can greatly reduce, and in some cases eliminate, occurrence of copper pitting, and provides insights to engineered and “natural” inhibitors of pitting. Dosing of phosphate above 1 mg/L (as P) prevented the initiation of pits; but, under-dosing of phosphate and other inhibitors had little benefit and, in some cases, decreased time-to-pinhole leak failure versus conditions without inhibitors, consistent with theory. Initiation of pitting was more rapid at higher levels of free chlorine, but even moderate levels of free chlorine (i.e., 0.4 mg/L) initiated pitting in this aggressive water under extreme conditions of continuous flow. Increased alkalinity decreased pit propagation, but did not prevent formation of pits.

INTRODUCTION

Copper pitting corrosion in potable water plumbing systems is problematic because it can lead to fully-penetrating pinhole leaks, which burden consumers with the expenses and frustrations of repairing or replacing plumbing materials, water damage and mold growth.¹ While there is ample reason to believe that there are at least a few "causes" of pitting, only that of aggressive water characterized by high pH, free chlorine and low alkalinity has been reproduced in the laboratory using synthesized waters.²⁻⁵ Potential mitigation strategies that can counter the corrosivity of these waters have not been examined in detail.

Generally speaking, mitigation strategies involving water chemistry modifications are very attractive because the risk of pinhole leaks could be reduced for homes throughout an entire distribution system. This is much more appealing than expecting consumers to treat their water to reduce corrosivity, or to gradually replace or repair their plumbing systems. Depending on the extent of pitting in a system, water chemistry modifications may also represent relatively low-cost solutions. In addition to the obvious possibilities of reducing free chlorine residual or pH,² recent research by Lytle and Schock has suggested that increasing alkalinity can reduce pitting rates in high pH waters with chlorine.³ Several other constituents including phosphate,^{3,5-7} silica (silicate at high pH),^{5,8} and natural organic matter (NOM)⁹⁻¹¹ may also act as inhibitors to pitting at ambient concentrations or those achieved by inhibitor dosing. Although most of the pipe-loop data collected to date does not provide mechanistic insights to pitting reactions, insights from older theory,^{12,13} as refined and confirmed in recent electrochemical studies,^{4,14} provides a conceptual framework for interpreting and analyzing pipe-loop data relative to pit initiation and propagation phases.

Copper Pit Initiation and Propagation

Copper pitting is generally regarded as a two-step process in which pits are first formed (i.e., initiation) and then gradually penetrated through a metal surface (i.e., propagation). While initiation mechanisms are not well understood, and likely vary depending on physical and chemical exposure conditions, propagation is believed to proceed via coupling of anodic reactions (i.e., copper oxidation) occurring at small anode sites (i.e., the pits) with cathodic reactions (i.e., oxygen or chlorine reduction) occurring on relatively large surface areas.¹⁵ This differs from uniform copper corrosion, for which anodic and cathodic reactions effectively occur equally over the pipe surface (Figure 2.1). Pits can initiate at specific locations, including imperfections or breakdowns in the passive film layer that naturally occurs on copper surfaces in potable water, or under particulate deposits that have settled onto the pipe surface.

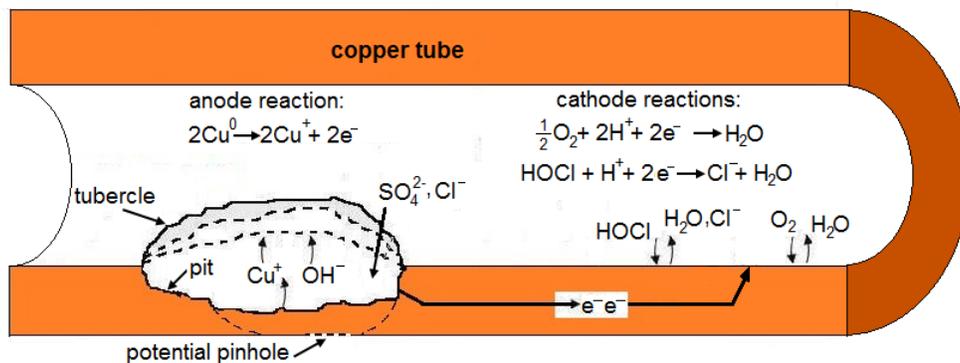


Figure 2.1: Simplified depiction of pitting corrosion of a copper tube. Electrons produced at the anode are consumed at the remote cathode.

After initiation, pit propagation can be enhanced by differential concentration cells, due to dramatic chemical changes that occur in the very small volume of water localized inside the growing pit. Specifically, the pit water becomes very acidic due to Lewis acidity of released Cu^{+1} and Cu^{+2} ions, and salty due to the increasing anion (e.g., Cl^- and SO_4^{2-}) concentrations drawn

into the pit to maintain electro-neutrality.^{13,15,16} In some cases the acidic and salty environment can promote sustained corrosion in the pit, and precipitation of copper salts (e.g., CuOH) forms a distinct mound of corrosion by-products (i.e., a tubercle).

It has been hypothesized that a characteristic rise in corrosion potential (i.e., E_{corr}) that proceeds beyond a critical value (i.e., E_{pit}) indicates the onset of copper pitting.^{13,17,18} Although this phenomenon may not be associated with all types of pitting in potable water systems,¹⁹ several studies have convincingly linked E_{corr} rise to pitting caused by the aggressive combination of high pH, low alkalinity and free chlorine.^{2,5} Moreover, Cong et al. has recently conducted elegant studies using cyclic voltammetry (CV) and coupled multi-electrode arrays (CMEA) which elucidated E_{pit} (or effective E_{pit}) values for copper in this water type.^{4,14} Thus, trends in E_{corr} can be applied to delineate the distinct phases of pitting during pipe-loop testing, and to help quantify pit initiation times and pit propagation rates.

Anodic and Cathodic Inhibitors

Inhibitors may prevent pitting by interfering with any aspect of the electrochemical cell including: 1) preventing the transport of anions into the pit, or 2) blocking the oxidation and/or reduction reaction sites. A basic example of the former mechanism would be alkalinity inhibiting pitting by buffering against pH change in the pit water. With respect to the latter, in simplest conceptualizations, it is hypothesized that “anodic pitting inhibitors” are negatively charged species (e.g., PO_4^{3-} , SiO_3^{2-}) that would be drawn to the net positive charge at an anode site (i.e., where Cu^+ and/or Cu^{2+} cations are being released), whereas “cathodic pitting inhibitors” are positively charged species (e.g., Zn^{2+}) that are drawn to the net negative charge at cathode sites (Figure 2.2). If pitting corrosion is limited by the rate of cathodic reactions, as is often assumed to be the case, any dose of cathodic inhibitor(s) is expected to reduce initiation and propagation

of pitting. However, at low enough dosages of anodic inhibitors, inactivating some of the pit sites could increase the cathodic driving force for corrosion at a few surviving sites, thereby accelerating the rate of pit growth relative to a condition without any inhibitor at all.²⁰ For this reason, very low doses of anodic inhibitors might actually decrease the time-to-failure; so only at dosages sufficient to inactivate all anodic sites, are anodic inhibitors considered "safe." Beyond the straightforward categorization of inhibitors presented above, it should be noted that some anions may function as cathodic inhibitors and some cations may function as anodic inhibitors if, for example, either is taken up into a protective film or passive scale layer that effectively protects an entire metal surface. In this case, the effective constituents may be called "passivating" inhibitors.²¹

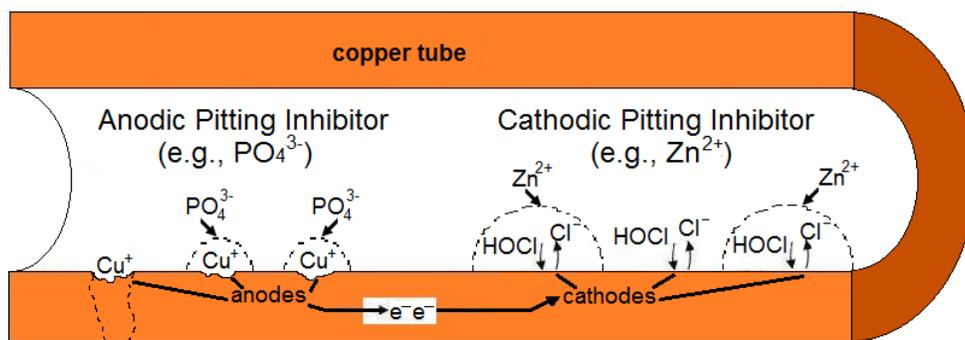


Figure 2.2: Simplified, speculative depiction of pit inhibition by anodic and cathodic inhibitors.

Phosphate and silica are currently used by utilities to control various types of corrosion in potable water distribution systems (e.g., corrosion of iron mains).²² Their potential beneficial effects on copper pitting mitigation have been suggested by several authors,^{3,5,6} and favorable data from full-scale testing.²³ Some research has also demonstrated that anionic NOM may also function as a very effective pitting inhibitor, even at relatively small concentrations.^{9,11,12,24} However, to date, the dependency between dose and effectiveness for each of these constituents has not been established, nor has substantive information been gathered as to their specific

functions (i.e., as anodic or cathodic pitting inhibitors, or both). It is also of considerable interest to determine whether very low levels of these constituents might actually worsen pit propagation rates.

This research is aimed at: 1) determining the role of free chlorine residual in initiating and/or propagating pitting in high pH, low alkalinity water; 2) confirming the efficacy and dose-response effects of phosphate, silica, NOM, and increased alkalinity in inhibiting pitting; 3) drawing preliminary conclusions regarding possible mechanisms of inhibition, and whether certain inhibitor dose ranges may actually increase pit growth rates, and 4) applying insights from prior electrochemical studies to interpret data in the context of pit initiation and propagation.

MATERIALS AND METHODS

Both large- and small-scale pipe-loop tests were conducted to examine the dose-response effects of free chlorine, alkalinity and inhibitors and on copper pitting caused by the aggressive combination of high pH, low alkalinity and chlorine in potable water. The large-scale loops exemplified more realistic conditions with respect to a copper plumbing system (e.g., practical flow velocity, copper tube size and wall thickness, etc.), whereas the small-scale loops were designed to accelerate the time to observation of fully- penetrating leaks (e.g., higher flow velocity, thinner copper tube wall). Prior work demonstrated that both pipe-loops could provide relatively reproducible results, and that the small-scale loops can be particularly useful for gaining insights in short time periods.⁵ A total of 10 large-scale tests with durations between 189 and 490 days, and 21 small-scale tests with durations between 86 and 220 days were conducted.

Water Qualities and Inhibitor Dosages

The control water quality (Table 2.1) was identical to the high pH, high free chlorine water first shown by Marshall² to cause pitting and pinhole leaks in copper, except that it did not contain aluminum solids. Only high and low concentrations of the test variables were investigated in the large-scale loops, but ranges of concentrations were tested in the small loops (except for in the case of alkalinity). Additionally, three different types of organic matter were tested in the small loops: natural organic matter (NOM), ozonated NOM, and a combination of acetate and glucose.

Table 2.1: Experimental conditions for large- and small-scale tests.

Test Variable	Water Quality	
	Large-scale Tests	Small-Scale Tests
control	pH 9.2, 4 mg/L free chlorine, 17 mg/L Ca ²⁺ , 16 mg/L Na ²⁺ 20 mg/L Cl ⁻ , 13 mg/L SO ₄ ²⁻ , 34 mg/L alkalinity as CaCO ₃ (4.1 mg/L as DIC)	
free chlorine adjusted	0.4mg/L as Cl ₂	0.5 - 8 mg/L as Cl ₂
ortho-phosphate added	0.1, 1 mg/L as P	0.015 - 1 mg/L as P
silica added	0.5, 5 mg/L as Si	0.1 - 10 mg/L as Si
organic matter added	0.01 ^a , 0.1 ^a mg/L as TOC	0.005 ^a - 0.05 ^{a,b,c} mg/L as TOC
alkalinity adjusted	10, 150 mg/L as CaCO ₃	none

^a Natural organic matter ^b Ozonated natural organic matter ^c Sodium acetate/d-glucose

Automatic feed systems were utilized in conjunction with manual adjustment (at least four times per week) to maintain targeted pH and free chlorine residuals. pH was measured using a double-junction Ag-AgCl electrode, and was generally maintained within 0.4 units of the target (i.e., 9.2 ± 0.4). Free chlorine residual was measured using a DPD (diethyl phenylene diamine) colorimetric test (per Standard Method 4500-Cl G)²⁵ with a Hach Chlorine Pocket Colorimeter II, and was maintained within 0.3 mg/L (standard deviation) of the targets (e.g., 4.0 ± 0.3 mg/L).

Water was changed either weekly, every two weeks, or every three weeks in the large-scale loops to control the rate of chloride build-up due to free chlorine decay; this approach ensured that chloride did not increase beyond three times its initial value. Bulk water was changed weekly in all small-scale loops, which had relatively small surface areas of exposed copper and low rates of chloride build-up. Just before each water change, test waters were made-up using deionized water and dry reagent-grade sodium or calcium salts. Free chlorine was added as sodium hypochlorite from a concentrated bleach stock (i.e., 6% NaOCl solution). pH was adjusted using sodium hydroxide and nitric acid. Water samples were analyzed via inductively coupled plasma mass spectrometry (ICP-MS) for quality assurance.

Ortho-phosphate and silica were dosed as sodium phosphate and sodium silicate, respectively. A natural organic matter stock solution was made by chlorinating and filtering (through a 0.45 μm pore size) a concentrated humic stock, such that the solution was relatively stable and homogeneous. Part of this NOM stock was then ozonated for several hours to break down the long chains of humics, such that the resulting NOM solution (referred to herein as ozonated NOM) had only 33% of the UV_{254} absorbance of the un-ozonated NOM stock. To test the effects of model low molecular weight organic compounds on copper pitting, a solution of sodium acetate and d-glucose (equimolar on the basis of mass organic carbon) was used.

Pipe-Loops

Each large-scale pipe-loop (Figure 2.3, left) consisted of a 94L polypropylene plastic reservoir, from which water was continuously recirculated through three (1' or 30.5 cm) lengths of $\frac{3}{4}$ " (1.9 cm) diameter Type M copper tubing at a velocity of about 4.5 ft/s (1.3 m/s). Another short (2" or 5.1 cm) length of the same copper tubing was located out-of-flow (i.e., at the dead-end T in Figure 2.3). All copper sections were physically separated using short lengths of clear

vinyl tubing, but were electrically connected via external copper wires. Vinyl tubing also was used to connect copper to recirculation pumps (magnet-drive, centrifugal with polypropylene construction) and to complete flow loops. Reservoirs were closed to limit atmospheric influences on water quality.

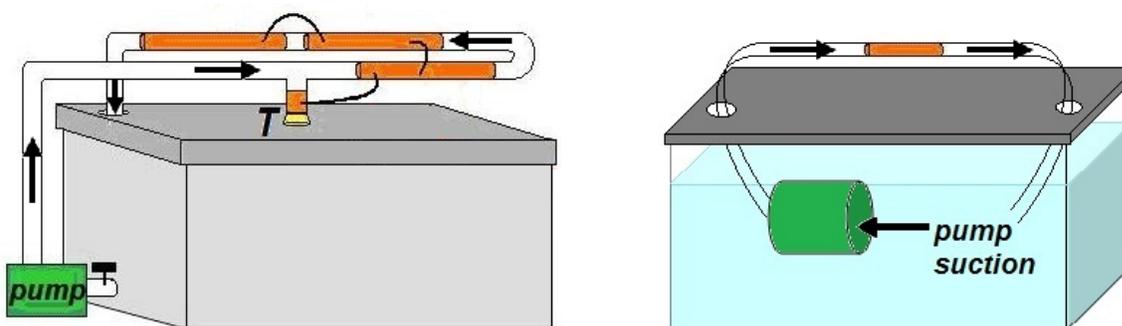


Figure 2.3: Large and small pipe-loop apparatuses; flow direction is indicated by arrows.

Small-scale pipe-loops (Figure 2.3, right) were similar in construction to the large loops, but consisted of 30 L reservoirs and had only one short (3" or 7.6 cm) length of ¼" (0.63 cm) diameter copper tubing. Water was continuously recirculated by submersible pumps (magnet-drive, centrifugal; polypropylene and stainless steel construction) at a velocity of approximately 5.0 ft/s (1.5 m/s). While the small-diameter tubing used in these loops was about 2.5x thinner than the Type M in the large loops (i.e., wall thickness of about 0.013" or 0.033 cm vs. 0.032" or 0.082 cm), both were C12200 (phosphorous deoxidized) copper. And all copper tubing was de-burred, rinsed with de-ionized water, allowed to dry and weighed prior to assembling the pipe-loops.

Data and Analyses

Changes in electrochemistry and chemistry were monitored in-situ throughout testing, and copper tubes were subject to forensic analyses at the conclusion of the tests.

Corrosion Potential

Corrosion potential (E_{corr}) was measured once per water change cycle for the large-scale tests, and two or three times per week for the small-scale tests. E_{corr} was measured against Ag-AgCl reference electrode using a Fluke 189 True RMS multi-meter with internal resistance $<100 \Omega$. In the convention utilized for this work, positive E_{corr} values indicate an overall cathodic activity on the exposed copper.

Chlorine Demand

Changes in chlorine concentration may be linked to the copper cathodic reaction rate and, therefore, provide some indication of pitting activity.¹⁸ Based on the hypothesis that, if present, chlorine will act as the oxidizing agent for pitting, the rate of chlorine consumption should be correlated to the overall pitting rate. A simple mass balance can be used to determine the rate of chlorine decay or, in tests where chlorine residual is maintained, the mass addition rate of chlorine needed to maintain a target residual. The latter has been termed “chlorine demand” and shown to be useful in monitoring copper pitting in high pH, low alkalinity water.⁵

In this work, chlorine demand (mg/week/cm^2) was determined for each test once per water change cycle, using Equation 2.1:

$$\text{chlorine demand} = \frac{V_B(C_{Bi} - C_{Bf}) + V_F C_F + V_S C_S}{t(A)} \quad (\text{Eq. 2.1})$$

where t is elapsed time (weeks), A is copper surface area exposed to water (cm^2), V_B is bulk water volume (L), C_{Bi} and C_{Bf} are initial and final bulk chlorine concentrations (mg/L), V_F and C_F are volume (L) and chlorine concentration (mg/L) of feed solution automatically added, and V_S and C_S are volume (L) and chlorine concentration (mg/L) of stock solution manually added.

Forensic Analyses

Forensic examination of copper tubes included quantitative characterization of pit depths and growth rates, and qualitative characterization of corrosion scales. At conclusion of tests, tubes were removed from pipe-loops and allowed to dry prior to being cut lengthwise and cleaned. Corrosion scales were removed chemically using Twinkle brand household copper cleaner from tubes in small-scale tests; scales were removed mechanically using a Dremel tool with a fine-bristle steel brush in large-scale tests. A digital, fine-tipped Mitutoyo micrometer (0.001 mm resolution) was used to measure tube-wall thicknesses (as guided by ASTM G46)²⁶.

Maximum and average overall pit growth rates ($\mu\text{m}/\text{day}$) were computed to determine the rapidity at which pits penetrated through copper in each test using Equations 2.2 and 2.3, respectively:

$$\text{maximum pit growth rate} = \frac{MPD}{X} \quad \text{or} \quad \frac{MPD}{Y} \quad (\text{Eq. 2.2})$$

$$\text{average pit growth rate} = \frac{APD}{Y} \quad (\text{Eq. 2.3})$$

where *MPD* and *APD* are the maximum and average pit depths (μm) measured in a given test, *X* is the failure time (days) (i.e., the time-to-first pinhole leak failure, if one occurred), and *Y* is the total test duration (days). In tests where at least one pinhole leak occurred, the fastest growing pit could only grow through the copper from the start of the test until the failure time, so the maximum pit growth rate was calculated using *X*; in tests where a leak did not occur, this pit was allowed to grow throughout the test, so the rate was calculated using *Y*.

RESULTS

Very large differences in time-to-failure (leak), trends in E_{corr} , chlorine demand and other factors were observed during the large- and small-scale tests (Table 2.2). Many tests (e.g., control) ended with either fully-penetrating pinhole leaks or very severe pitting, but others (e.g., high phosphate) produced no detectable pitting whatsoever (Figure 2.4). Pits were generally observed beneath tubercles, as expected; in tests that did not produce pits, corrosion scales tended to be relatively smooth and uniform.

The sections that follow describe trends in failure times, overall pit growth rates and in-situ data, followed by presentation of pit initiation and propagation results based on interpretation of E_{corr} rise data.

Failure Times and Overall Pit Growth Rates

The control condition was amongst the fastest to produce pinhole leaks; failure times for the large- and small-scale control tests occurred at 207 and 38 days, respectively (Table 2.2). Tests with reduced alkalinity, or dosing of low levels of phosphate, silica, or NOM also produced pinholes, generally within similar time frames as the control tests. In contrast, tests with higher concentrations of inhibitors did not produce leaks during the test. The time-to-failure was found to be inversely related to free chlorine concentration in the small-scale tests with residuals of 2 mg/L or higher, but neither pinhole failures nor pitting occurred at lower residuals (i.e., 1 or 0.5 mg/L) within the 140-day tests. This does not mean that chlorine levels of 1 mg/L or less should be considered “safe” under continuous flow conditions; in fact, just 0.4 mg/L chlorine caused some deep pits to form during a 490-day large-scale test. Instead, taken together, these results strongly suggest that, given a long enough time, even low levels of chlorine can cause pitting.

Table 2.2: Summary of experimental results. Tests are grouped by respective adjustments to control water quality and large-scale results are shaded. The large-scale control, 1 mg/L phosphate and 5 mg/L Si test data has been partially published elsewhere⁵ in a different context, and is included here for completeness and comparison.

Test		Duration	Failure Time	Avg. Overall Pit Growth [†]		Max. Overall Pit Growth	Avg. [‡] System E _{corr} (vs. Ag-AgCl)		Avg. [‡] Chlorine Demand		
adjustment to control water	No.	days	days	µm/day	95% Cl	µm/day	mV	95% Cl	mg/week/cm ²	95% Cl	
none	control	S1	86	38	3.4	0.2	8.6	549	11	9.1	0.2
	control	L1	210	207	2.2	0.2	3.8	458	34	3.2	0.4
free chlorine (mg/L as Cl ₂)	0.5	S2	124	-	0.0	0.0	0.1	127	8	1.6	0.1
	1	S3	124	-	0.0	0.0	0.1	140	10	1.6	0.0
	2	S4	220	212	0.7	0.2	1.5	223	24	3.1	0.1
	3	S5	88	82	1.9	0.4	4.0	380	56	6.1	0.1
	8	S6	88	34	2.6	0.5	9.6	625	28	10.1	0.3
	0.4	L2	490	-	0.3	0.0	0.5	179	14	0.1	0.0
ortho-phosphate (mg/L as P)	0.015	S7	88	48	2.5	0.4	6.8	488	70	4.7	0.1
	0.025	S8	88	54	2.5	0.4	6.1	316	40	4.3	0.2
	0.1	S9	88	-	0.1	0.1	0.0	142	7	2.3	0.1
	0.25	S10	88	-	0.1	0.1	0.0	117	6	2.8	0.2
	0.5	S11	88	-	0.0	0.0	0.0	121	5	2.2	0.1
	1	S12	88	-	0.1	0.1	0.0	117	4	1.8	0.1
	0.1	L3	490	357	1.4	0.1	2.2	301	44	2.3	0.6
	1	L4	490	-	0.1	0.0	0.2	88	5	0.3	0.2
silica (mg/L as Si)	0.1	S13	86	43	3.1	0.3	7.6	637	11	9.3	0.1
	0.5	S14	86	34	2.1	0.5	9.6	634	9	5.0	0.1
	2.5	S15	86	-	0.1	0.0	0.2	115	6	5.1	0.1
	10	S16	86	-	0.1	0.0	0.3	113	4	2.7	0.1
	0.5	L5	490	357	0.9	0.1	2.2	356	31	2.2	0.3
	5	L6	490	-	0.2	0.0	0.3	139	16	0.3	0.2
organica matter (mg/L as TOC)	0.005 ^a	S17	86	46	2.3	0.5	9.1	574	12	6.9	0.1
	0.01 ^a	S18	86	38	2.6	0.3	6.8	521	18	6.4	0.2
	0.05 ^a	S19	86	-	0.8	0.1	1.4	220	6	3.8	0.1
	0.05 ^b	S20	86	-	1.3	0.2	2.1	276	10	4.8	0.1
	0.05 ^c	S21	86	53	3.5	0.3	6.2	471	11	7.1	0.1
	0.01 ^a	L7	210	193	1.9	0.2	4.1	366	34	2.3	0.3
	0.1 ^a	L8	490	455	1.1	0.1	1.7	245	13	0.4	0.2
alkalinity (mg/L as CaCO ₃)	10	L9	189	172	2.6	0.2	4.6	511	37	6.0	1.1
	150	L10	490	-	0.5	0.0	0.7	593	73	0.7	0.3

S Indicates small-scale pipe-loop

L Indicates large-scale pipe-loop

^a NOM

^b Ozonated NOM

^c Sodium acetate/d-glucose

[†] Average pit growth rates computed from 24 (small-scale tests) or

48 (large-scale) deepest pits measured on copper surfaces contacted by flow

[‡] Average of measurements from week 3 (small-scale tests) or for weeks 5-22 (large-scale)



Figure 2.4: Representative photographs of copper from selected tests following scale removal. Photos are grouped by respective adjustments to control water quality, and arrows indicate some of the pinhole leaks that formed during testing. All photos show copper from small-scale tests, except for those in the variable alkalinity group.

On the basis of failure times, test durations and final pit depths, overall maximum and average pit growth rates (Table 2.2) were found to increase with increasing chlorine, and decrease with increasing phosphate, silica, NOM or alkalinity (e.g., Figure 2.5, top). At small-scale, the fastest average growth rates occurred in the control and 0.05 mg/L acetate and glucose tests, while the fastest maximum growth rates (i.e., fastest failure time) occurred in the 8 mg/L chlorine and 0.5 mg/L silica (as Si) tests. At large-scale, the fastest maximum and average rates

occurred in the 10 mg/L alkalinity (as CaCO₃) test – and the next fastest were in the control and 0.01 mg/L NOM (as TOC). At 150 mg/L alkalinity, significant pitting did occur, although overall pit growth rates were markedly reduced (e.g., the average growth rate was only 20% of that in the control test). This is consistent with hypotheses of Lytle and Schock³ and Cong et al.⁴ regarding benefits of higher alkalinity.

Phosphate completely inhibited pitting at high enough dosages (i.e., >0.025 mg/L at small-scale and >0.1 mg/L at large-scale), such that overall pit growth rates were negligible. A similar case was seen for silica, which inhibited all pitting in the small-scale tests with >0.5 mg/L (as Si) and only allowed minor pitting in the large-scale test with 5 mg/L. Although increasing NOM decreased pit growth rates, no level of NOM was tested that completely inhibited pitting. Furthermore, results clearly showed that the type of organic matter is critical to the efficacy of pitting inhibition. As compared to the average pit growth rate in the control (i.e., no organic matter added), 0.05 mg/L un-ozonated NOM resulted in greater than 75% deceleration, while an equal dose of ozonated NOM only resulted in about 60% deceleration, and an equal dose of the acetate and glucose mixture did not decelerate the pitting rate at all.

In-situ Data

Generally speaking, the overall pit growth rates correlated well with average system E_{corr} (i.e., rest potential of all copper surfaces exposed to test water vs. Ag-AgCl reference) (Figure 2.6) and chlorine demand (Table 2.2), except for a few isolated cases. For example, the high alkalinity condition consistently had high E_{corr} but produced relatively shallow pits within the test duration, albeit at a very high density (see Figure 2.4). This can be attributed to the fact that, although many pits were being initiated (as suggested by the high E_{corr} and confirmed by later visual observation), pits did not propagate rapidly. We speculate that this might be due to

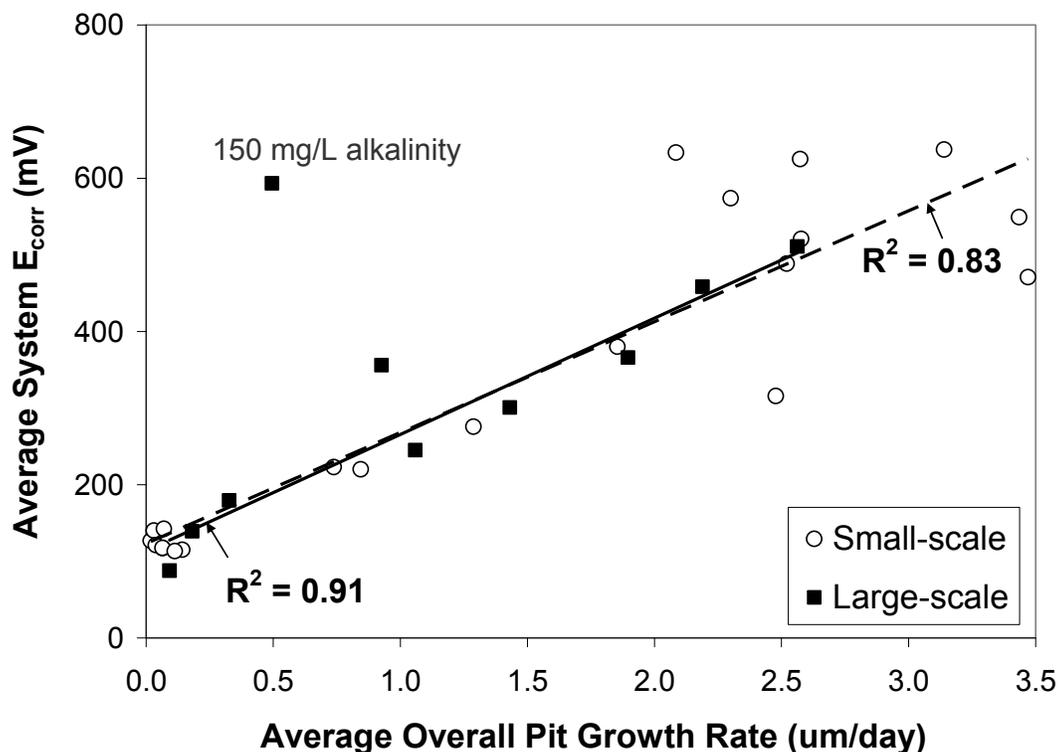


Figure 2.6: Average system E_{corr} vs. overall pit growth rate for all tests. The 150 mg/L alkalinity condition did not follow the same trend as other data, and is not included in the computed R^2 value for the large-scale tests.

Pit Initiation and Propagation

In the preceding sections, trends were based on overall results, and no attempt was made to distinguish between pit initiation and propagation phases. However, it is possible, even likely, that the rates of pit initiation and propagation did indeed vary as a function of water chemistry. Assuming the conventional electrochemical interpretation is correct – that a critical potential does indicate the onset of copper pitting in aggressive waters like those tested in this work – the time-to-pit initiation and the duration of pit propagation during each experiment can be estimated from simple plots of E_{corr} versus time for each test (e.g., Figure 2.7).

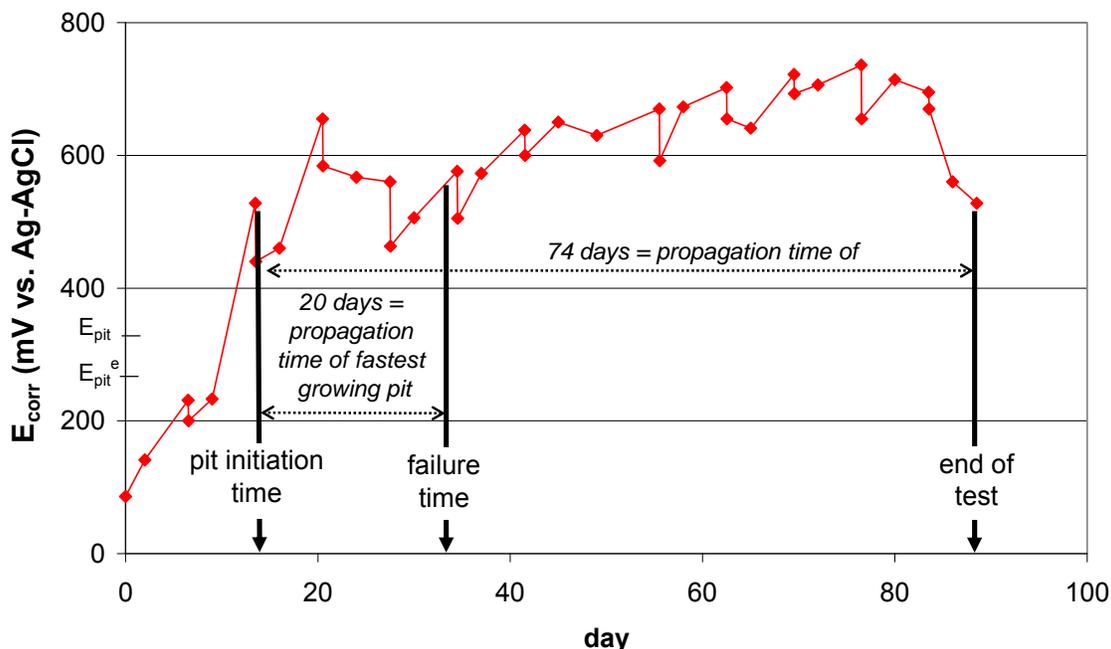


Figure 2.7: E_{corr} vs. time for small-scale test with free chlorine residual adjusted to 8 mg/L. Using $E_{pit} = 325$ mV (vs. Ag-AgCl), the pit initiation time (14 days) and the relative times available for maximum (20 days) and average (74 days) pit propagation were estimated.

The critical potentials for analyses in this work were selected by interpolating results from recent works by Cong et al.^{4,14} In one study, CV was used to define E_{pit} at several pH's (i.e., from 7.4 to 11) in a similar water quality to that used here (i.e., control water in this study without free chlorine).⁴ By interpolating results from that study, E_{pit} at pH 9.2 is approximately 325 mV (vs. Ag-AgCl). However, in a later study, CMEA's were used to investigate pitting across a similar pH range (i.e., from 7 to 10) in the same water with free chlorine and aluminum solids, and results indicated that pitting can actually occur at somewhat lower potentials than the previously defined E_{pit} values.¹⁴ Consequently, an effective E_{pit} (termed E_{pit}^e herein) at pH 9.2 may be as low as about 260 mV (vs. Ag-AgCl). In support of this hypothesis, the E_{corr} of each test that produced significant pitting in this work was observed to rise to and, at least temporarily, remain above these approximated E_{pit} and E_{pit}^e values. If the time of the first measurement at or above one of these values is considered to be the pit initiation time, maximum

and average pit propagation rates (i.e., rate of pit penetration through the copper tube wall) after initiation, can then be computed over the time span from initiation to either the time of failure or end of a test, respectively. Pit initiation times and propagation rates were computed using both E_{pit} and E_{pit}^c (Table 2.3) and results were quite similar due to the very rapid E_{corr} rise exhibited by tests that caused pitting. Thus, only the analyses based on E_{pit} will be discussed in detail from here.

Pit Initiation Times

Perhaps not surprisingly, many conditions (e.g., 8 mg/L chlorine at small-scale) that appear to have initiated pits quickly also tended to have rapid overall pit growth rates (Figure 2.5) and failure times. In contrast, conditions that had relatively slow pit growth rates (e.g., 0.4 mg/L chlorine) appear to have significantly delayed pit initiation (vs. conditions that did fail). Again, the high alkalinity condition was an exception; while the overall pit growth rates in this test were very slow, the pit initiation time was estimated to be similar to that in the control and low alkalinity tests.

At the lowest chlorine levels in the small-scale tests (i.e., 0.5 and 1 mg/L), and the highest dosages of phosphate (i.e., > 0.25 mg/L) and silica (i.e., > 2.5 mg/L) in both large and small tests, E_{corr} was never observed to reach or exceed the critical 325 mV value, and pits were not observed on copper from these conditions – with the exception of some very shallow pits in the 5 mg/L silica test at large-scale. The highest E_{corr} measured in this test was approximately 240 mV, which may mean that the actual E_{pit} was somewhat lower in this condition than was presumed in this analysis, or that the peak E_{corr} values in this test were simply not measured. The latter is entirely possible considering that electrochemical data were only collected once every three weeks for the test. Moreover, the maximum E_{corr} measured in the 2.5 mg/L silica small-

scale test (two or three measurements per week) was about 245 mV, but no pits formed in that condition.

Table 2.3: Estimated pit initiation times and computed pit propagation rates based on $E_{\text{pit}} = 325$ mV (bold) and $E_{\text{pit}}^e = 260$ mV (vs. Ag-AgCl). Tests are grouped by respective adjustments to control water quality; large-scale results are shaded.

Test		Initiation Time (days)		Propagation Rate ($\mu\text{m}/\text{day}$)			
				Max.		Avg.	
		E_{pit}	E_{pit}^e	E_{pit}	E_{pit}^e	E_{pit}	E_{pit}^e
con.	S1	10	10	11.7	11.7	3.9	3.9
	L1	42	35	4.8	4.6	2.7	2.6
chlorine	S2	-	-	-	-	-	-
	S3	-	-	-	-	-	-
	S4	141	97	8.0	3.8	3.3	1.7
	S5	49	45	9.9	8.8	4.2	3.8
	S6	14	14	16.4	16.4	3.1	3.1
	L2	407	407	3.2	3.2	1.9	1.9
	S7	28	25	16.4	14.2	3.7	3.5
phosphate	S8	32	32	14.9	14.9	3.9	3.9
	S9	-	-	-	-	-	-
	S10	-	-	-	-	-	-
	S11	-	-	-	-	-	-
	S12	-	-	-	-	-	-
	L3	77	77	2.8	2.8	1.7	1.7
	L4	-	-	-	-	-	-
	S13	14	14	11.3	11.3	3.8	3.8
silica	S14	16	16	18.2	18.2	2.6	2.6
	S15	-	-	-	-	-	-
	S16	-	-	-	-	-	-
	L5	77	35	2.8	2.5	1.1	1.0
	L6	-	-	-	-	-	-
	S17	21	21	16.7	16.7	3.0	3.0
organic matter	S18	14	14	10.8	10.8	3.1	3.1
	S19	48	44	3.1	2.8	1.9	1.7
	S20	28	26	3.2	3.1	1.9	1.8
	S21	20	20	8.7	8.7	4.5	4.5
	L7	70	29	6.5	4.9	2.8	2.2
	L8	217	71	3.3	2.1	1.9	1.2
	L9	35	15	5.8	5.1	3.1	2.8
alk.	L10	35	15	0.7	0.7	0.5	0.5

Even very small amounts of (un-ozonated) NOM appear to have delayed pit initiation substantially. As compared to the control, 0.1 mg/L NOM in the large-scale test increased the estimated initiation time by a factor of about four, and just 0.05 mg/L NOM in the small test

increased the initiation time by a factor of about five. By comparison, an equal dosage of ozonated NOM only increased the initiation time by about three, and the same dosage of the acetate and glucose mixture only by a factor of 2.

Estimated pit initiation times (i.e., the rate of E_{corr} rise) were typically faster in small-scale tests than in large-scale for identical or similar water quality conditions (e.g., 10 vs. 42 days for control). This discrepancy is most likely related to differences in the pipe-loop apparatuses (e.g., exposed copper surface area to bulk water volume ratio), operating conditions (e.g., flow velocity) and/or water change schedules. It is also possible that some of the small tests that did not exhibit a rise in E_{corr} or produce pitting would have done so if test durations had been longer. For example, E_{corr} in the 1 mg/L chlorine test was slowly rising and reached a maximum value of 248 mV just 20 days before the test conclusion. Similar trends were observed for the 0.5 mg/L chlorine and 1 mg/L phosphate tests, which had maximum E_{corr} values of 204 and 184 mV, respectively.

Pit Propagation Rates

Pit propagation rates and chlorine demand were also a strong function of water chemistry (Figure 2.8). For tests with variable alkalinity or with added phosphate, silica or organic matter, average chlorine demand was well correlated with computed average pit propagation rates (i.e., the penetration rate of the average pit). However, this was not the case for tests with variable free chlorine residuals, probably due to auto-decomposition kinetics of chlorine (i.e., the reaction is non-zero order, so the rate of chlorine decay is dependent on chlorine concentration).

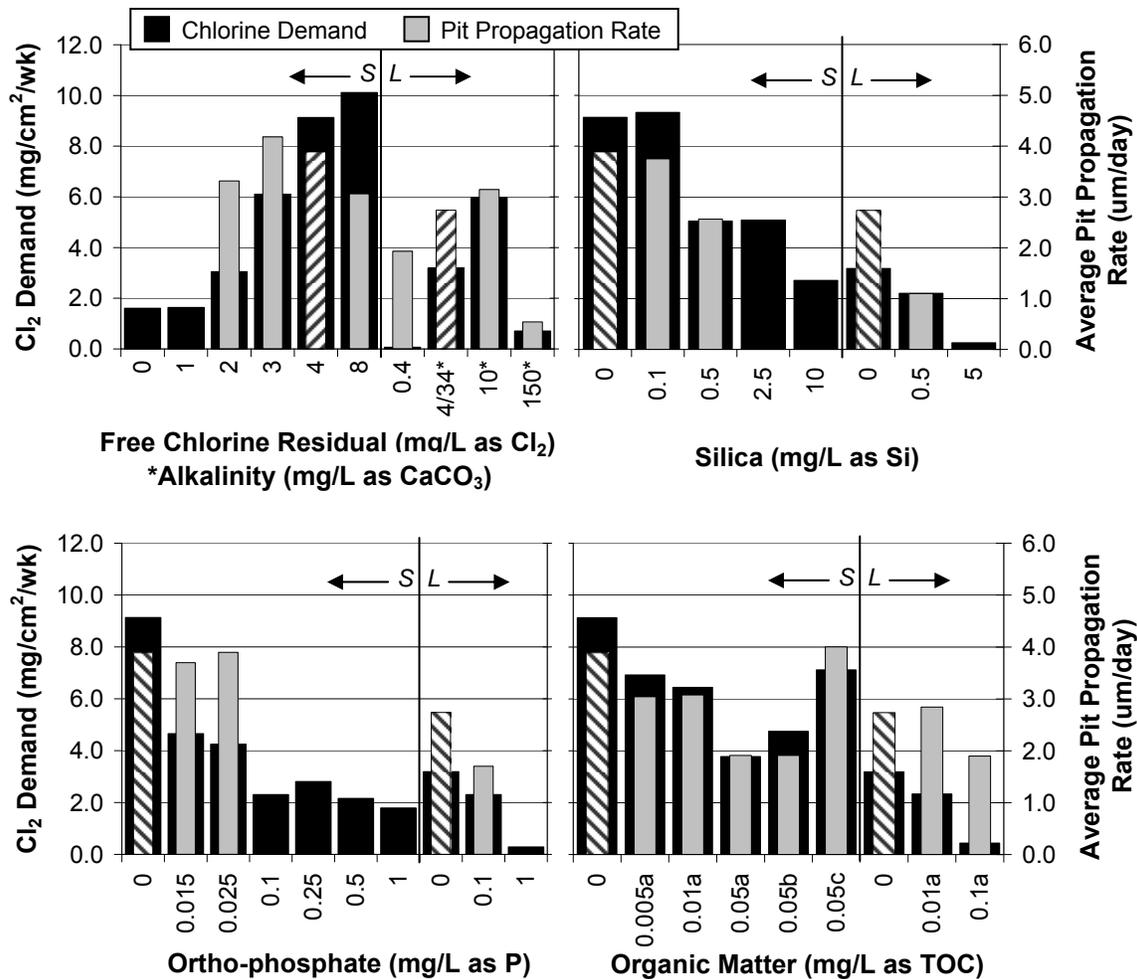


Figure 2.8: Chlorine demand (dark shading) and computed average pit propagation rates (light shading) based on $E_{pit} = 325$ mV (vs. Ag-AgCl). No propagation rate is shown for tests in which E_{pit} was not observed. Conditions are grouped by respective changes to the control water quality, and the control tests are shown with hash marks in each grouping. S and L indicate small- and large-scale tests, respectively.

Interestingly, although chlorine seems to have had a controlling impact on pit initiation time, it does not appear to have greatly influenced pit propagation rates. Of the small-scale tests with variable chlorine that exhibited E_{corr} rise and produced pits (i.e., 2-8 mg/L chlorine tests), average pit propagation rates only varied by about 25% (based on $E_{pit} = 325$ mV); and at large-scale, the rate of the 0.4 mg/L chlorine test was only about 30% lower than the control, which had ten times more chlorine. Furthermore, the maximum pit propagation rates (i.e., the penetration rate of the fastest growing pit) also appear to have been very similar, especially

considering the dramatically different pit initiation and failure times with variable chlorine. For instance, while the time-to-failure for the 3 and 8 mg/L chlorine test were separated by a factor of roughly 2.4 (i.e., 82 vs. 34 days), the computed maximum pit propagation rates only differed by a factor of 1.6 (i.e., 16.4 vs. 9.9 $\mu\text{m}/\text{day}$). For situations in premise plumbing, in which water flow is not continuous and chlorine can decay rapidly during stagnation, it might be expected that pit initiation would be a critical factor. This might explain why, in some real systems that have experienced outbreaks of pitting, much higher incidence of pinholes have been reported near the treatment plant where levels of chlorine are much higher.²⁷

At very low dosages of phosphate (i.e., 0.015 and 0.025 mg/L), silica (i.e., 0.5 mg/L) and NOM (i.e., 0.005 mg/L), maximum pit propagation rates in the small-scale tests were 27-56% higher than in the control condition. This supports the hypothesis that these constituents were functioning, at least in part, as anodic pitting inhibitors, reducing the number of pits and focusing the cathodic reaction on a smaller number of anode sites (i.e., pits). As further direct evidence for this effect, the proportion of measured pits penetrating deep into the copper tube wall was indeed much smaller in the very low-dose inhibitor tests than in the control, even though these conditions failed more quickly. For example, only 25-36% of the pits in these tests with low levels of inhibitors penetrated 80% of the wall, whereas 75% of the pits did in the control. The low NOM (i.e., 0.01 mg/L) test at large-scale also appears to have accelerated the maximum pit propagation rate; and, in this case, just 6% of pits penetrated 80% of tube wall while 14% of pits did in the corresponding control.

At higher dosages of phosphate, silica and NOM, and when E_{pit} was reached and pits formed, computed maximum and average pit propagation rates were reduced significantly. Chlorine demand data indicates that these constituents cathodically inhibited pitting in these

cases, in addition to any anodic inhibition that occurred. Not only was the average chlorine demand lower in the tests with higher inhibitor dosages (Figure 2.8), but so was the initial chlorine demand measured after just 72 hours (not shown). This suggests that the inhibitors were directly preventing the chlorine reduction (i.e., cathodic) reaction. Mechanistically, phosphate, silica and/or NOM inhibitors probably form a protective film or scale that hinders chlorine interaction with the copper surface. Because each of these species is anionic at high pH – as is hypochlorite (OCl^-) – it is also possible that they are drawn to a net positive copper surface, and are held there in the electrical double layer, where they repel hypochlorite and effectively reduce chlorine the chlorine- copper interaction.

Although ozonated NOM was unable to delay pit initiation to the same degree as un-ozonated NOM, its effects on pit propagation rates were nearly identical to those of un-ozonated NOM. Both reduced the average propagation rate by about 50% (vs. control). In contrast, the acetate and glucose mixture did not reduce the average pit propagation rate whatsoever. This suggests that certain fractions of organic matter present in potable water may have different dose-response behavior.

Increased alkalinity also appears to have reduced pit propagation rates, which is consistent with the idea that pits grew very slowly (or stopped growing soon after initiation) in this test, despite probably being initiated at similar times as in the control. The relatively low chlorine demand in this test (Figure 2.8) corresponds to a reduced rate of the cathodic reaction, which in turn reduces the rate of pit growth.

DISCUSSION

Free Chlorine

In distribution systems with water characterized by high pH and low alkalinity, decreasing free chlorine residual across the system (e.g., reduced dosing at the treatment facility perhaps with use of booster stations to achieve adequate disinfection) would probably reduce but not eliminate pitting attack. Based on results of this work, a “safe” lower limit on free chlorine to prevent pitting in this water type cannot be ascertained under continuous flow conditions, and if it exists, the "safe" level of chlorine would be less than 0.4 mg/L. Since most test work to date has been conducted at continuous flow^{3,5,16} – which markedly increases pitting,² but is only representative of specific sections (e.g., hot water recirculation lines) of premise plumbing systems – more research is needed to investigate dose-response effects of chlorine at less frequent flow. This presents a real challenge for future practical studies because it will surely necessitate very long test durations.

The present findings with respect to the effects of free chlorine residual on copper pitting are consistent with some prior observations. Lytle and Schock demonstrated that free chlorine residuals of just 0.3-0.8 mg/L could cause some pits in high pH (i.e., ~9) and low alkalinity (i.e., ~40-80 mg/L as CaCO₃) waters in continuously recirculating pipe-loops at relatively low flow velocity (i.e., ~1.1 ft/s) over a 99 day experimental time.³ These pits were relatively shallow compared to those produced herein, with the deepest reported as 0.2 mm deep. Lytle and Nadagouda reported that an Ohio community experiencing copper pitting problems in high pH (i.e., ~8.3) and low alkalinity (i.e., ~40 mg/L) waters had a free chlorine residual of only about 0.5 mg/L; the water also had a natural silica concentration of about ~4.7 mg/L (as Si).¹⁶ Interestingly, pitting was limited to cold water lines and measured free chlorine in hot water lines

was less than in cold (i.e., 0.3 vs. 0.5 mg/L). Additionally, copper pinholes were reported to occur roughly 4-6 years after plumbing installation. In other field accounts of copper pinholes where free chlorine residual is higher, leaks have been reported to occur much faster.¹ On the basis of free chlorine residual, the above observations are not inconsistent with the present findings that higher chlorine can initiate pitting more quickly than lower chlorine.

Using CMEA's in relatively short-term experiments, Cong and Scully demonstrated that chlorine levels as low as 1 mg/L could cause copper pitting in a similar water quality as that used in the present work (i.e., control water with aluminum solids added).²⁸ They also showed that pitting severity (based on a computed "pitting factor" and maximum total anodic charge) increased with chlorine concentration, which may have been partially related to the short duration of the experiments (6 days) or the near stagnant conditions (i.e., chlorine levels depleted more rapidly at copper surface for low chlorine residual tests). The authors acknowledged that differing flow conditions and exposure times may alter their prediction. Thus, at higher flow and with longer exposure time, the level of chlorine needed to induce pitting in the CMEA experiment may be lower. The impacts of exposure time illustrated in the present work are certainly consistent with this hypothesis. The impacts of flow have been reported elsewhere,^{2,7,18} and increased velocity and frequency were found to increase pitting propensity.

Alkalinity

Higher alkalinity did reduce pit propagation rates, unlike free chlorine, which seemed to be primarily related to pit initiation. Large increases in alkalinity (i.e., 150 vs. 34 mg/L as CaCO₃ in the control) slowed pit propagation – consistent with observations of Lytle and Schock³ – but severe pitting occurred over the 490-day test duration nonetheless. Alkalinity did not seem to significantly influence pit initiation time, and it is likely that pitting would eventually

initiate in high pH, higher alkalinity waters (i.e., similar to the high alkalinity condition herein) even at lower chlorine residuals. Further work is certainly necessary to elucidate the competing effects of chlorine to initiate pits and alkalinity to reduce pit propagation, and to determine if a threshold ratio for pitting exists between these two constituents. To date, pitting has not been shown to initiate without free chlorine in high pH waters, although very long experiments (i.e., on the order of years to decades) may be needed to confirm that pitting does not occur without chlorine.

Phosphate and Silica

Overall, for pitting caused by high pH, free chlorine and low alkalinity, phosphate or silica inhibitor dosing was confirmed to be a relatively effective mitigation strategy, as has been reported elsewhere.^{3,5-7} At sufficient dosages, these constituents might completely inhibit pitting by hindering the cathodic reaction (i.e., chlorine reduction), and preventing initiation of pits. If pits do initiate (or initiated prior to inhibitor dosing), phosphate or silica may reduce pit propagation rates, or perhaps stop propagation entirely. However, it is difficult to predict what the threshold dosages may be due to discrepancies between small- and large-scale tests. For example, just 0.1 mg/L phosphate was sufficient to inhibit pitting in the small pipe-loop (86 day test), but pits and ultimately pinholes developed in the large loop with the same phosphate dose (490 day test). This highlights the potential importance of exposure time and copper tube length in precisely determining the effectiveness of an inhibitor at a given dose.

In the case of silica, there does seem to be a minimum dosage which had no effect on pitting (i.e., 0.1 mg/L as Si in the current work). Practically, this could also be the case for phosphate, and may explain why, despite naturally occurring levels of these constituents, some distribution systems experience copper pitting incidents. As mentioned above, this was indeed

the case for an Ohio community investigated by Lytle and Nadagouda which experienced copper pitting problems despite a natural silica level in water of about 4.7 mg/L (as Si).¹⁶ Another example is a Maryland distribution system that has been plagued by copper pinholes, attributed to high pH, free chlorine and aluminum solids, which has a natural silica level of about 3-3.5 mg/L (as Si).²⁹ Alternatively, mechanisms initiating and propagating pitting during stagnation could be quite different than those for continuous flow. For example, prior work under conditions more representative of flow in premise plumbing suggested that aluminum solids would markedly increase pitting,^{2,18} but later work that has been conducted under continuous flow has indicated the aluminum solids are not necessary and may even have an inhibiting effect.^{3,8,30}

Practically, phosphate inhibitors have successfully been introduced to real distribution systems in attempt to mitigate pitting. At the Maryland system mentioned above, marked reductions in pinhole failures were reported since introducing ortho-phosphate.²³ In two Tennessee distribution systems, wherein copper pinholes were suspected to be caused by high pH and high free chlorine residual, dosing of ortho- or ortho/poly-phosphate blends (in combination with pH reduction) also seemed to quickly reduce pitting problems.³¹ Additionally, Lytle and Nadagouda anecdotally reported that, in comparison to the Ohio community that was experiencing pinhole failures and had no detectable phosphate in the water, a neighboring community with very similar water quality (i.e., pH, chlorine, alkalinity) except for the presence of phosphate (i.e., about 0.4 mg/L as P from poly-phosphate dosing) did not generally have pinhole leaks.¹⁶

Despite several successful efforts to mitigate copper pitting in potable water systems with phosphate inhibitors, it should be noted that phosphate (and likely silica) may not perform as

desired in cases where pitting is caused by factors other than chlorinated, high pH and low alkalinity water. For example, a Florida utility attempted to mitigate a pinhole leak outbreak by dosing ortho- and then poly-phosphate inhibitors, but little, if any, reduction in leaks was observed thereafter.³² This could be due to the fact that a different mechanism of pitting may be occurring in this water (e.g. sulfate-reducing bacteria or SRB),¹ or for other reasons that are poorly understood. The key point is that phosphate is not a cure to all pitting problems.

Utilities should also remain mindful of the possibility of an “optimally bad” dose of phosphate, silica or other inhibitors conventionally categorized as anodic inhibitors. As illustrated by work presented herein, it does appear that at very low concentrations, these inhibitors may indeed accelerate the time-to-pinhole leak failure, even as they reduce the overall number of pits on a copper surface. However, further research is certainly needed to determine what threshold values might be applicable in real potable water systems and at other pHs.

Natural Organic Matter

It has previously been suggested that recent trends in NOM removal from potable water may render some waters susceptible to copper pitting.¹⁰ The current work does confirm that NOM may well reduce pitting, at least to some extent, in high pH waters with free chlorine. Results of the current work showed that even very low levels of NOM (i.e., 0.05-0.1 mg/L as TOC) could significantly delay pit growth – presumably by delaying the time-to-pit initiation and decelerating pit propagation. Ultra-low levels (i.e., 0.005-0.01 mg/L) appeared to actually make pitting worse (in terms of maximum pit propagation rate), indicating that an optimally bad level of NOM may exist.

It appears that ozonation of NOM, as is commonly practiced in water treatment, reduces the capability of the resultant NOM to delay pit initiation. And short-chained, generic organics

(i.e., as represented by acetate and glucose here) are even less effective. Practically, this may explain why certain waters with relatively higher organic carbon concentrations (i.e., TOC) in the form of low molecular weight organics might still be very susceptible to copper pitting corrosion, and also highlights a challenge in determining threshold levels of organic matter (as measured by TOC) that may be needed to inhibit pitting in specific waters. Moreover, maintaining higher NOM concentrations in finished waters with free chlorine residual would certainly represent a controversial mitigation strategy due to increased potential for disinfection by-product (DBP) formation. Even if threshold levels of NOM are determined, further analysis is needed to weigh the costs and benefits of targeting higher levels of NOM to inhibit pitting.

SUMMARY AND CONCLUSIONS

Pitting corrosion can lead to rapid failure of copper plumbing tubes, and one proven cause is aggressive potable water, characterized by high pH, low alkalinity and free chlorine residual. Potential mitigation strategies were investigated in this work, and results indicated that:

- Decreasing free chlorine residual reduces the rate and extent of pit initiation. But, under conditions of continuous flow after 15 months, pits could still initiate even with moderate levels of free chlorine (i.e., 0.4 mg/L) in an aggressive water.
- Increasing alkalinity may decelerate the rate of pit propagation; however even very high alkalinity may not completely inhibit pitting.
- Addition of sufficient phosphate or silica concentrations can completely inhibit pitting in aggressive waters by hindering pit initiation; and at moderate concentrations, pit propagation may be slowed even if pits are initiated. But, at very low levels, these constituents may actually reduce time-to-pinhole leak failures.

- Relatively low concentrations of NOM (as TOC) can dramatically slow both pit initiation and pit propagation. It is unclear how much NOM may be needed to completely inhibit pitting, especially considering that some fractions of organic matter may have a much lesser ability to stop pit initiation.

Given experimental results and the success of field trials discussed here, phosphate inhibitors currently appear to be the best alternative for copper pitting mitigation in systems with chlorinated, high pH and low alkalinity waters.

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CHAPTER 3: REVIEW OF BRASS DEZINCIFICATION CORROSION IN POTABLE WATER SYSTEMS

Emily Sarver, Yaofu Zhang, and Marc Edwards

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ABSTRACT

Brass dezincification corrosion is re-emerging as a significant problem in potable water systems due to corrosion product (meringue) build-up and pipe blockage, fitting bursts, lead contamination events and pitting failure. Dezincification can occur as a uniform or localized process, with or without meringue build-up. While resistant brasses have been developed and are available for use in potable water systems, it has become commonplace in many markets to use alloys susceptible to dezincification due to their low cost. It is accepted that high chloride, low hardness and low alkalinity waters are especially prone to dezincification, but little research has assessed influences of modern potable water practices, such as chloramination or addition of constituents such as corrosion inhibitors. Moreover, there has been virtually no research directed at evaluating impacts of physical exposure conditions, such as brass location within a system, as a contributing factor to service failures. This paper provides a comprehensive overview of dezincification in potable water systems and summarizes prior work regarding effects of water chemistry. A conceptual framework is also developed to understand the potential roles of various physical factors (e.g., flow conditions and galvanic connections) as contributors to rapid dezincification. Finally, strategies for avoiding or overcoming dezincification problems in potable water systems are discussed.

INTRODUCTION

Brass failures in building plumbing systems resulting from dezincification corrosion can be expensive, result in water resource loss, create conditions suitable for mold growth, and decrease consumer confidence in the safety of the public water supply. There are also health concerns due to links between dezincification and increased lead contamination of potable water from brass./1, 2, 3/

For many decades, well-established problems associated with brass dezincification corrosion in potable water were considered “solved” by use of low-zinc or dezincification resistant (DZR) brass alloys. However, there has been a resurgence in use of high-zinc brass fittings in some countries (e.g., the United States) which are relatively inexpensive and easy to manufacture, in both plastic tube (e.g., cross-linked polyethylene) and traditional copper pipe plumbing systems. In fact, there have recently been several high profile class-action lawsuits in the United States related to failures resulting from use of the high-zinc brasses. For example, a lawsuit surrounding hundreds of sub-divisions (more than 30,000 individual homes built between 2001 and 2004) impacted by dezincification failures in Nevada was recently settled with damages approaching 100 million dollars./4/

When outbreaks of dezincification failures occur in a locality, there is widespread confusion amongst all stakeholders (homeowners, water utilities, contractors, etc.) as to the factors contributing to dezincification failures, terminology, and possible remedial strategies. This paper provides an overview of existing understanding of dezincification in potable water systems and summarizes key research results, which generally pertain to the brass alloy itself and water chemistry. Additionally, hypotheses are developed regarding underappreciated physical factors associated with modern plumbing practice, which have not been specifically researched

to any great extent. Finally, means for avoiding dezincification are reviewed and discussed, and arguments are made for more stringent plumbing codes associated with use of brass alloys in potable water systems and development of standard test methods for determining dezincification propensity of potable waters.

Manifestations of Dezincification Corrosion in Water Systems

Dezincification is a dealloying process resulting from the selective leaching of zinc from brass (a Cu-Zn alloy). Dezincification can be localized to certain parts of the brass, resulting in deep regions of spongy brittle copper, which appear as red patches on the brass surface. This is termed “plug” dezincification (Figure 3.1). Plug dezincification can lead to component failures if the affected regions penetrate deep enough within the metal to compromise mechanical integrity. Dezincification can also attack brass surfaces more uniformly, in which case it is referred to as “layer” dezincification. This tends to result in shallow regions of porous copper, which also exhibit a characteristic uniform red color. Layer dezincification can contribute to brass fitting fragility and increase the likelihood of fracture under mechanical stress.

There have been considerable efforts dedicated to differentiating between the plug and layer types of dezincification and to determining under what conditions each might develop, but solid conclusions have yet to be reached. For example, Nicholas observed from field experience that dezincification attack is often non-uniform, and there is no clear evidence of fundamentally different mechanisms in these two types of attack.⁵ Regardless of attack mechanism, it is clear that substantial and costly damages can result from dezincification failures and associated leaks, especially when failures occur in buildings.

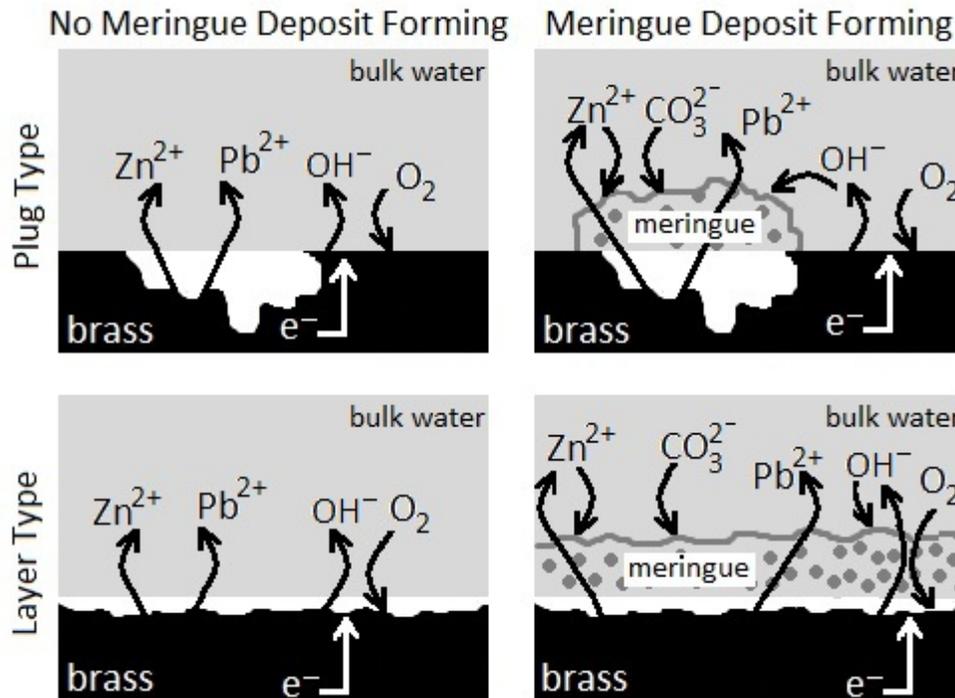


Figure 3.1: Dezincification can occur as either the plug (upper left) or layer (lower left) type, either of which may or may not lead to meringue deposition (right). Plug dezincification affects isolated areas of the brass and penetrates into the brass surface, whereas layer dezincification attacks the surface fairly uniformly.

The most commonly cited problem associated with dezincification is the formation of “meringue” deposits on brass components, which can physically block water flow (Figure 3.2). Meringue is a characteristic white, voluminous and tenacious deposit that is visually reminiscent of a meringue dessert topping. It tends to form when pH is relatively high (above about pH 8.3) and zinc solubility is low, and is typically a basic zinc carbonate/6/ but may incorporate dissolved constituents of the brass itself or constituents of the system water. Meringue deposition can occur as part of either plug or layer dezincification, and in extreme situations the deposit can completely stop water flow through the brass device and associated plumbing line.

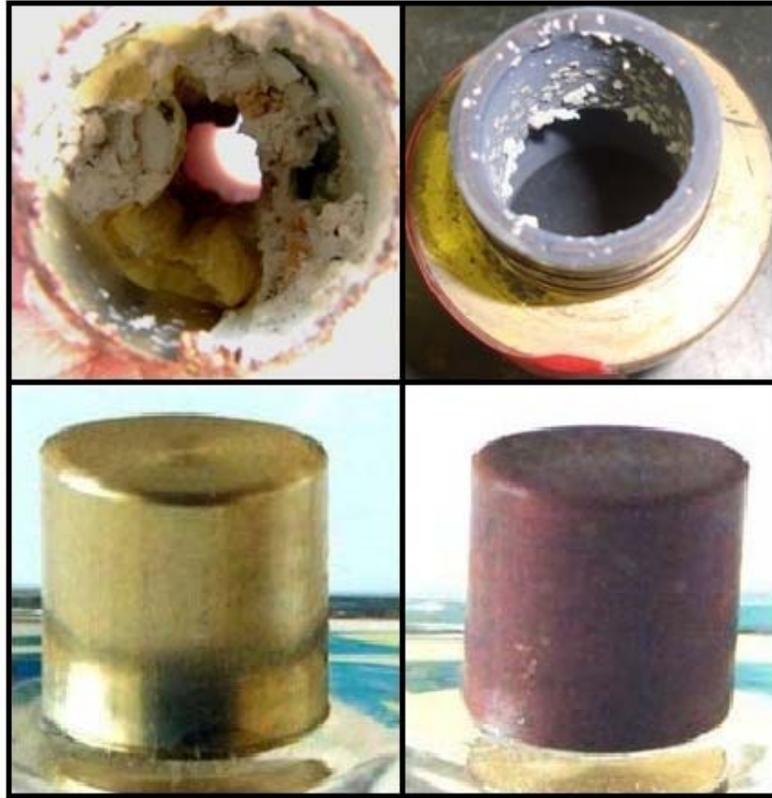


Figure 3.2: Meringue build-up inside a brass fitting can effectively block flow (upper left). After several months of plug dezincification, meringue build-up is evident on a brass fitting (upper right). As brass undergoes layer dezincification, its characteristic yellow surface (lower left) turns to a reddish color due to copper enrichment (lower right).

In addition to component failures and associated water damage, release of minor brass alloy constituents is also possible (Figure 3.1). Lead is a component in many brasses manufactured for use in potable water and even brass advertised as “lead-free” can legally contain up to 8% lead. The potential for lead release via brass corrosion is increasingly of concern/^{7/}, and the literature suggests a relationship between the occurrence of dezincification and persistent lead leaching in many potable water systems/^{1, 2, 3, 8/} and in “green” buildings./^{9/} Unfortunately, relatively little research has been conducted conclusively tying the two phenomena together. Some have hypothesized that lead is present in brass alloys as small “islands”, rather than being well mixed into the solid solution of copper and zinc, and that the

porous structure produced by dezincification may allow lead to be released more rapidly than would occur otherwise./10, 11/ Work by Triantafyllidou et al. (2007) demonstrated that lead leaching could increase with time when dezincification was occurring in low alkalinity waters/1/, and this trend was confirmed by Maynard et al./10/ The latter study speculated that the porous surface structure produced by dezincification may promote lead release either by enhancing diffusion or allowing lead particulates to detach from the surface.

In practice, the different types of dezincification can occur concurrently in the same water or even on the same fitting, due to different local chemical, physical and hydraulic conditions on the exposed surface. While some earlier research associated meringue-type blockage with layer dezincification/12/, Nicholas noted that if meringue was removed from a brass component plug-type red pits were often observed underneath./5/ Nicholas also argued that conditions favoring meringue deposits (e.g., high pH and low zinc solubility) are often independent from those thought to encourage the underlying plug or layer dezincification, (e.g., somewhat occluded vs. fully exposed brass surfaces).

Basic Electrochemical Reactions Driving Dezincification

The fundamental mechanisms by which dezincification will occur are relatively well understood. The simplest is a singular mechanism, in which the only significant anodic reaction involves zinc metal oxidation and dissolution from the brass surface (Table 3.1). The electrons released by this reaction are consumed by a cathodic reaction via reduction of either oxygen or chlorine supplied from the bulk electrolyte (i.e., water).

Dezincification can also occur by a dual mechanism, in which both copper and zinc are oxidized and dissolved from the brass surface. As the soluble copper accumulates in the water near the dezincifying surface and if oxidation-reduction potential is low enough, an equilibrium

between the cupric ion in the water and metallic copper is established. In that event, a substantial fraction of the copper that dissolves will re-deposit or “plate” back onto the dezincifying metal surface, and the net material loss is still via leaching of zinc (Table 3.1).

Table 3.1: Key electrochemical half-reactions generally associated with brass dezincification in potable water.

Half Reaction	Standard Potential (vs. SHE)	Name	Location
$Zn^0 \rightarrow Zn^{2+} + 2e^-$	0.762V	Zinc Oxidation	Dezincifying Surface
$\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$	0.814V (pH=7)	Oxidant Reduction	Cathodic Surface
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36V		
$Cu^0 \rightarrow Cu^{2+} + 2e^-$	-0.340V	Copper Oxidation	Dezincifying Surface
$Cu^{2+} + 2e^- \rightarrow Cu^0$	0.340V	Copper Deposition	Dezincifying Surface

Regardless of whether dezincification is occurring via the singular or dual mechanism, the key point is that zinc is preferentially leached from the metal relative to copper. If dissolution of both metals occurs without re-deposition of copper, electrochemical corrosion is still occurring but is defined as uniform brass corrosion and is not dezincification. Uniform brass corrosion generally seems to be self-limiting and, in the context of plumbing system performance and longevity, is usually preferred to dezincification-type attack.

The corrosion mechanism is controlled by both the oxidation-reduction potential (ORP) and the water chemistry at the dezincifying surface. Thus, it is useful to consider the potential-pH conditions under which each mechanism is thermodynamically predicted to occur (Figure 3.3).

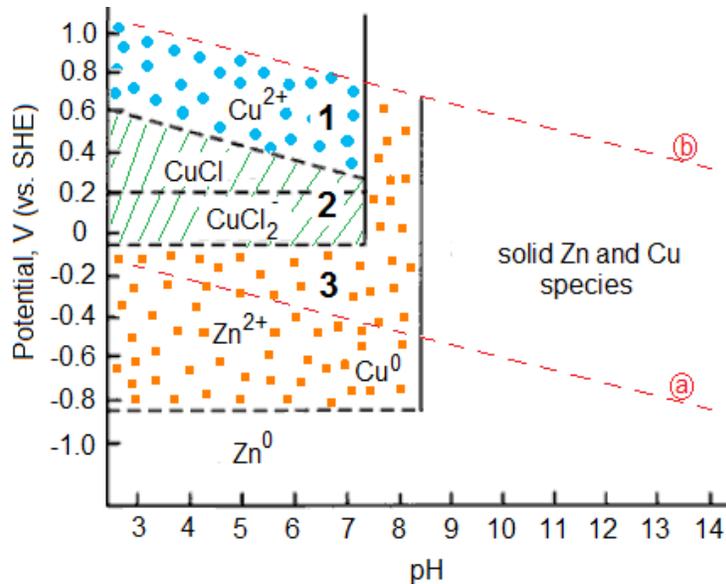


Figure 3.3: Illustrative potential-pH diagram for 70-30 brass in 0.1M chloride solution (adapted from Heidersbach & Verink 1972/18/). Region 1 represents uniform brass corrosion via copper and zinc dissolution with no copper re-deposition; 2 represents dezincification via copper and zinc dissolution with copper re-deposition; and 3 represents dezincification via selective zinc leaching alone. 2 is particularly relevant to localized environments where chloride concentrations are elevated and pH is reduced. Between lines a and b water is stable. Depending on water chemistry (e.g., chloride concentration) and brass composition, regions will shift.

FACTORS AFFECTING BRASS DEZINCIFICATION

Experience and electrochemical considerations indicate that the key factors which determine the type and rate of dezincification include the alloy type, water chemistry and physical factors. Each of these issues is addressed separately in the sections that follow.

Alloy composition

“Brass” refers broadly to a range of alloys with varying ratios of copper and zinc. Brasses may also contain a variety of other elements, which may be naturally present or intentionally added to the alloy. The convention in naming brass alloys is to refer to their relative percentages of copper and zinc. For example, 70-30 brass refers to a common alloy which is approximately

70% copper and 30% zinc. Alloy composition is a critical factor in determining the susceptibility of brass to dezincification corrosion.

Zinc Content

The zinc content of brasses typically ranges from 3 – 45%, and the percentage of zinc controls many physical properties of the alloy. With zinc content lower than about 30%, the brass generally exists in a single alpha phase, and both tensile strength and elongation ability tend to improve as zinc content increases./13, 14, 19/ When the zinc content is between about 30 to 40%, tensile strength and machineability improve with higher zinc, but elongation ability is reduced./14/ Such brasses generally have two phases (i.e., alpha and beta) and are therefore termed “duplex” brasses. In addition to having good surface finishes, duplex brasses are well-suited for forging (hot stamping), which tends to make manufacturing less expensive than those brasses requiring casting methods./11, 14/ When the zinc content rises above 45%, the alloy tends to become very brittle which is problematic for use in plumbing systems./14/

Zinc content is also a key factor in determining the susceptibility of brass to dezincification (Figure 3.4). Brasses with zinc content below about 15% are generally considered resistant to dezincification/15, 16, 17/; this threshold is based mostly on field experience, but it is rare that brass with less zinc exhibits serious dezincification problems. Brasses with higher zinc contents, including alpha brass with 15-30% zinc and duplex brass (> 30% Zn), can be susceptible to dezincification attack under some circumstances./16/

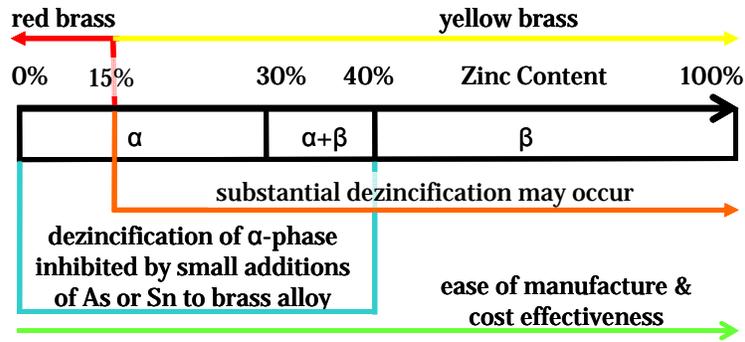


Figure 3.4: General trends for brass alloys as zinc content is varied.

Effects of Alloy Additives

A substantial amount of effort has been invested in attempting to inhibit dezincification by adding trace constituents directly to the alloy as per a prior review article/16/; a summary of key results is provided in Table 3.2. While some constituents may render alpha brass (and the alpha phase of duplex brass) relatively immune to dezincification/6, 18, 16/, inhibiting the dezincification propensity of beta brass has proven more difficult./5, 18/ Arsenic and tin are the most common alloy additives, which can profoundly inhibit dezincification of alpha brass even at trace levels, and benefits from these constituents have also been observed for duplex brass./19/

Table 3.2: Observed effects of various alloy additives on brass dezincification propensity; partially summarized from Copper Development Association report./16/

Additive	Observed Effect on Dezincification Propensity	Researcher(s)	Source Cited
Arsenic	Inhibits dezincification of 70-30 alpha brass	Bengough and May (1924)	Bengough and May (1924)
	Increases dezincification rate of 60-40 brass at 0.25% As	Sullivan (1971)	CDA (1993)
	Variable results for 70-30 and 60-40 brasses	Lombardi (1954)	CDA (1993)
	Inhibits dezincification	Nothing (1962)	CDA (1993)
	Inhibits dezincification of 70-30 alpha brass up to 0.05% arsenic	Ming and Ruon (1963)	CDA (1993)
	Negligible effects up to 0.014% As; inhibits dezincification of all tested brasses at 0.024% arsenic	Crampton and Burghoff (1941)	CDA (1993)
	Inhibits dezincification of 70-30	Pryer and Giam (1982)	CDA (1993)
	Inhibits dezincification of 60-40 brass with 0.1% As, and navel brass with 0.05% As and	Karpagavalli et al. (2006)	Karpagavalli et al. (2006)

	1% Sn		
Antimony, Phosphorous	Variable results for 70-30 and 60-40 brasses	Lombardi (1954)	CDA (1993)
	Inhibits dezincification	Nothing (1962)	CDA (1993)
Aluminum	Inhibits dezincification of 70-30 alpha brass	May (1938)	CDA (1993)
	Negligible effects for alpha or duplex brass	Kenworthy and O'Driscoll (1955); Heidersbach (1968)	CDA (1993)
	Negligible effects for duplex or beta brass	Weldon (1957)	CDA (1993)
	Retards dezincification of alpha and beta brass	Oishi et al. (1982)	CDA (1993)
	Retards overall brass corrosion	Beccaria et al. (1989)	CDA (1993)
Tin	Inhibits dezincification for 60-40 brass with 2% Sn, but accelerates dezincification of 60-40 leaded brass	Karpagavalli et al. (2006)	Karpagavalli et al. (2006)
	Inhibit beta brass and deteriorate alpha brass	Desch and Whyte (1913)	CDA (1993)
	Inhibits dezincification of alpha brass	Bengough and May (1924)	Bengough and May (1924)
	Inhibit dezincification of 70-30 alpha brass	Pchelnikov and Marshakov (1986)	CDA (1993)
	Negligible effects for duplex or alpha brass from 1.2 to 3.2% Sn	Weldon (1957)	CDA (1993)
	Inhibits dezincification of 70-30 brass when added with Al	Beccaria (1989)	CDA (1993)
	Optimal dezincification inhibition of 60-40 brass at 1% Sn in sea water	Pai et al. (1987)	CDA (1993)
	Inhibits dezincification of navel brass with 0.5 % Sn and Ni	Sukegawa and Watanabe (1982); Oishi et al. (1982)	CDA (1993)
Silicon	Results in severe susceptibility of 60-30 brass to dezincification at 0.33% Si	Weldon (1957)	CDA (1993)
	Inhibition of dezincification increases with Si content up to 3.7% Si	Staley and Davies (1988)	CDA (1993)
	0.5% Si inhibits dezincification of 60-40 brass, but dezincification proceeds in 70-30 brass	Oishi et al. (1982)	CDA (1993)
Iron, Manganese, Nickel, Cobalt	Fe accelerates dezincification of beta brass	Desch and Whyte (1913)	CDA (1993)
	Fe accelerates dezincification of 70-30 brass	Bengough and May (1924)	Bengough and May (1924)
	Fe/Mn and Fe/Ni both result in brass susceptibility to dezincification	Bailey (1960)	CDA (1993)
	0.5% Fe or 0.5% Mn accelerates dezincification of 60-40 and 70-30 brass	Oishi et al. (1982)	CDA (1993)

	0.5-1% Ni inhibits dezincification of 70-30 brass	Bengough and May (1924); Oishi et al. (1982)	Bengough and May (1924); CDA (1993)
Tungsten	Inhibits dezincification of 70-30 brass at 0.5% W	Bengough and May (1924)	Bengough and May (1924)
Lead	Negligible effects	Colegate (1948)	CDA (1993)
	Inhibits dezincification of 70-30 brass	Bengough and May (1924)	
	Inhibits dezincification of 70-30 brass	Desch and Whyte (1913)	CDA (1993)
	Accelerates dezincification of 60-40 brass	Sullivan (1971)	CDA (1993)
	Negligible effects	Heidersbach (1968)	CDA (1993)
Bismuth	Accelerates dezincification of 70-30 and 60-40 brasses	Price and Bailey (1942)	CDA (1993)
	Negligible effects	Staley and Davies (1988)	CDA (1993)
Others	Yttrium accelerates dezincification of 60-40 brass, but inhibits dezincification of arsenical 60-40 brass	Sullivan (1971)	CDA (1993)
	0.1% Mischmetal (rare earth metals) reduced dezincification rate of 60-40 brass	Sullivan (1971)	CDA (1993)
	Gold and silver both inhibit brass dezincification	Kondrashin et al. (1989)	CDA (1993)

Water chemistry

Even if a brass alloy is considered highly susceptible to dezincification, the water chemistry to which the metal is exposed will play a key role in determining the type and extent of corrosion problems. The effects of individual water constituents on dezincification have received a considerable amount of attention; but synergistic effects and the complexities involved with film (or scale) formation are still largely undefined. Indeed, passive film formation by reaction with the water may exert significant control over the mechanisms of corrosion which are operative, in some cases completely protecting the brass whereas in other cases dramatically accelerating the attack. This section details general observations of dezincification propensity under varying water quality conditions and important effects of physical factors are described in a section that follows.

Prior research concluded that increasing chloride tends to increase dezincification propensity, particularly when hardness or alkalinity of the water is low. Other influential factors have also been identified, including pH, temperature, aeration, disinfectant type and concentration, other anions, and the chemical make-up of surface films or scales. Conclusions as to the role of individual constituents can vary from study to study, most likely because the scope, experimental methods and specifics of exposure have also varied widely. Table 3.3 summarizes the effects of individual water constituents and/or parameters on brass dezincification reported in the literature.

Table 3.3: Key observations regarding effects of water quality on brass dezincification.

Constituent/ Parameter	Researcher(s)	Dezinc. Type(s) Investigated	Key Observation(s)	Evaluation Method(s)
Chloride and Alkalinity	Turner, 1961	Meringue	High chloride to temporary hardness ratios promote meringue dezincification.	Visual observation; Field experience.
pH	Turner, 1965	Meringue	Meringue dezincification may occur in both hot and cold systems at high pH; Meringue only formed in hot systems at low pH.	Visual observation.
	Turner, 1961	Meringue	Meringue dezincification occurs at pH 8.3 or above.	Visual observation.
	Oliphant & Shock, 1996	Plug; Meringue	Meringue dezincification occurs at pH 8.2 or above; plug dezincification penetration occurs between pH 7.6-8.2.	Experience; Literature review.
	Jester, 1985	Plug; Meringue	Meringue dezincification occurs above pH 7.8.	Visual observation and experience.
	Simmonds, 1967	Non-meringue; Meringue	Meringue dezincification likely above pH 8.0.	Visual observation and experience.
	Nicholas, 1994	Plug; Layer; Meringue	Meringue dezincification occurs between pH 7.5-9; Brass surface passivates above pH 9.5; Critical pH is dependant on specific water.	Corrosion currents equated with meringue build-up.

Temperature	Lucey, 1973	Meringue	Increased temperature promotes hardness-salt precipitation and increased pH, which both support meringue dezincification.	Experience.
	Simmonds, 1967	Non-meringue; Meringue	Protective scale does not form in cold water, thus dezincification continues unchecked.	Visual observation and experience.
	Nicholas, 1994	Plug; Layer; Meringue	Increased temperature accelerates dezincification.	Corrosion currents equated with general dezincification rates.
	Oliphant & Shock, 1996	Plug; Meringue	Increased temperature accelerates dezincification.	Experience; Literature review.
	Abbas, 1991	Plug; Layer	Increased temperature accelerates dezincification, but not zinc dissolution.	Visual observation; Metal leaching data; Corrosion potential data.
Aeration	Turner, 1965	Meringue	Oxygen is necessary for meringue dezincification.	Visual Observation.
	Kelly, 1980	Non-meringue	Increased oxygen levels (via increased flow velocity) accelerates dezincification.	Corrosion currents were equated with general dezincification rates.
Free Chlorine	Ingleson, 1949	Un-specified	Chlorine (up to 0.4 mg/L) accelerates dezincification; effect of chlorine is minor compared to other water constituents.	Visual observation.
	Nicholas, 1994	Plug; Layer; Meringue	Chlorine (1-2 mg/L) doubles dezincification corrosion currents.	Corrosion currents equated with general dezincification rates.
	Risbridger, 1951	Un-specified	Chlorine leads to rapid corrosion of brass ball-valve seats.	Visual observation.
Chloramine	Stuart, 1988	Un-specified	Increased chloramine (between 0.1-1.0 mg/L) linearly increases dezincification depth.	Dezincification depth measurements.
	Moore, 1998	Un-specified	Chloramine increases dezincification as compared to (un-chloraminated) raw water	Dezincification depth equated with dezincification rate.
Sulfate and Chloride	Turner, 1961	Meringue	At moderate chloride to temporary hardness ratios, increased sulfate worsens	Visual observation.

			meringue dezincification.	
	Lucey, 1973	Meringue	Depending on sulfate concentration, chloride can either accelerate or not affect dezincification rate.	Corrosion currents equated with meringue dezincification rates.
	Oliphant & Shock, 1996	Plug; Meringue	Depending on chloride concentration, sulfate can either inhibit or promote meringue dezincification.	Experience; Literature review.
Nitrate	Turner, 1961	Meringue	Nitrate (up to 100 mg/L) has negligible effects on meringue dezincification.	Visual observation.
	Lucey, 1973	Meringue	Nitrate slightly reduces meringue dezincification.	Corrosion currents equated with meringue dezincification rates.
	Oliphant & Shock, 1996	Plug; Meringue	Nitrate reduces meringue dezincification, especially at high sulfate levels.	Experience; Literature review.
Fluoride	Turner, 1965, 1961	Meringue	Fluoride (up to 2 mg/L) does not affect dezincification.	Visual observation.
Silica	Turner, 1961	Meringue	Silica (up to 20 mg/L) has limited effects on meringue dezincification.	Visual observation
	Oliphant, 1978	Un-specified	Silica, when combined with zinc, can effectively inhibit dezincification.	Visual observations; Corrosion currents equated with unspecified dezincification rates.
Ortho-phosphate	Turner, 1961	Meringue	Orthophosphate (up to 1 mg/L) does not influence meringue dezincification.	Visual observation.
	Lucey, 1973	Meringue	Orthophosphate appreciably increases propensity for meringue dezincification.	Corrosion currents equated with meringue dezincification rates.
	Oliphant & Shock, 1996	Plug; Meringue	Orthophosphate, even at low levels, significantly increases dezincification rates.	Experience; Literature review.
	Oliphant, 1978	Un-specified	Orthophosphate stimulates dezincification.	Visual observations; Corrosion currents equated with unspecified dezincification rates.

Poly-phosphate	Oliphant, 1978	Un-specified	Polyphosphate, when combined with zinc, effectively inhibits dezincification.	Visual observations; Corrosion currents equated with unspecified dezincification rates.
Zinc	Oliphant, 1978	Un-specified	Zinc, when combined with silicate or polyphosphate, may effectively inhibit dezincification.	Visual observations; Corrosion currents equated with unspecified dezincification rates.
Conductivity	Jester, 1985	Plug; Meringue	High conductivity generally stimulates dezincification, but no quantitative relationship has been established.	Visual observation and experience.
	Simmonds, 1967	Non-meringue; Meringue	For non-meringue dezincification, low conductivity usually leads to slow corrosion, and high conductivity leads to rapid failure; for meringue dezincification, lower conductivity water may still cause failure.	Visual observation; Experience.
	Tabor, 1956	Meringue	Some ions accelerate dezincification and some retard it.	Weight loss; Experience.
Scale formation	Kumar et al., 2006	Un-specified	Sulfides can form a porous surface scale (or film), which may greatly accelerate the rate of dezincification	Corrosion currents equated with dezincification rates.
	de Sanchez & Schiffrin, 1982	Un-specified	Sulfide films accelerate corrosion of aluminum brass (22% Zn), perhaps by electro-catalyzing oxygen reduction,	Visual observation; corrosion currents equated with corrosion rates.
	Valcarce et al., 2005	Un-specified	Scales inoculated with <i>pseudomonas fluorescens</i> promote dezincification.	Corrosion currents equated with dezincification rates; Weight loss.

Chloride and Alkalinity

To provide a rule of thumb, the ratio of chloride to temporary hardness is widely cited as a key determinant in a given water's ability to support dezincification.^{/15/} "Temporary hardness" is an archaic measure of water chemistry, in which the amount of hardness (e.g., Ca^{+2} , Mg^{+2}) lost via precipitation upon heating is quantified. Dependent on circumstance, temporary hardness is sometimes well correlated to modern chemical measures that include alkalinity or total hardness of a water supply. The chloride to temporary hardness ratio was first suggested as a primary criterion for dezincification by Turner, who observed that waters with relatively high chloride and low temporary hardness (Table 3.3), and having a pH of about 8.3 or greater, were prone to causing meringue build-up.^{/20/} Using both laboratory and practical data, Turner empirically developed a diagram (simplified version shown in Figure 3.5) to indicate water quality regimes in which dezincification problems will likely occur based solely on chloride and temporary hardness concentrations.^{/20/} Turner's diagram has been adopted as a standard in predicting dezincification propensity based on water chemistry.

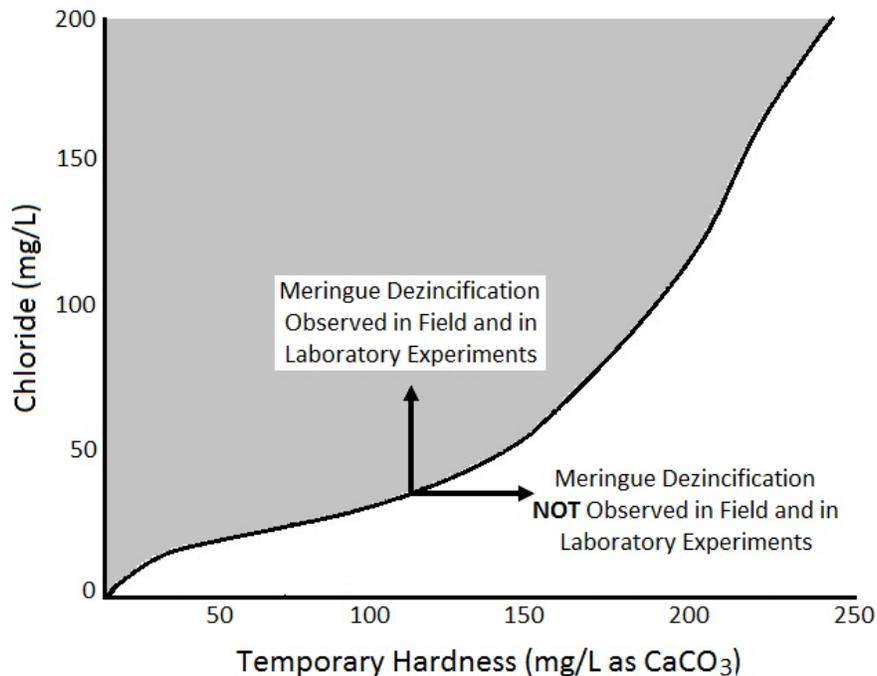


Figure 3.5: Simplified version of Turner's diagram for predicting meringue dezincification based on chloride and temporary hardness concentrations (adapted from Turner, 1961/20/). Waters in the shaded area are considered likely to produce meringue dezincification at pH 8.3 or above.

Because the work of Turner is cited so frequently (and often inappropriately) in relation to dezincification failures, it is worth noting the limitations of the work. First, the diagram was developed based on observations from particular regions in Great Britain which were impacted by a specific type of dezincification problem: blockage of hot water pipes by meringue build-up. Consequently, Turner's laboratory tests were primarily limited to synthesized water and natural waters that contributed to pipe blockage. Tests were generally conducted at or near pH 8.3, temperatures around 90°C, and with a galvanic connection between 60-40 duplex brass and copper. A second limitation of Turner's work is that it only assessed meringue dezincification, which is only one manifestation of dezincification-induced failures. Furthermore, the extent of dezincification was determined by visual observation of meringue-type corrosion products under low-power binocular microscope. No data on weight loss or metal leaching that would have

provided insights into other modes of dezincification were collected. A third limitation is that Turner's diagram does not account for many water constituents encountered in modern potable water systems including corrosion inhibitors (e.g., orthophosphate or zinc orthophosphate), secondary disinfectants such as free chlorine or chloramine, or natural organic matter – each of which may be expected to influence dezincification.

Additionally, Turner found that meringue build-up was accelerated in short-term testing if brass was galvanically connected to copper, and therefore, he conducted all tests under this condition. Recent research has demonstrated that, in some waters, the long-term effect of a galvanic connection to copper may be very different than the short-term effect, and the connection can also exert considerable influence on the mode of attack./1, 15/ Thus, dezincification of brass might proceed differently with and without a galvanic connection to copper.

The above is not a criticism of Turner's landmark work, which sheds considerable light on the problem of dezincification of brass in premise plumbing systems and has withstood the test of time. It is simply meant to highlight the fact that Turner's diagram and interpretations can only be applied with any confidence to a narrow range of systems and conditions. For dezincification problems not occurring as the result of meringue formation, such as lead leaching./1, 3, 10/ and brass failure from plug dezincification below pH 8.3, a relationship between Turner's diagram and real dezincification propensity and associated failures has not been established./5, 21/

pH, Temperature and Aeration

For meringue dezincification, Turner's field experience/20/ and further laboratory tests/22/ indicate that deposit build-up is favored at relatively high pH. Based on the experience

of actual water systems in the Mildura Urban Water Trust of Melbourne, Australia, Simmonds recommended that water authorities maintain pH below 8.0 to avoid meringue build-up./6/ While pH 8.3 is commonly cited as the level above which serious meringue deposits will occur, researchers tend to disagree on an exact value, probably due to significant differences in experimental techniques and waters tested (Table 3.3). For example, some authors have reported meringue formation in waters with pH only 7.5-7.8, and noted that below this range dezincification without meringue is favored./5, 15/ Jester concurred that meringue could form below pH 8.3, but he added that from pH 7.6-8.3 plug dezincification is favored at the lower end of the range while layer dezincification is favored at the higher end./12/ However, Nicholas determined that corrosion of brass between pH 7.5-9.0 occurred as general dezincification, meaning the pH did not specifically control the mode of attack./5/

Dezincification occurs both in cold and hot water systems, however, many authors have noted that leaks due to dezincification are relatively more common in hot systems./15,16/ This may be due to the fact that hot water systems are often seen to exacerbate the problem of meringue deposits. Simmonds and Lucey both found that heating enhanced dezincification by precipitating hardness salts (e.g., calcium carbonate) and increasing pH./6, 21/ Other researchers also observed that increased temperature accelerates dezincification rates./5, 15, 23/ For example, research by Nicholas indicated that dezincification rates doubled when the temperature was increased from 20 to 70°C./5/

Aeration can also significantly influence dezincification by mixing and by affecting the dissolved oxygen concentration in water. Turner's tests indicated that oxygen is necessary for occurrence of meringue dezincification, and he found that by replacing dissolved air in water with nitrogen gas the formation of meringue was eliminated./22/ Even low levels of dissolved

oxygen have been shown to support significant amounts of meringue dezincification, albeit at lower rates than when higher oxygen levels are present./17,22/ Jinturkar et al. studied brass corrosion in sulfuric acid solutions and also found that increased dissolved oxygen enhances corrosion./24/ Ingleson et al. reported that free carbon dioxide promotes dezincification as well./25/

Free Chlorine Residual and Chloramine

Free chlorine is often added to distributed water as a disinfectant. In some systems, free ammonia is also added to the water, in which case the chlorine and ammonia react to form chloramine. Both chlorine and chloramine are oxidants which can drive dezincification if they are reduced at a cathodic site (e.g., accept electrons released when zinc is oxidized). Due to their relatively high oxidizing power, either disinfectant may dramatically accelerate dezincification rates as compared to those achievable with dissolved oxygen alone.

Using visual observation as an indicator of dezincification rate, Ingleson et al. found chlorine concentrations up to 0.4 mg/L accelerate dezincification of duplex brass (Table 3.3)./25/ The beta phases of the brass were severely attacked leaving behind a spongy deposit of copper. Despite these results, the researchers believed that the effect of chlorination on dezincification rates was small relative to the impact of other factors in the water. Another study in Britain confirmed the deleterious and significant effects of chlorine: the corrosion of both cast and stamped brass was greatly accelerated by the presence of 1 ppm free chlorine./26/ Nicholas also concluded that chlorine worsens dezincification; he determined that addition of 1.0-2.0 mg/L generally doubled or tripled corrosion currents versus those obtained in the presence of oxygen alone./5/

Several studies have also looked at the effects of chloramination on dezincification (Table 3.3). Stuart, as cited by Nicholas⁵, observed that the penetration depth of dezincification increased linearly with chloramine concentration from 0.1-1.0 mg/L.²⁷ Shortly thereafter, Moore reported that, per weight loss measurements, an excessive dose of 5.6 mg/L chloramine to a raw water supply was surprisingly determined to be less aggressive than the raw water itself.²⁸ Moore surmised that a significant pH increase caused by chloramination possibly played a key role in this experiment, and upon later testing Moore observed that chloramination (at 4 mg/L) did indeed increase dezincification of brass as compared to raw water when pH was controlled.²⁹

In terms of relative aggressiveness of chlorine versus chloramine, the interpretation is quite complicated by the practical behavior of these oxidants and dosing strategies in real systems. For example, although the oxidizing power of chlorine is higher than that of chloramine, the practical circumstances under which each may be present will likely control the overall effects on dezincification. Often, chloraminated water is distributed at higher pH than is chlorinated water, which could directly impact meringue dezincification problems. Moore's observation of apparent decrease in corrosivity of raw water upon chloramination via weight loss measurements²⁸ might be explained by the fact that at increased pH, meringue was actually forming from the leached zinc. Thus, net weight loss in that study was low, despite potentially higher rates of dezincification due to the presence of chloramines which might be masked by greater meringue buildup.

Additionally, free chlorine tends to decay in distributions systems faster than chloramine, and is usually dosed at much lower levels to the water. The overall result may be that a switch from chlorine to chloramine might significantly increase the levels of total chlorine oxidant that

actually contacts brass in building plumbing. This could potentially result in increased dezincification failures of brass via meringue build-up in situations where use of chlorine disinfectant caused few problems. Indeed, a rash of brass faucet failures in the 1940's and 1950's was attributed to many utilities switching from chlorine to chloramine disinfectant./25, 26, 30/ On the other hand, increased pH of chloraminated waters may decrease occurrence of non-meringue dezincification – depending of course on other water quality parameters. Little research has been done so far on this topic, although it deserves consideration. Many utilities are switching from chlorine to chloramine disinfectant in the United States to control disinfection by-products and some are experiencing increased problems with corrosion of other metals like copper./31/

Finally, the observed effects of chlorine and chloramine on lead release from brass should be noted. Ingleson et al. showed that, despite the impacts on dezincification propensity, the presence of chlorine did not tend to significantly affect lead release from alpha phase brass, because the lead was released in both the presence and absence of chlorine./25/ Edwards and Dudi found that chloramine typically increased lead leaching from brass samples versus the same water with free chlorine alone./32/ However, they reported that the difference between the two scenarios was sometimes only within an 85% confidence interval, thus highlighting the need for further work in this area.

Other Water Quality Parameters

In addition to chloride, the effects of several other common anions have been considered, albeit to a lesser extent (Table 3.3). The influence of sulfate on dezincification is not straightforward. In Turner's original work, the presence of some sulfate was found to lower the amount of chloride required to cause dezincification, but exact sulfate concentrations were not

specified./20/ Lucey's findings appear to show a synergistic effect between sulfate and chloride./21/ He reported that, depending on sulfate concentration, the effects of chloride on dezincification could range from substantial to insignificant based on electrochemical measurements between experimental brass samples and copper pipe cathodes. For example, when sulfate concentration was less than 60 mg/L, chloride could be up to 250 mg/L without rendering the water aggressive. However, when sulfate was above 60 mg/L, chloride concentrations of just 60 mg/L were deemed problematic.

Turner reported that nitrate up to 100 mg/L has negligible effects on the build-up of meringue./20/ Alternatively, Lucey reported that nitrate slightly reduced a water's dezincification propensity at a given chloride level, especially if the water had a high sulfate content./21/ Oliphant's findings agreed with Lucey's with respect to the role of nitrate in reducing dezincification rates./13/

Turner also reported on the effects of fluoride on brass dezincification, and noted that the addition of fluoride up to 2 mg/L did not impact meringue formation./20, 22/ It is generally accepted that fluoride at or below 1 mg/L has negligible effects./5/

Based on measured galvanic corrosion currents between copper cathodes and brass samples, Oliphant concluded that silica may temporarily inhibit dezincification./13/ He suggested that in his experiments, lasting up to 48 days, silica may have changed over time from an ionic to colloidal form, as phenomenon previously asserted by Lehrman./33/ Furthermore, Oliphant reported that if the addition of silica is combined with approximately 1 mg/L zinc, stable and strong inhibitive effects were achieved./13/ This was concluded from a separate 25-day experiment, in which corrosion currents were measured to indicate dezincification rates, Based on visual observations of meringue build-up, Turner found, however, that silica has very

limited effects up to 20 mg/L./20/ The influence of silica on dezincification and meringue deposit formation deserves further study.

Phosphate corrosion inhibitors have been found to result in differing effects on dezincification, depending on the type and concentration of phosphate added to water (Table 3.3). Turner determined that 1 mg/L or less orthophosphate had no observable effects in a 30-day experiment as assessed by meringue formation./20/ However, Lucey determined that increasing orthophosphate concentrations from 1 ppm (as PO_4^{3-}) to 8 ppm generally led to substantial increases in dezincification propensity./21/ Lucey's results were based on data from a 4-day experiment. He computed a "corrosion index" (integration of measured corrosion currents over time) to theoretically determine the mass of metal oxidized. Oliphant's findings pointed in yet another direction: by relating corrosion currents to dezincification rates he found that 5 mg/L polyphosphate (as P) and 1 mg/L zinc markedly reduced dezincification in a water that otherwise caused serious problems. Effects of more realistic polyphosphate doses (up to 0.3 mg/L as P) have not been reported.

The discrepancies between the above findings may simply reflect the fact that form and function of corrosion inhibitors may change over time. It is also possible that the mechanisms by which poly- and orthophosphate operate in zinc rich solutions are different. Clearly, further studies are necessary to determine the efficacy of any type of phosphate as an inhibitor for dezincification corrosion.

As a general rule, it is believed that most anions, though not all, tend to increase dezincification propensity of brass. This effect is attributed to increased conductivity, although studies by Jester found no linear relationship between conductivity and the development of dezincification./12/ Indeed, Simmonds' field experience suggested that dezincification failures

can also occur at the lower end of the typical conductivity spectrum for potable water./6/ Tabor theorized that some decisive anions (e.g., chloride) are more important than others (e.g., nitrate) for initiating and propagating dezincification, as would be expected based on prior research in other fields./34/

Water chemistry can also influence dezincification by controlling formation of scales and deposits on a brass surface; the actual mechanisms by which scales might affect dezincification are discussed in a following section. It has been shown that scales contaminated with sulfides may form a porous layer of cuprous sulfide, which can greatly accelerate the rate of dezincification on the brass beneath./35/ de Sanchez and Schiffrin reported that corrosion of aluminum brass (22% Zn) is accelerated specifically by the ability of the sulfide film to electrocatalyze oxygen reduction./36/ In addition, scales laden with bacteria may also promote dezincification, as observed by Valcarce et al./37/ Compared with a sterile control condition, the presence of *pseudomonas fluorescens* in a surface oxide film increased the weight loss of 70-30 brass by a factor of nearly seven. In the sterile condition, pitting corrosion occurred on the brass surface, but both pitting and dezincification were observed in the condition inoculated with the bacteria.

Physical Factors

It is often observed that nearly identical brass components in a given building plumbing system can fail by dezincification at markedly different rates, even though they are obviously exposed to the same water. This suggests an inherent dependence of dezincification on local physical and environmental factors, which can include flow rate, galvanic connections between brass and other materials, surface condition and structure of the brass, and even the placement of brass within a system. Most prior research on dezincification in potable water has emphasized

the role of alloy composition and water chemistry, and relatively little work has been done which directly relates physical factors to dezincification. However, the work of the preceding sections can be synthesized and logically developed to provide a conceptual framework to explain how previously underappreciated physical factors may influence dezincification.

Separation of Anodic and Cathodic Sites and Development of Concentration Cells

If a clean piece of brass is placed into aerated flowing or stagnant water, both copper and zinc may dissolve from the brass surface until all the oxygen is consumed (Figure 3.6). The anodic and cathodic reactions will occur relatively uniformly over the entire surface. With time and upon exposure to additional oxidant (e.g., dissolved oxygen or free chlorine) during flow, the brass will gradually become completely coated with relatively thick zinc and copper scales, which greatly limit access of the oxygen to the cathodic sites, and thus the rate of corrosion will decrease. While some dezincification can and does occur in these situations, the corrosion is relatively more uniform and problems are less severe than for other situations discussed below.

If anodic and cathodic sites become separated for any reason, dezincification can accelerate and become self-perpetuating. At the anode, the pH drops markedly due to the Lewis acidity of the oxidized zinc and copper species, and chloride and other anions are actively transported to the anode from the bulk water and concentrated (Figure 3.6). To the extent that a mercuric (or other) deposit forms over the anode surface, that water at the anode tends to maintain an even lower pH and higher levels of chloride and soluble copper (cuprous and cupric). This is because diffusion of corrosion products from the anode via flow turbulence is reduced. At the distant cathode, the metal surface is protected from corrosion by connection to the anodic area, resulting in formation of very little protective scale. The lack of scale at the cathode also dramatically enhances the transport of oxidant to the cathodic surface, and removal

of the reaction products (i.e., hydroxide anions) from the surface (Figure 3.6). The net result is the formation of a very strong “concentration cell” with a self-perpetuating galvanic reaction that can maintain very high dezincification rates.

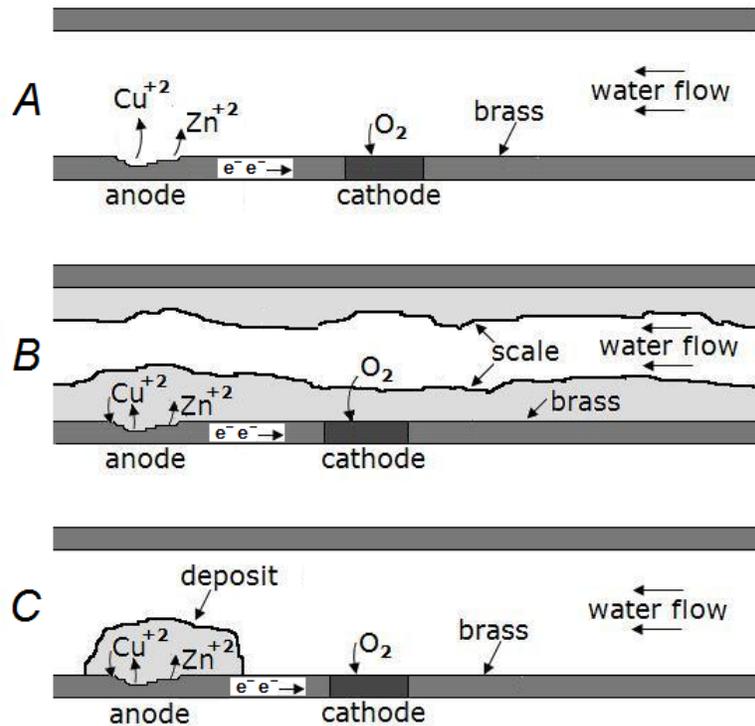


Figure 3.6: Potential manifestations of dezincification for a single piece of brass in potable water. On clean brass with or without flow, the anode and cathodes are located very near each other and corrosion proceeds uniformly (A). With time, deposits may grow and completely coat the brass surfaces (B), reducing diffusion of oxidant to the cathode and slowing dezincification. But if deposits form selectively at parts of the surface, then dezincification can be accelerated due to the low pH and high chloride near the anode (C). The lack of scale at the cathode can then allow for very high cathodic reaction rates.

Variable or Differential Flow in Case of Single Piece of Brass

Water flow has typically been treated as an “on/off” parameter in prior dezincification research, and most experimental work has been done under low-flow or stagnant conditions. Indeed, corrosion textbooks state that dezincification is encouraged by such conditions./38, 39, 40/ Seemingly in direct contrast with many textbooks are practical observations that brass corrosion (including dezincification corrosion) is often accelerated by water movement and

flow./17, 41/ This discrepancy is noted by Kelly et al. and is not inconsistent given considerations of separate anodic and cathodic areas used in the different experimental setups./17/

Specifically, any factor that tends to reduce the flow rate at the anode surface, or increase the flow rate at the cathodic surface, will promote dezincification. Lucey asserted that dezincification is typically under cathodic control./21/, or that the overall dezincification rate at the anode is controlled by the rate of oxidant reduction at the cathode. Thus, anything that increases the net cathodic reaction will worsen dezincification.

For a single piece of brass in isolation, three representative extremes may be defined for exposure in potable water (Figure 3.6). First, if the anode and cathode are both exposed to significant flow as in case *A*, rapid dezincification is not expected because corrosion is relatively uniform. If the oxidation-reduction potential of the system is relatively low, some layer-type dezincification may occur, but the rate will be low because a differential aeration cell does not develop.

In case *B* neither the anode nor the cathode is exposed to significant flow due to stagnation or formation of a thick scale layer (e.g., both sites are beneath a surface oxide film), and the scale restricts mass transport. In such situations, the corrosion rate is slow and is limited by hydrodynamic delivery of oxidant to the metal surface./42/ Soluble cuprous and cupric species may be at local equilibrium with the metallic copper, and some re-deposition may occur. Hypothetically, if zinc and or copper form non-porous precipitates, dezincification and/or uniform corrosion may be inhibited.

C represents a potential worst-case scenario for a single piece of brass because the rate of dezincification is highest due to rapid cathodic reactions and the attack is localized. As per case

B, when soluble copper reaches equilibrium with metallic copper, zinc is leached preferentially. But unlike *B*, there is a locally low pH, higher level of chloride and lower oxidant level at the anode, which could worsen dezincification by orders of magnitude. Plug-type dezincification is expected in this case, followed by meringue build-up if the water chemistry favors formation of basic zinc carbonate precipitates.

The bulk water chemistry can exert a strong influence on the strength of the dezincification reaction illustrated in case *C*. For example, high alkalinity water has a high buffering intensity, and can therefore maintain a much higher pH at the dezincifying (anode) surface. The ratio of chloride to other constituents such as bicarbonate and sulfate can determine the extent to which chloride is concentrated near the anode surface. This can have important implications relative to formation of cuprous chloride and other chloride complexes with oxidized zinc and copper species. Noting the high affinity of chloride for cuprous and cupric species, Lucey proposed that the formation of solid cuprous chloride (CuCl), in particular, on the dezincifying surface is especially important in promoting dezincification via the dual mechanism discussed previously./43/ Newman et al. agreed with the general effect of chloride but argued that it is the cuprous chloride anion (CuCl_2^-) which accelerates dezincification./44/

There are a number of circumstances by which scenario *A* or *B* may develop into *C* in potable water systems for an isolated piece of brass. For example, if turbulent flow were to remove a large piece of scale from *B*, non-uniform corrosion might then be induced with a cathode developing on the exposed brass surface. Or, between two threaded brass parts, a crevice exists that is naturally screened from the water and isolated from flow./45/ Finally, surface imperfections or deposits on the device might act to initiate scenario *C* when the brass would otherwise tend to corrode uniformly.

Following these lines of logic, text suggests surface cleaning of brass would remove scale and reduce the rate of dezincification./46/, but this is impractical for potable water systems. Cigna and Gusmano found that sandblasted brass surfaces were unable to develop a surface film of comparable protection to that of initially clean or oxidized surfaces in stagnant conditions./42/, as the film developed on the rough surface was not compact. While dezincification corrosion was not specifically studied, the above results suggest that rough brass surfaces (as opposed to smooth) may promote dezincification by encouraging localized environments beneath a porous scale. Minor defects in the brass surface may not pose such a problem; Bengough and May observed that superficial flaws in 70-30 brass condenser tubes did not usually cause serious corrosion./41/

Variable or Differential Flow in Case of Multiple Devices in a Plumbing System

Kelly et al. created and tested a scenario analogous to *C* using multiple pieces of brass in a pipe network./17/ This might mimic brass devices which are located throughout the plumbing network in homes or buildings. Sometimes a water line branch in a building is in service (i.e., water is flowing), whereas an adjacent water line may be completely stagnant. In such situations, the entire brass device located in the service line will be subject to flow, whereas those brass devices in the stagnant line will be out of flow. If they are electrically connected via conductive copper tube the brass devices out-of-flow will become anodic relative to those in-flow.

To measure the possible impacts of the above idea on brass corrosion, a series of experiments was conducted in a re-circulating flow apparatus with 60-40 brass electrodes./17/ Some brass specimens were exposed to flow (cathodes) but were electrically connected to others which were recessed from flow (anodes), As expected, the in-flow brass became highly cathodic relative to the out-of-flow brass. Moreover, as a cathode was subjected to increased flow rate, the

galvanic current between the cathode and anode increased. This observation was attributed to the increased availability of dissolved oxygen at the cathode. The authors also observed that when transitioning from laminar to turbulent flow conditions at the cathode, the corrosion current density at the anode increased by over an order of magnitude. It was asserted that the increased electron flow from the anode to the cathode indicated accelerated dezincification on the anodes, which seems highly likely given the above conceptualization. The authors noted that the anodes exhibited a characteristic red color of dezincification, although no soluble ion concentration or other data was used to verify the belief that zinc was leaching selectively.

Other Effects of Flow

In addition to the primary role of flow in removal and/or delivery of electrochemical constituents in potable water systems, other effects may be seen. In an early report on the topic of brass corrosion, Bengough and May recognized in 1924 the importance of flow with respect to air bubbles.^{/41/} They noted that impingement of bubbles could often remove the protective scale that sometimes develops on condenser tube brass, especially the tube end first contacted by water where more turbulent conditions were observed. Additionally, they reported that the corrosion rate tended to increase with the flow velocity, and the acceleration was primarily due to entanglement of air in the flow. Houghton came to similar conclusions.^{/47/} As discussed above, when only parts of a scale are removed from a single piece of brass, localized environments may more easily develop underneath the remaining scale as illustrated by case *C* in Figure 3.6.^{/48/}

Additionally, erosion corrosion should be considered. In this case, the shear stress and turbulence of the flow still acts to mechanically remove protective surface scale from part of the brass surface, revealing bare metal which is subsequently corroded when exposed to the water. In some situations the bare metal can become highly anodic (instead of cathodic as in case *C*),

while the metal beneath the remaining scale continues to be protected. Sakamoto et al. conducted laboratory tests wherein both 60-40 and dezincification resistant brasses were subjected to high-velocity water jets, which impacted the brass surfaces perpendicularly./49/ They reported that flow-induced localized corrosion (or erosion-corrosion), identified by the presence of ring-shaped grooves, was occurring in the vicinity of the jet impact for both types of brass. Furthermore, dezincification, identified by a distinct change in surface color, occurred along with the erosion corrosion on the 60-40 brass specimens. Weight loss data suggested that the corrosion rate increased with exposure time.

Moore and Beckwith also directly linked dezincification with erosion-corrosion in their investigation of brass tap-seat failures./50/ They cited deep radial grooves across the surface of the failed brass components and concluded that dezincification resulted in a fragile copper surface structure which was subsequently eroded by high-velocity water. Grzegorzewicz and Kuznicka linked accelerated turbulence to brass tube failures in heat exchangers/51/ and Efrid reported on critical shear stress for wall impingement of aluminum brass (22% Zn)./52/ Both of the aforementioned suggest the importance of erosion corrosion type phenomena in brass failures, albeit neither commented on dezincification specifically.

Concentration Cell Development Via Galvanic Connections

Dezincification on a single piece of brass, or between two pieces of brass exposed to differential flow, results via a concentration cell based on water chemistry differences at the surface of a single type of metal. A voltage drop or electrical current is present that can sometimes be measured experimentally as electrons flow between the anode and cathode sites. In most potable water systems, brass is often connected to copper, in which case dissimilar metal galvanic corrosion can occur. Copper is the more noble metal and may function as the cathode,

while the brass is the anode and is sacrificed. Due to these differences in electrochemical activity, galvanic connections between brass and other metals can dramatically increase the rate of dezincification.^{/53/} Additionally, the large surface area of the copper pipe network can also increase the rate of dezincification, since the copper pipe is the site of the cathodic reactions which are often rate limiting. Indeed, as mentioned previously, some researchers have purposefully connected copper to brass in their experiments in order to promote more rapid dezincification.^{/13, 21/}

Galvanic connections between copper and brass may also help to initiate rapid dezincification. For example, Nielsen and Rislund observed that when brass samples were attached to copper hooks, dezincification initiated more rapidly than in the instance of brass alone.^{/45/} As for the instance of a single piece of brass, three general scenarios may exist for the instance of a galvanic connection between brass and another metal. Figure 3.7 illustrates these scenarios for a connection with copper.

For a direct galvanic connection between clean pieces of brass and copper (case *D*), both copper and zinc may dissolve in aerated water due to the oxidation reduction potential at the cathode, as in case *A* of Figure 3.6. Larger cathode to anode surface area ratios will accelerate the intensity of electrochemical attack on the brass. Zinc may also dissolve preferentially due to the galvanic current alone. The difference in the standard potentials of the copper and zinc will be the driving force for dezincification, and should be generally dependent on the zinc content of the brass alloy (e.g., brasses with higher zinc contents behave more like zinc). If pH reduction and chloride build-up at the brass surface are minimized, the rate of dezincification in case *D* is expected to be slow.

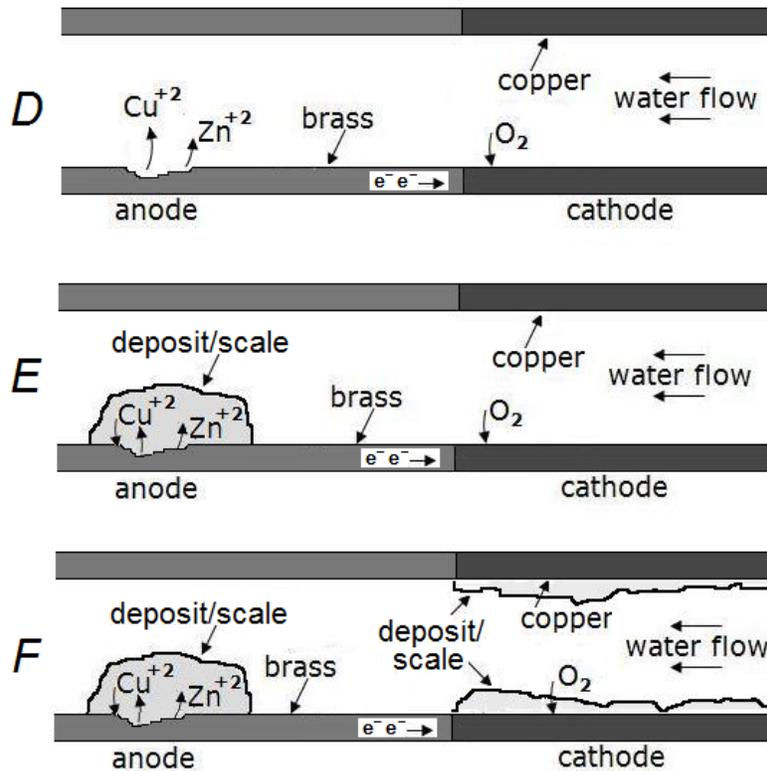


Figure 3.7: Potential manifestations of dezincification for a galvanic couple between brass and copper in potable water. D represents slow dezincification; E represents severe dezincification whereby a localized environment develops at the anode while the copper cathode is supplied with oxidant; and F represents dezincification as in E, only it is somewhat slowed by the loss of active surface area on the cathode.

In *E*, similar to case *C* in Figure 3.6, a localized environment develops at the anode (e.g., under a deposit or scale) while the cathode remains relatively clean such that there is little resistance to oxygen reduction. This represents the worst-case scenario in Figure 3.7, since the cathodic reaction is allowed to proceed at a high rate. In some situations, however, case *F* develops when the copper cathode is oxidized and covered with a scale that can be more or less protective, in which case the rate of the cathodic reaction is limited.

Some of the most comprehensive work regarding the effects of water composition on dezincification was carried out by the British Non-Ferrous Metals Technology Center (which has changed names numerous times throughout its existence), and much of that research was done

using galvanic connections between duplex brass and copper. In work by both Lucey and Oliphant, experimental set-ups analogous to D (except for variable cathode to anode ratios) were employed and the measured current between the metals was used to assess dezincification rate./13, 21/ Oliphant noted that dezincification of duplex brass became anodically controlled (i.e., controlled by the rate of zinc dissolution) when the copper cathode surface was more than eight times larger than the brass anode./13/ This observation is likely to depend on the specific system and is deserving of additional research, because in most practical situations the copper to brass surface area ratio far exceeds the 8:1 ratio.

Case of Differential Flow and Galvanic Connections

The case of combined conditions of differential flow and a galvanic connection between brass and a more noble metal represents a hypothesized “worst-case” scenario with respect to dezincification potential (e.g., Figure 3.8). Such a case is commonly encountered in traditional copper domestic plumbing systems wherein large sections of copper are directly connected to brass components. If, as shown in Figure 3.8, the brass is completely removed from frequent flow, but is electrically connected to copper that is exposed to water flow, rapid dezincification may occur. Driven by both the differential aeration/concentration and galvanic cell development, the anode will develop a locally low pH and oxidant concentration, but high anion and soluble metal concentrations. Meanwhile, the cathode surface will be maintained with bulk water-level oxidant concentrations as it is exposed to continuous flow. Meringue-type dezincification is expected to progress rapidly in this situation, perhaps leading to a blockage within the brass component.

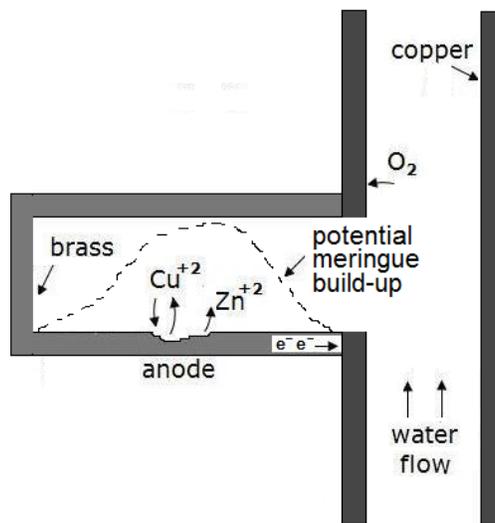


Figure 3.8: Hypothesized worst-case scenario for dezincification in the case of a galvanic couple between brass and copper in potable water. Due to its position in the system, the brass is removed from flow and a localized environment may quickly develop to promote dezincification and eventual meringue build-up.

COMBATING DEZINCIFICATION IN POTABLE WATER SYSTEMS

Considering the influence of alloy composition, water chemistry and physical factors highlighted above, it is possible that brass dezincification can be avoided or overcome by controlling factors in any or all of these three categories. A range of approaches have been proposed for mitigating dezincification in potable water systems (Table 3.4)./6, 7, 14, 13, 29, 46, 50, 54, 55, 56, 57, 58/ The most common recommendation by far is to simply use unsusceptible brass alloys (see Alloy Composition section), which are typically below 15% zinc content or are up to 30% zinc with small additions of arsenic. At present, use of dezincification resistant alloys is probably the most practical solution for many systems, especially new plumbing installations or individual households or buildings served by municipal water distribution. As an alternative to fully replacing brass plumbing components with resistant alloys, Moore and Beckwith reported

that certain dezincified brass tap-ware can be reinstated via re-surfacing or use of re-newable brass, stainless steel or acetyl plastic tap seats. /50/

In light of historical dezincification problems, some countries have actually adopted recommendations or requirements to use dezincification resistant materials, and this has proven largely successful. For example, following decades of dezincification outbreaks and much research, Australia has implemented requirements (e.g., AS 3500, AS 3718) stipulating dezincification resistance of copper alloys /29, 59, 60/, including components used in plastic tube systems (e.g., /61/). Realizing the potential corrosivity of soils in addition to waters, many standards specify that copper alloys in contact with soil must also be dezincification resistant./59/ To comply with these rules, alloys must conform to AS 2345, the Australian standard test method for determining resistance to dezincification corrosion.

Table 3.4: Summary of recommendations for avoiding brass dezincification in potable water systems.

Researcher(s)/ Author(s)	Recommendations
During (1997)	Use of inhibited brass or copper; prevention of deposit formation on brass surface
Kuppan (2000)	Use of unsusceptible alloys
Marshakov (2005)	Use of unsusceptible alloys, such as those containing additions of As, Sn, Al; remove oxygen from water
Moore (1998)	Continued mandatory use of dezincification resistant alloys in water supplies in Australia
Moore & Beckwith (1982)	Use of dezincification resistant alloys such as gunmetal, alpha or arsenical brasses for tapware; use of re-newable components made of either brass or alternate materials like acetyl plastics or stainless steel
Nicholas (1983)	Bicarbonate dosing to corrosive water supplies.
Oliphant (1978)	Maintain sufficient carbonate hardness to ensure non-dezincifying water according to Turner's Diagram (Figure 3.5); maintain pH 8.3 or less to prevent meringue dezincification, but must ensure that accelerated corrosion rates of brass and other system materials are acceptable; blend naturally-inhibited waters with dezincification-prone waters; use polyphosphate and zinc inhibitor treatment
Oliphant (2003)	Use of dezincification immune (e.g., arsenical alpha brass) or resistant brasses in waters known to initiate or propagate dezincification
Selvaraj et al	Use of unsusceptible alloys such as those containing additions of As,

(2003)	Sn, B, Mn and Bi
Simmonds (1967)	Maintain pH 8 or less to prevent meringue dezincification
Uhlig (1985)	Use of unsusceptible alloys such as red brass or admiralty (Sn) brass
Waterton (1973)	Adjust alkalinity to maintain satisfactory temporary hardness to chloride ratio to ensure non-dezincifying water; avoid increasing chloride concentration during water treatment

Furthermore, Scottish and Irish water codes mandate that any concealed (though not necessarily underground) fittings or backflow prevention devices are manufactured of dezincification resistant materials./62, 63/ The UK Water Industry provides specifications for dezincification immune or resistant copper alloys for use in valves in contact with potable water (e.g., /64/). Sweden has recommended use of dezincification resistant materials for some water valves /45/, and has required their use in specific instances. /65/ Again, standard test methods (e.g., British standard BS 2872) must be used to certify the dezincification resistance of the alloy.

In the United States, dezincification in potable water systems was once a significant problem that was considered solved by use of low-zinc brass through guidance such as AWWA C800./12/ However, such standards are unfortunately limited only to copper alloys placed underground and controlled by municipalities. With respect to brass components installed within premise (e.g., home or building) plumbing systems, there are no published requirements for use of alloys that are unsusceptible to dezincification in the United States – even though their use was apparently once common./66/ Recently, trends in use of susceptible alloys (i.e., high-zinc and/or uninhibited brass) has led to many dezincification outbreaks in the United States./66/ In many ways, this equates to a costly way of re-learning past lessons. Incorporation of formal standards in to the United States plumbing codes, such as those used in Australia, should be strongly considered.

Now that high-zinc brasses have been installed throughout newer housing developments in the United States, water chemistry modifications to mitigate dezincification problems might

be desirable or necessary (Table 3.4). Practically speaking, these modifications may be considered where point-of-use water treatment is employed or a significant number of municipal water customers are affected by dezincification problems. For example, in cases where high chloride is suspected to contribute to brass dezincification, simply switching from chloride- to sulfate-based coagulants might be expected to reduce the dezincification propensity of the water supply. Waterton suggested such modifications where applicable for problematic waters in the United Kingdom, but noted the relatively high associated costs.⁵⁸ On top of evaluating the advantages, expenses and/or complexities of changing treatment processes to modify water chemistry, potential effects on water quality and other materials in a distribution system should also be considered. For instance, the cost attractiveness of chemical dezincification control strategies which use additive inhibitors may be increased if the inhibitors could benefit system materials other than brass (e.g., copper or concrete). Information on such inhibitors is lacking in the literature and is thus a topic for future research.

Moreover, in order to ensure that water chemistry modifications are well-informed, development of standard methods to test the dezincification propensity of a specific water supply would be very useful. To date, standard methods that rely on accelerated testing of alloys in aggressive solutions are available to certify specific brasses as dezincification resistant (e.g., AS 2345, ISO 6509, BS 2872). However, no test method has yet been established to examine the relative aggressiveness of specific potable waters or to gauge the effectiveness of corrosion inhibitors. This might explain the limited scope of adopted recommendations and regulations (i.e., only the alloy is targeted). Given this, and the fact that resistant alloys are not currently required in most countries (e.g., the United States) even for new installations, both water utilities and consumers are at a disadvantage in diagnosing and resolving dezincification problems.

A few researchers (e.g., /20, 67/) have essentially “standardized” their own tests, exposing certain brass alloys to different waters in order to identify potentially “dangerous” waters and rank their propensity to cause dezincification. Turner’s diagram is, in fact, an illustration of this type of work, which enabled him to effectively explain meringue dezincification problems within his geographic region of interest in Great Britain./20/ Zhang recently conducted similar tests to those of Turner using waters from across a wide geographic region of the United States./67/ In addition to visual observations of dezincification like Turner, Zhang’s tests included other analyses (e.g., cumulative weight loss of alloy specimens, soluble metal concentration measurements) which may be quite useful in assessing the relative aggressiveness of given water chemistries and all manifestations of dezincification corrosion. Continued development of standardized test protocols is highly desirable.

Finally, modifications to physical factors in potable water systems which are suspected to influence propensity for brass dezincification (see *Physical Factors* section) should be considered. Oliphant noted the importance of plumbing system configuration in dezincification testing, and attempted to build a representative test apparatus./13/ And Nicholas reported that investigations of actual dezincification occurrences suggest that a number of variables (not just chemical) are influential./56/ Additionally, Zhang found that when identical brass alloys were subjected to a matrix of waters from locations both with and without known dezincification problems, results were not well correlated with field failure reports; waters from locations reporting most severe dezincification problems were not necessarily the most aggressive to the tested brass with respect to dezincification, and vice versa./67/ Zhang concluded that other factors, perhaps physical factors of actual plumbing systems, must be significant. However, the current lack of research results in this area makes it difficult to confidently recommend specific

system configurations (e.g., avoiding differential flow patterns or decreasing design flow velocity) or materials (e.g., dielectric components between dissimilar metals). Following development of a standardized test to determine the dezincification propensity of a given water, tests might also be developed to pinpoint critical physical factors and suggest optimal plumbing design modifications.

SUMMARY AND CONCLUSIONS

Brass is a key component of many intricate and critically important mechanical devices in premise plumbing. Line blockage and failures due to dezincification can be difficult and costly to repair, and sometimes cause catastrophic failures. Additionally, preliminary data suggest that dezincification might contribute to elevated lead in drinking water in at least some circumstances.

Given the multitude of factors that may influence dezincification of brass in potable water systems, it is clear that predicting the initiation and propagation is not an easy task. Fortunately, it may be possible to identify the predominant controlling factors to better assess the likelihood of dezincification occurrence and consequences. Various authors have reported strategies for avoiding dezincification; use of alloys which are not susceptible to the problem is highly recommended where possible.

Based on a comprehensive review of the literature, the following statements may generally be made regarding dezincification in potable water systems:

- Dezincification may occur by either a singular or dual mechanism, depending on the water chemistry to which the brass is exposed and the oxidation-reduction potential
- Dezincification attack may manifest itself as either plug- or layer-type, and mercuric deposits may form under circumstances of low zinc solubility

- Brasses with zinc content lower than 15% are generally free from serious dezincification problems, and the alpha phase in brass can be inhibited effectively by adding arsenic and tin to the alloy.
- While high chloride and low temporary hardness do appear to enhance meringue dezincification, the Turner diagram is based on data that are limited in scope, and will not prove to be an acceptable predictor of dezincification problems in modern water systems.
- Meringue dezincification is favored by higher pH, temperature and aeration.
- Increased free chlorine and chloramine may promote dezincification.
- Most anions are believed to worsen dezincification. However, some prior work has indicated that nitrate and poly-phosphate may slightly inhibit dezincification in some cases.
- The effects of zinc and silica (as either natural constituents or added inhibitors) are largely unclear at this time. Based on limited data, both zinc and silica have been found to reduce the rate of dezincification in some circumstances,
- The influence of water flow on dezincification is expected to be highly dependent on the condition of the metal, galvanic connections and types of deposits present on the surface.
- Separation of anodic and cathodic areas promotes dezincification via development of differential concentration cells. Thus, scales, deposits and crevices tend to initiate and/or accelerate dezincification
- Galvanic connections between brass and other materials can promote dezincification via the difference in metal activities and increased cathode to anode surface area ratios. While the cathodic reaction is often rate limiting for brass in isolation, when coupled to long sections of copper pipe the anodic reaction may become rate limiting.

- The worst-case scenario for meringue buildup with respect to physical factors in a traditional plumbing system is hypothesized to be a case in which brass is out of flow but connected a larger, more noble pipe (e.g., copper) exposed to flow.
- Where possible, use of resistant alloys seems the most practical method of preventing dezincification at present. Modifications to water chemistry (e.g., increasing temporary hardness to chloride ratio) are also suggested to overcome the problem, but economic and technical feasibility should be considered. Due to limited research about the influences of physical factors, recommendations are largely unformed for modifications in this area.
- In response to severe dezincification problems, some nations have adopted recommendations or requirements that can help to avoid, reduce or overcome this type of corrosion in potable water systems. Such actions are highly desirable in the United States if future dezincification problems are to be avoided.
- A standard test method to determine the propensity of specific water chemistries for causing brass dezincification is needed.

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CHAPTER 4: EFFECTS OF FLOW, BRASS ORIENTATION, TUBE MATERIALS AND TEMPERATURE ON CORROSION OF BRASS PLUMBING DEVICES

Emily Sarver and Marc Edwards

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ABSTRACT

Several types of brass corrosion can occur in plumbing systems including dezincification, pitting and lead leaching. To date, little work has been aimed at understanding the effects of factors associated with specific plumbing installations. The roles of flow velocity, orientation of brass within a system, tube materials (i.e., copper vs. plastics), and temperature were investigated in a series of pipe-loop experiments. It was confirmed that increased flow velocity, via increased oxidant delivery rates to cathode surfaces, can increase brass corrosion rates; although flow velocity did not affect the corrosion type. Differential flow conditions were also observed to increase corrosion rates in some instances, but the impacts were more subtle. Galvanic connections between copper tubes and brass devices accelerated overall brass corrosion rates, but decreased selectivity for zinc. On the other hand, when galvanic connections did not exist, the effect of background copper levels (due to corrosion of copper tubes) was to increase selectivity of brass corrosion for zinc. Plastic tubing served to maintain oxidant (e.g., free chlorine) levels, and promoted build-up of corrosion by-products (i.e., “meringue”), which may partly explain

relatively high incidence of recent brass failures in PEX plumbing systems. Finally, it was found that increased temperature may significantly increase lead leaching from brass.

INTRODUCTION

Brass is a copper-zinc alloy, which contains small amounts of lead, iron and other trace elements. Brass devices (e.g., valves, couplings, faucets, etc.) are very commonly used in both copper and plastic premise plumbing systems due to their relative durability, machinability, intricate functionality and low costs [1]. Although brass corrosion does not present serious problems in most plumbing systems, certain types of non-uniform corrosion can significantly impact performance in some cases. Most notably, dezincification – a type of de-alloying corrosion wherein zinc is selectively dissolved – can leave brass porous and subject to leaks, and can also lead to clogged water lines and burst failures. In addition to economic consequences, water damage can result in potentially harmful mold growth [2]. Brass pitting, similar to copper pitting, is another type of non-uniform corrosion, which could also result in leak failures [3]. Moreover, waters that support dezincification or other brass corrosion may also cause lead leaching, which presents a potential health hazard if tap water is contaminated [4-8].

Red (i.e., low-zinc content) and dezincification resistant (called “DZR” or “inhibited”) brasses are made for use in plumbing applications [9]; however these alloys are not utilized in many cases in the US due to their relatively high costs, limited availability, or unfamiliarity. Recently, use of some inexpensive, yellow (i.e., high-zinc content) brasses has resulted in outbreaks of dezincification failures in specific areas – many in fairly new homes – and some product liability concerns [e.g., 10]. Additionally, while “lead free” brass alloys are now required for many potable water applications [11], these alloys can legally contain up to 8% lead and may not be adequately reducing lead leaching [12,13]. There is also some evidence that DZR brasses

may be more prone to lead leaching than un-inhibited brasses [8,14], and neither DZR nor “lead-free” brass specifically offers protection against pitting corrosion. So even though failures are relatively rare, brass alloys are subject to a wide range of corrosion issues and modes of attack.

In potable water systems, the type and extent of brass corrosion can be controlled by alloying constituents and metallurgy, and water chemistry (e.g., pH, alkalinity, chloride concentration), as reported elsewhere [e.g., 3,15-17]. Additionally, corrosion may also be influenced by physical or physiochemical factors associated with specific installations, including flow conditions, predominant tubing materials, orientation of brass within a system, the presence of galvanic connections, and water temperature.

Plumbing Tube Materials

Copper accounts for a large percentage (i.e., >40%) of the market share in premise plumbing tubes for new construction [18], although plastics, particularly cross-linked polyethylene (PEX), are growing in popularity [19]. On top of the potential for formation of galvanic connections (discussed below), two key differences between copper and plastic tubing can be readily noted that may impact brass corrosion. First, leached copper ions from copper tubing might influence the selectivity of corrosion for zinc, since basic solubility chemistry dictates as the background level of copper increases in the water near a brass device, less copper might dissolve from brass. Second, given the relatively large surface area ratios between plumbing tubes and brass devices, a tube material which depletes the water of oxidants (e.g., free chlorine, dissolved oxygen) which drive corrosion reactions might provide some protection of the brass. For example, long lengths of copper tubing may dramatically reduce chlorine residual in a plumbing system before water even reaches some brass components.

Flow

Corrosion textbooks often state that brass dezincification is promoted by slowly moving or stagnant water [e.g., 20,21], and much experimental work has indeed been carried out under these conditions [e.g., 3,22]. However, some researchers have made practical observations that dezincification is accelerated by water movement and flow [e.g., 23,24]. This discrepancy between theory and practice was noted by Kelly et al. [25] and may be logically explained in view of a physical separation of anodic and cathodic sites in affected systems. For example, a relatively small anode site may become isolated beneath a corrosion product deposit (i.e., “meringue”), while much larger cathode sites develop on brass surfaces exposed to bulk water. In such cases, water flow through a brass component may be expected to accelerate dezincification via increased delivery of oxidant to the cathode, which drives corrosion at the anode. Essentially, a differential concentration cell may develop as the bulk water quality is maintained, while the localized water at the anode becomes acidic, salty, and depleted of oxidant. Consistent with this theory, Tabor’s [24] work indicated that dezincification was intensified with build-up of corrosion deposits.

Depending on water chemistry (i.e., pH, oxidation-reduction potential, etc.) and alloy properties, flowing conditions could also promote selective lead leaching or brass pitting. Fundamentally, the process of lead leaching from brass might be somewhat similar to dezincification, caused by micro-galvanic cells that exist between dissimilar alloy constituents (i.e. noble copper in contact with more active metals like zinc or lead). Additionally, if brass pitting is mechanistically similar to copper pitting, as may be expected at least in some circumstances, flow in waters having relatively high pH and high oxidant concentrations should promote pitting [26].

Differential Flow

The above scenario of under-deposit brass corrosion illustrates the concept of *differential flow* (i.e., the cathode can be subjected to water flow while the anode is effectively shielded) at relatively small scale. Such conditions may also be present on a much larger scale in plumbing systems when, for instance, a brass “T” connection branches one water line off of another, as is commonly the case in plumbing systems using PEX tubing. While one brass surface might contain stagnant or intermittently flowing water (e.g., a line that terminates at a faucet), the other might experience continuous or frequent water flow (e.g., hot water recirculation line). If brass surfaces located in each section are electrically connected (e.g., in the case of a brass T), a large-scale concentration cell can develop (similar to that described above) wherein the in-flow brass becomes relatively cathodic and drives corrosion on the anodic out-of-flow brass.

Galvanic Connections

Galvanic connections are commonplace between brass and copper in premise plumbing systems, with copper generally expected to act as a cathode while brass functions as a sacrificial anode [27]. Given the relatively large copper to brass surface area ratios typically present in plumbing systems (e.g., a long length of copper tube connected to a small brass valve), the effects of these galvanic connections could be significant. Though some dezincification researchers have purposefully connected large pieces of copper to smaller pieces of brass to accelerate mercuric build-up [28,29], the potential impacts have never been examined in realistic long-term experiments.

Combination of Galvanic Connection and Differential Flow

Beyond the independent scenarios of differential flow or a galvanic connection between brass and a more noble metal, the combination may represent a “worst-case” scenario for some

types of brass corrosion. For example, Figure 4.1 illustrates how dezincification may be accelerated on a brass component completely removed from flow, and electrically connected to a copper cathode exposed to flow .

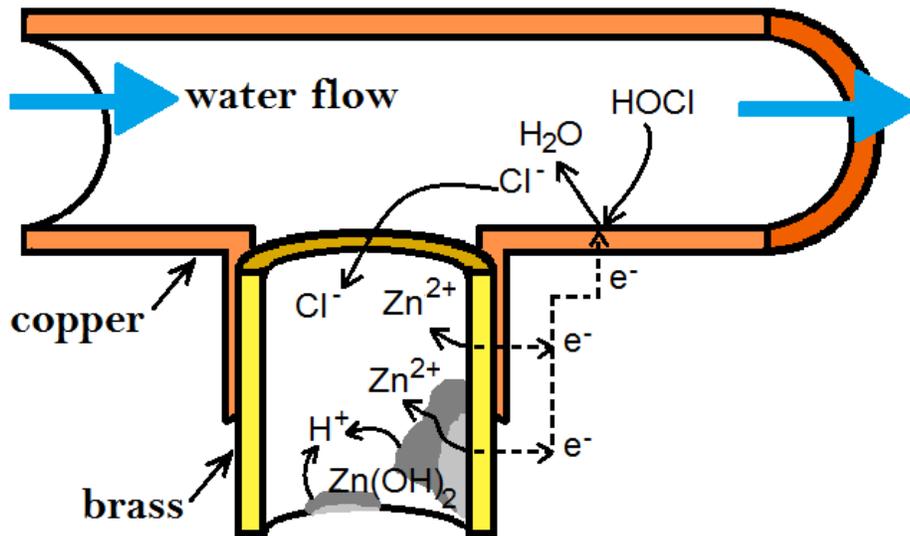


Figure 4.1: Hypothesized effects of differential flow and galvanic connection (with copper) on brass dezincification. Water flows through the copper tube, but is relatively stagnant inside the brass. The electrons liberated at the brass surface as zinc (or other alloy constituents) is oxidized are accepted at the copper surface where an oxidant (e.g., free chlorine as HOCl) is reduced. pH drops in the stagnant water due to Lewis acidity of zinc cations (Zn^{2+}), and salt content increases as chloride (Cl^-) and other anions are drawn in. In some cases, corrosion deposits (i.e., meringue) can build-up on brass surface. If flow velocity is increased or oxidant concentration is increased in the flowing water, corrosion (e.g., dezincification) on the brass surface is expected to accelerate, and vice versa.

Heating

Temperature might also play a large role in the type(s) and extent of brass corrosion that occurs in potable water systems. While it is accepted that hot water can worsen dezincification-related failures [30] via precipitation and accumulation of solids visually resembling meringue [31,32], or acceleration of zinc leaching [3,14], effects of temperature on other types of brass corrosion are not well understood under the chemical and physical conditions that may be encountered in real plumbing systems. For instance, some field data indicates that lead levels can

be higher in hot water tap samples than in cold when brass components are present [e.g., 33], and it is highly desirable to understand if lead-bearing brass is a probable culprit.

The objective of this work is to gain a broader understanding of practical effects of flow velocity, differential flow configurations, galvanic connections, plumbing tube material and temperature on the type(s) and extent of brass corrosion that may occur in potable water systems.

MATERIALS AND METHODS

Three experiments were conducted (Table 4.1) in pipe-loop apparatuses (Figure 4.2). The first experiment included short-term “proof of concept” tests, the second included long-term tests designed to investigate differences in brass corrosion between plumbing systems with copper and plastic tubes, and the third included long-term tests designed to isolate the effects of temperature and the individual physical factors described above on brass corrosion.

Pipe-Loops

New C36000 (i.e., yellow, high-zinc content) brass fittings and C12200 copper tubing (where specified) were used in the pipe-loops. The brass fittings were either couplings or plugs that would be practically utilized with $\frac{3}{4}$ ” PEX plumbing tube or to join PEX and copper. The actual elemental composition of the alloy was determined by a handheld X-ray fluorescence (XRF) instrument (Innov-X Systems, model Alpha 8000) as 58.8% Cu, 37.2% Zn, 3.1% Pb, 0.3% Sn, 0.3% Fe and 0.1% Ni. Prior to assembling the pipe-loops, copper tubing was cut and de-burred, and all components were rinsed with de-ionized water, allowed to dry and weighed.

Table 4.1: Synthesized water chemistries and physical conditions for three experiments.

Ex.	No.	Duration days	Test Condition	Flow velocity ft/s (m/s)	Water Chemistry Target (\pm st. dev.)		Water Change Cycle
					Maintained	Stable	
1	A	14	Loop 1 with variable free Cl ₂	7.0 (2.1)	variable Cl ₂ *	pH 7.6 (\pm 0.3) 11 mg/L alk.** (\pm 7) 38 mg/L Na ⁺ (\pm 5) 50 mg/L Cl ⁻ (\pm 10)	-
	B	14	Loop 1		4 mg/L Cl ₂ * (\pm 0.8)		weekly
	C	21	Loop 1 with brass located in-flow (no T)				weekly
2	D	490	Loop 2	4.5 (1.3)	pH 9.2 (\pm 0.3)	34 mg/L alk.** (\pm 12) 16 mg/L Na ⁺ (\pm 7) 20 mg/L Cl ⁻ (\pm 11) 17 mg/L Ca ²⁺ (\pm 4) 13 mg/L SO ₄ ²⁻ (\pm 6)	every other week
	E	490	Loop 2 without electrical connection		4 mg/L Cl ₂ * (\pm 0.5)		
	F	490	Loop 2 with PVC tubes in-flow				
3	G	150	Loop 3	6.0 (1.9)	pH 8.3 (\pm 0.2)	34 mg/L alk.** (\pm 10) 29 mg/L Na ⁺ (\pm 8) 40 mg/L Cl ⁻ (\pm 15) 17 mg/L Ca ²⁺ (\pm 2) 13 mg/L SO ₄ ²⁻ (\pm 5)	every other week
	H	150	Loop 3 at low velocity	2.0 (0.6)			
	I	87	Loop 3 at 45°C	6.0 (1.9)			
	J	150	Loop 3 without electrical connection	6.0 (1.9)			
	K	150	Loop 3 with galvanic connection to copper	4.5 (1.3)			

* free chlorine residual

** alkalinity as CaCO₃

All pipe-loops had continuously re-circulating flow of test water (velocities in Table 4.2) from polypropylene plastic reservoirs (30L in exp. 1, 94 L in exp. 2 and 3), which were closed to limit atmospheric influences on water quality (e.g., changes in alkalinity, temperature). Metal tube sections were physically separated using short lengths of clear vinyl tubing, but were electrically connected (unless specified otherwise in Table 4.1) via external copper wires. This allowed for collection of electrochemical data by temporarily replacing the wires with a multi-meter (as illustrated in Figure 4.2). Vinyl tubing was used to connect metal to recirculation pumps and to complete flow loops. Magnet-drive centrifugal pumps (polypropylene construction) were used to re-circulate water, except in the low velocity test (exp. 3, test H), which had a submersible pump (polypropylene and stainless steel construction).

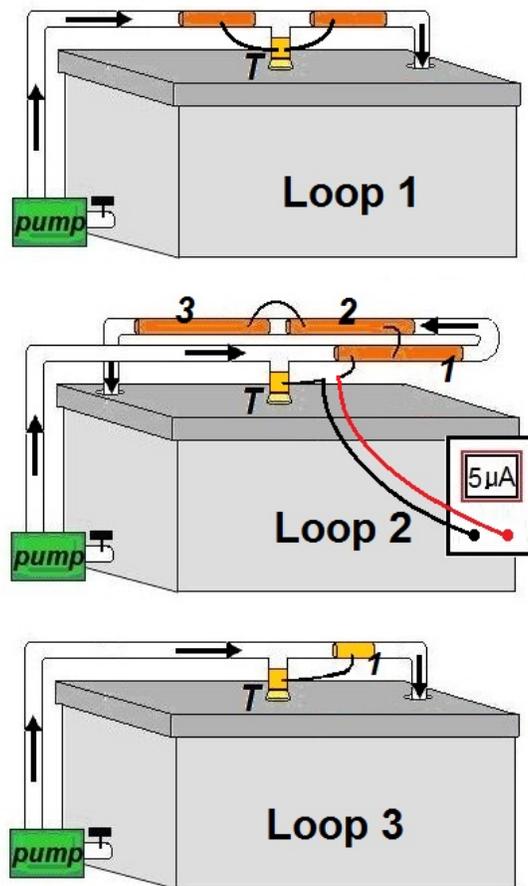


Figure 4.2: Pipe-loops for three experiments. Flow direction is indicated by arrows. The metal labeled T was brass in all loops. In Loop 1, in-flow tubes were copper in tests A and B; but in test C, the T section was completely removed and a brass tube was instead positioned in-flow. In Loop 2, the in-flow tubes were copper in tests D and E, and PVC in F. In Loop 3, the in-flow tube was brass in tests G-J, and copper in K.

In tests A and B in experiment 1, the pipe-loop (Loop 1 in Figure 4.2) had one brass coupling (1.75" or 4.5 cm long, 0.7" or 1.75 cm inner diameter) located out-of flow (i.e., the dead-end *T* in Figure 4.2), and 2' (61 cm) of 3/4" (1.9 cm) diameter Type M copper tubing located in-flow. Half of the copper tubing was upstream of the brass T, and half was downstream. In test C, no tubing was positioned out-of-flow (i.e., there was no differential flow); instead, a brass coupling (identical to above) was positioned in-flow. In experiment 2, the pipe-loops had three 1' (30.5 cm) lengths of 3/4" Type M copper or polyvinyl chloride (PVC) tubing located in-flow, and one brass coupling (1.75" or 4.5 cm long, 0.7" or 1.75 cm inner diameter) located out-of flow. In

experiment 3, the pipe-loops had one brass coupling (dimensions above) located in-flow, and one brass plug (0.5” or 1.3 cm long, 0.5” or 1.3 cm inner diameter) located out-of flow. The only exception was test K, in which the brass coupling was replaced with a 1.75” (4.5 cm) length of ¾” Type M copper tubing in-flow.

Water Chemistry

At the beginning of a test, or just before each water change (cycles given in Table 4.2), waters were synthesized using de-ionized water and reagent grade sodium and/or calcium salts. Free chlorine was added as sodium hypochlorite from a concentrated bleach stock (i.e., 6% NaOCl solution). Where applicable, pH was adjusted using NaOH and HNO₃ stock solutions. Water samples were analyzed using Thermo Electron X-Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) for quality assurance. pH was measured using a double-junction Ag-AgCl electrode, and free chlorine residual was measured with a Hach Chlorine Pocket Colorimeter II using a DPD (diethyl phenylene diamine) colorimetric test per *Standard Method* 4500-Cl G [34]. Except for test I (exp. 3), in which water temperature was maintained at 45 °C by an immersion heater, temperature was governed by ambient room temperature and the recirculation pumps. Temperature ranged from 24-33 °C in experiment 1, and from 24-28 °C in experiments 2 and 3.

In experiment 1, the test water had a relatively high chloride to alkalinity ratio (Table 4.1) with a high dezincification propensity [14]. The water was synthesized using only sodium salts (i.e., it had no hardness), and had a relatively stable pH of 7.6, which was not purposefully maintained. Chlorine was not initially dosed to test A, but on day 3, free chlorine (as NaOCl) was dosed to the water to achieve a 4 mg/L residual. This was manually maintained until day 6,

at which time the chlorine was allowed to decay until the end of the test. In tests B and C, chlorine was manually maintained throughout the test according to Table 4.1.

The water quality in experiment 2 was a synthesized potable water with high pH, high free chlorine water and low alkalinity, known to cause pitting of copper [36]. Given its aggressiveness toward copper, it was expected to also attack brass. In experiment 3, a similar water was used, except that it had lower pH (i.e., 8.3 instead of 9.2) and higher chloride (i.e., 40 instead of 20 mg/L). These conditions were expected to produce severe meringue dezincification based on prior studies [e.g., 14,15]. In experiments 2 and 3, pH and chlorine targets were maintained via automatic feed systems in conjunction with manual adjustment (at least four times per week).

Data and Analysis

Corrosion currents (I) were monitored in-situ for all tests with multiple pieces of metal in electrical contact. Measurements were taken at least once per water change cycle using a Fluke 189 True RMS multi-meter with internal resistance $<100 \Omega$. In the convention utilized for this work, positive I values indicate anodic behavior of a given metal sample vs. all other metal in a system (e.g., T vs. electrically connected copper tubes 1-3 as shown in Figure 4.2). Additionally, bulk and T water samples were collected regularly (i.e., weekly in exp. 1, every 6 weeks in exp. 2, and every 4 weeks in exp. 3) for metals (i.e., zinc, copper and lead) analysis via ICP-MS.

At the end of each test, metal samples were subject to forensic inspection. They were removed from pipe-loops and allowed to dry prior to being cleaned and cut lengthwise for visual and elemental analyses. Corrosion scales were removed chemically using Twinkle brand household copper cleaner from experiment 1 and 3 samples; scales were removed mechanically using a Dremel tool with a fine-bristle steel brush from experiment 2 samples. Copper

enrichment (i.e., the relative increase in copper fraction of the brass surface after testing), and zinc and lead depletion (i.e., the relative decrease in the zinc or lead fraction of the brass surface after testing) were determined by comparing elemental analyses (obtained via the XRF instrument described above) of un-exposed brass surface areas with (cleaned) areas which were obviously corroded during testing. The XRF instrument analyzes about an 8 mm² area, to a penetration depth of 1 μm or more. Enrichment and depletion were computed using Equations 1 and 2:

$$E_M = 100\% \frac{M_C - M_U}{M_U} \quad (\text{Eq. 1})$$

$$D_M = 100\% \frac{M_U - M_C}{M_U} \quad (\text{Eq. 2})$$

where E_M and D_M are the percent enrichment or depletion in a given element, M (e.g., Cu), during testing, respectively; M_C is the percentage of that element on the corroded brass surface; and M_U is the percentage of that element on the brass surface not exposed to test water. Selected samples from experiment 3 were also imaged and analyzed using an FEI Quanta 600 FEG environmental scanning electron microscope (ESEM), equipped with a Bruker Quantax 400 energy dispersive X-ray spectroscope (EDX) (penetration depth of 1 μm). This allowed for precise geometric measurements and elemental analyses of specific regions of interest (e.g., plug dezincification); surface areas of about 0.005-0.05 mm² were investigated. Equations 1 and 2 were also used to calculate enrichment and depletion values from ESEM-EDX data. Additionally, corrosion scales from experiments 2 and 3 were dissolved and analyzed for metal contents (e.g., zinc, copper and lead) via ICP-MS.

RESULTS

Dezincification was observed in all tests, though the severity of attack and particular manifestations (i.e., layer, plug and/or meringue) varied (Table 4.2). Brass pitting was also observed in some tests (i.e., G, H and K in exp 3), and selective lead leaching was evident from water, scale and brass surface analyses in another (i.e., I, exp. 3). The sections below provide detailed results from each of the three experiments.

Experiment 1: Proof of Concept

Results from experiment 1 confirmed that the general hypothesis presented in Figure 4.1 (i.e., acceleration of brass corrosion via combination of differential flow and galvanic connection to copper) is valid, at least for the brass alloy and water quality conditions tested. In test A, the galvanic corrosion current density (brass *T* vs. copper in-flow) was closely related to the free chlorine concentration in the bulk water (Figure 4.3), demonstrating that corrosion on the anodic brass surface was directly related to supply of oxidant to the cathodic copper. When chlorine dosing began on day 3, the current jumped and then rose over about a two-day period, reaching a peak of nearly $14 \mu\text{A}/\text{cm}^2$; when chlorine dosing was stopped on day 7, the current fell slowly with chlorine residual and stabilized around $0.8 \mu\text{A}/\text{cm}^2$ on day 12. No meringue formed in this test (or other tests in exp. 1), but based on metal leaching (not shown), visual observations and XRF data (Table 4.2), the measured galvanic corrosion currents can be attributed to dezincification of the brass.

Table 4.2: Summary of selected results for all tests.

Test	Current Density		Weight Loss		Observed [\] Corrosion Type(s)		Zinc Depletion [†]		Copper Enrichment [†]		Lead Enrichment [†]		Corrosion Scale Constituents [‡]						
	<i>T vs. In.</i>		<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	<i>T</i>	<i>In.</i>	
	$\mu\text{A}/\text{cm}^2$	95% Cl	% / year				%		%		%		% Zn		% Cu		% Pb		
Exp. 1	A	NA		ND	NA	LD (shallow)	NA	18.1	NA	10.6	NA	41.5	NA	ND					
	B	5.9	1.0			LD (shallow)	NA	ND											
	C	3.2	0.5			NA	LD (shallow)	ND											
Exp. 2	D	0.9	0.1	1.2	NA	MD, LD (shallow)	NA	35.9	NA	22.9	NA	26.6	NA	47.6	NA	4.7	NA	2.9	NA
	E	NA		1.0	NA	MD, LD (shallow)	NA	69.5	NA	42.5	NA	88.3	NA	57.1	NA	0.6	NA	2.3	NA
	F	NA		0.9	NA	MD, LD (shallow)	NA	53.9	NA	35.3	NA	23.6	NA	56.8	NA	0.1	NA	2.6	NA
Exp. 3	G	0.8	0.5	1.3	1.9	BP, PD, LD (shallow)	LD (shallow)	30.6	51.8	20.1	30.9	-15.8	19.0	48.8	46.9	2.0	4.1	1.0	2.6
	H	0.2	0.2	0.8	1.8	LD (shallow)	BP, LD (shallow)	29.8	47.5	18.4	31.0	10.4	-8.6	49.3	52.1	5.6	3.1	1.4	2.2
	I	0.5	1.3	1.5	2.1	MD, PD, LD (deep)	MD, LD (shallow)	19.0	28.9	13.9	21.4	-43.5	-32.7	64.6	47.9	5.4	1.0	4.4	3.1
	J	NA		1.3	2.0	PD, LD (deep)	LD (shallow)	35.1	37.0	21.0	23.3	14.8	22.1	58.9	40.0	5.1	7.8	1.3	2.7
	K	2.7	2.0	1.7	NA	BP, LD (deep)	NA	16.3	NA	8.4	NA	10.4	NA	44.8	NA	12.2	NA	1.4	NA

NA Not applicable

ND Not determined

T Brass located out-of-flow

In. Brass located in-flow

MD Meringue dezincification

PD Plug dezincification

LD Layer dezincification

BP Brass pitting

[\]Based on visual inspection of cross-sectioned samples

^{||} Average of measurements from week 8 through end of testing

[†]Computed from XRF data as the % increase or decrease of element on exposed brass surface (vs. un-exposed surface of same sample); negative enrichment values indicate depletion of element from brass surface

[‡] Computed from ICP-MS data as the % of each element contained in solid scale removed from brass sample following testing

In test B, in which chlorine concentration was maintained over the test duration, comparison of the stagnant water localized inside the brass *T* to the bulk water proved that a large-scale differential concentration cell did indeed develop as hypothesized. Water samples were taken on days 7 and 14, and on both occasions the water in the *T* had lower pH (i.e., by 0.4 pH units) and the free chlorine residual was lower (i.e., by 1.1-1.3 mg/L) than that of the bulk water. Additionally, comparison of current densities from tests B and C, indicated that dezincification was more severe when the brass was located out-of-flow (as pictured in Figure 4.1, Loop 1) than when it was located in-flow (not pictured) (Figure 4.3). The average current density was about $5.9 \mu\text{A}/\text{cm}^2$ in test B, but was only about $3.2 \mu\text{A}/\text{cm}^2$ in test C.

While brass exposed to stagnant water (tests A and B) developed a relatively smooth scale that was easily removed, brass exposed to flow (test C) developed a rough scale (i.e., high density of tiny corrosion deposits) that was very tenacious. This texture was not observed in any other tests, and may be due to the high test velocity or sustained exposure to chlorine at pH ~ 7.6 . Once corrosion scales were removed, the brass surfaces from tests A, B and C all looked very similar. The entire exposed surface was reddened indicating that layer dezincification occurred; however the depth of dezincification into the brass wall was too shallow to measure, at least on the two planes (i.e., wall thicknesses) exposed by cross-sectioning the brass samples lengthwise. Significant lead leaching was not observed in any of these short-term tests.

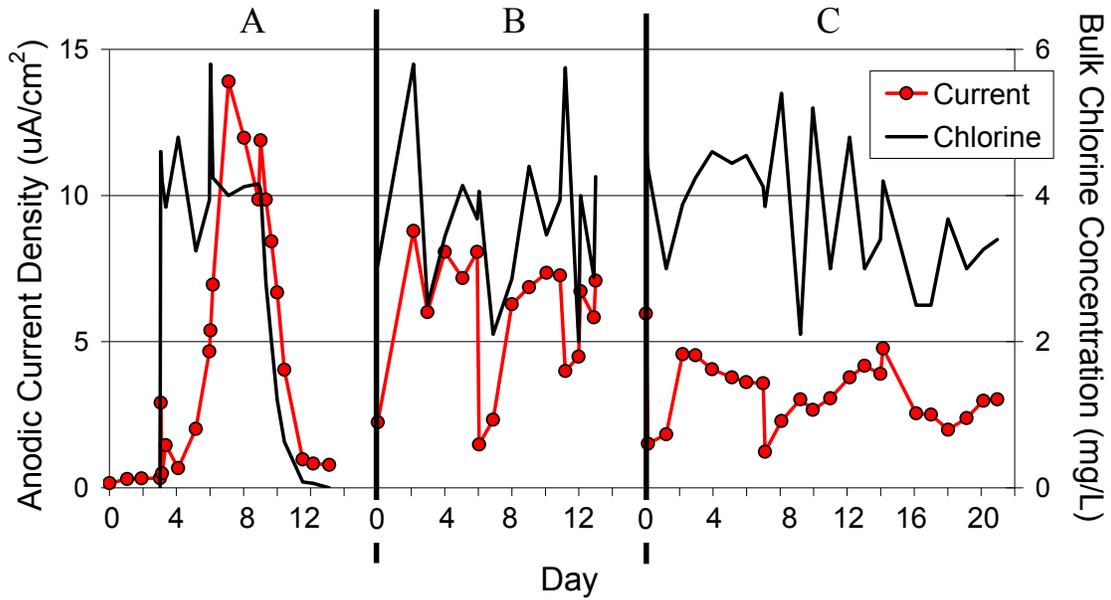


Figure 4.3: Brass current density (vs. in-flow copper) and bulk chlorine residual over time for tests A, B and C.

Experiment 2: Plastic vs. Copper Plumbing Systems

In experiment 2, meringue build-up was quite severe (Figure 4.4), and was visually worst in the test (F) with PVC tubes in-flow instead of copper. While this condition had the least brass weight loss (Table 4.2), it maintained the highest pH levels in the stagnant *T* water (Table 4.3), so the increased build-up of scale at higher pH is likely due to reduced solubility despite the lower overall corrosion rate. In contrast, the brass *T* that had a galvanic connection to copper (test D) had the least meringue build-up, the greatest weight loss, the greatest pH drop in the stagnant water, and the greatest average zinc leaching (Figure 4.5). Beneath the meringue and other corrosion scales, the brass surfaces in all three tests exhibited shallow layer dezincification, which covered large, non-uniform areas (Figure 4.4); but, the depth of dezincification was too small to be quantified. Somewhat surprisingly, brass pitting was not observed in this experiment even though the copper tubes in-flow (tests D and E) were severely pitted and produced multiple pinhole leaks. Apparently, the combination of pH and free chlorine residual inside the *T*'s was

not supportive of brass pitting. At lower pH's (i.e., ~ 7.5) and similar chlorine residuals in the *T* waters in experiment 3, some pitting was observed (discussed below).

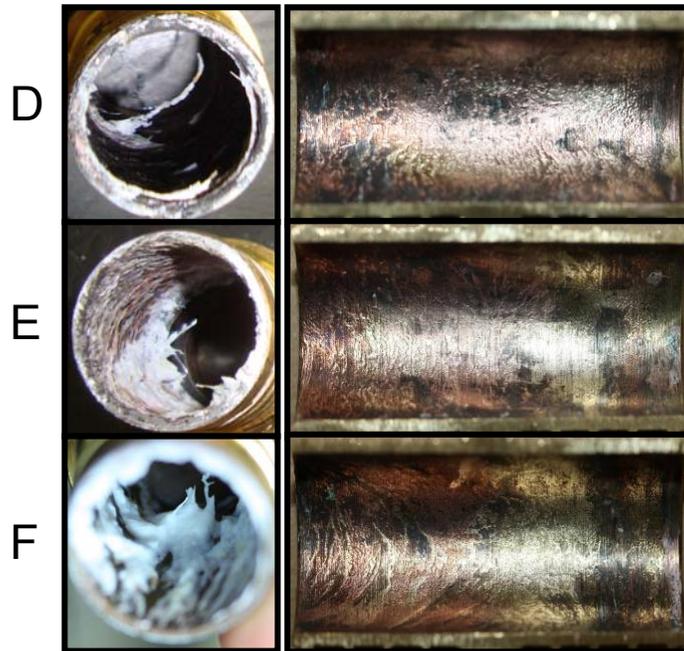


Figure 4.4: Meringue scale build-up (left) and non-uniform layer dezincification (right) revealed after scale removal on brass *T*'s from tests D (top), E (middle) and F (bottom).

Table 4.3: *T* water chemistry and chlorine consumption rates in experiment 2 tests.

Test	Avg. <i>T</i> Water Chemistry						Avg. Cl ₂ Consumption*
	pH	Cl ₂	Cl ⁻	Zn	Cu	Pb	
		mg/L					
D	8.6	1.4	54	280	417	1.3	7.8
E	8.7	2.0	44	210	580	0.5	8.7
F	8.9	2.5	9	208	2	1.2	0.5

* rate of chlorine addition required to maintain target concentration in bulk water

As expected, the overall decay rate of free chlorine (as indicated by the rate of chlorine consumption in Table 4.3) was much lower (i.e., by a factor of more than 15) in the test with PVC tubes in-flow (F) than in the tests with copper tubes (D and E), and the chlorine residual remained relatively high in the *T* water (Table 4.3). This is seemingly contradictory to the relatively low weight loss measured for the brass in test F as compared to its counterpart in E (i.e., 0.9 vs. 1.0%, respectively), but the extreme difference in chloride concentrations in the *T*

waters in these tests may have played a role; the chloride build-up in test E was very high due to high chlorine decay rates (which necessitated high rates of chlorine addition to maintain the target residual), and could have increased the corrosion rate of the brass. Additionally, even though zinc leaching (the major source of weight loss) appears to have been similar between tests E and F, it is highly possible that a significant fraction of the zinc leached in test E was taken up by the thick corrosion scale formed on the in-flow copper tubes; only a very thin film layer formed on the PVC tubes in test F.

The primary source of the large amounts of copper present in the *T* waters in tests D and E (Figure 4.5) was undoubtedly the copper tubes located in-flow, which were severely corroded. Perhaps due to cathodic protection of the copper by the brass in test D, the *T* water was somewhat lower in dissolved copper than that of test E (non-galvanic system with copper tubes in-flow). However, there was a significantly higher fraction of copper in the corrosion scale from the galvanic test – about 4.7% vs. 0.7% copper by mass, respectively (Table 4.1). This suggests the brass in test D may have actually leached much more copper than its counterpart, and, as a result, corrosion was less selective for zinc. Zinc depletion and copper enrichment data (as indicated by XRF) also supported this finding (Table 4.2). Alternatively, with no galvanic connection, but very high amounts of copper in the *T* water, brass corrosion in test E was highly selective for zinc. In fact, this test produced the most severe general dezincification (in terms of zinc depletion on the brass surface as indicated by XRF) of any test presented herein. In test F, which was not influenced by a galvanic connection or high background copper levels, corrosion was relatively selective for zinc, and nearly no copper was found in the *T* or bulk water, or in the corrosion scale.

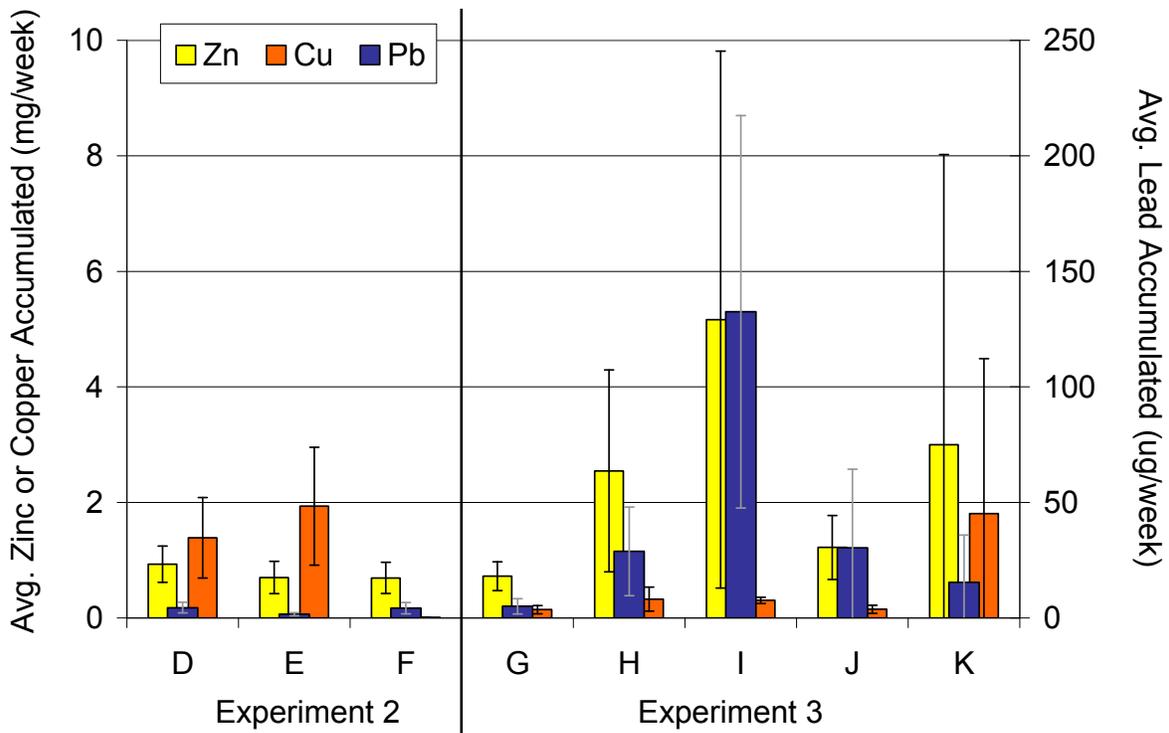


Figure 4.5: Average zinc, copper and lead accumulated (either due to leaching or settling from bulk water) in stagnant *T* waters in experiments 2 and 3. Data are normalized based on *T* water volume and sampling frequency; error bars show 95% confidence intervals.

From the perspective of lead leaching, which has been of recent concern [e.g., 5-7], all tests in experiment 2 behaved relatively similarly (e.g., Figure 4.5). In addition to concentrations of lead measured in the *T* and bulk waters (i.e., about 0.5-2 mg/L and 0.1-1 µg/L on average, respectively), lead was also found in the meringue deposits in each condition. It ranged from about 2.3-2.9% by mass, which is relatively similar to the mass fraction of lead in the brass alloy itself. Interestingly, it was also found that lead and zinc depletion were inversely related, such that as brass corrosion became more selective for zinc, it became less selective for lead, and vice versa (Figure 4.6).

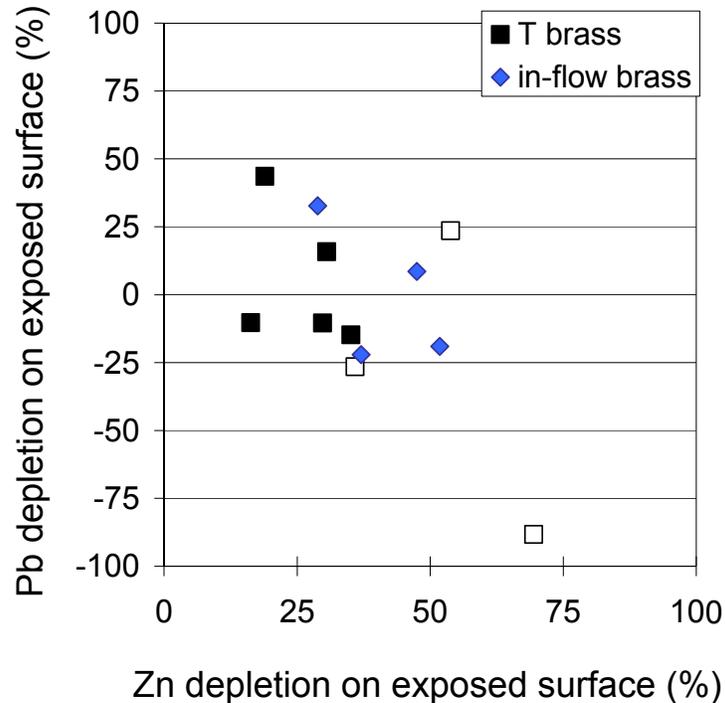


Figure 4.6: Zinc vs. lead depletion on exposed brass surfaces from experiments 2 (un-filled points) and 3 (filled points). Negative lead depletion values indicate lead enrichment.

Experiment 3: Isolated Factors

Tests in experiment 3 produced widely varying types of brass corrosion (Table 4.2), despite several disruptions to the testing. First, the de-ionized water system utilized for these tests temporarily leached silica (i.e., 3-15 mg/L as Si) which briefly affected all tests in experiment 3 between the first and second water changes (i.e., days 14-28). Second, a decision was made to interrupt chlorine dosing between the third and fourth water changes (i.e., days 28-42), during which time it was confirmed that electrochemical activity was significantly depressed in all tests. Figure 4.7 shows the effects of the above events on the brass current density in test K (galvanic connection between brass *T* and copper in-flow). Additionally, test I (heated water) was only run for 87 days (vs. 150 days for other exp. 3 tests); and due to the high rate of chlorine

auto-decomposition in this test, the average chlorine residual in the bulk water was only about 2.6 mg/L (vs. the maintained 4 mg/L target in all other conditions).

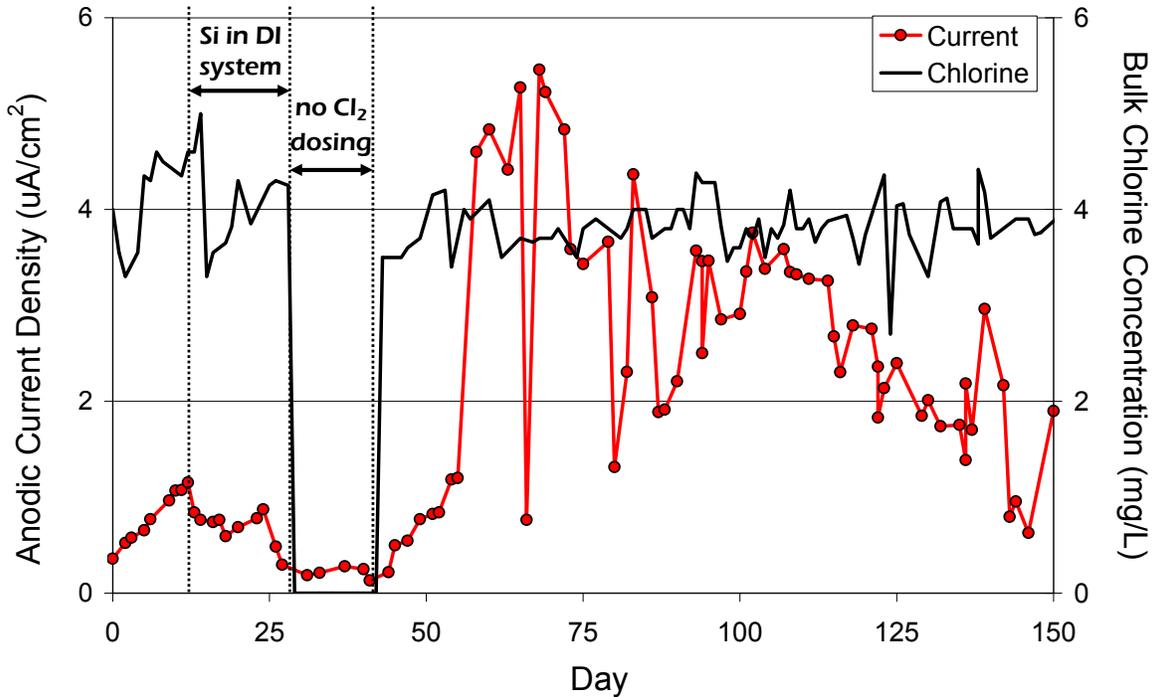


Figure 4.7: Brass current density (vs. in-flow copper) and bulk chlorine residual over time for test K. Periods of silica contamination and chlorine dosing interruption are indicated.

Weight loss was similar for similar brass samples (i.e., T or in-flow) in experiment 3 (Figure 4.8), and higher current densities tended to correlate to higher weight losses for the T 's (Table 4.2). However, despite the fact that the T 's were generally anodic to the in-flow brass and that the stagnant T waters maintained consistently lower pH than the bulk waters (not shown), the T 's lost *less* weight in every test condition than the in-flow brass. The severity of dezincification (based on zinc depletion and copper enrichment as indicated by XRF data) was also determined to be lower on the T than on the in-flow brass in all tests. Thus, even though corrosion rates on the T 's were accelerated via connection to in-flow brass (or copper in test K), the overall corrosion rates were still lower than those of the in-flow metals. This is likely due to the fact that the in-flow metals were exposed to relatively high, constant chlorine concentrations,

whereas chlorine levels in the brass *T*'s were consistently much lower (i.e., about 2 mg/L, on average).

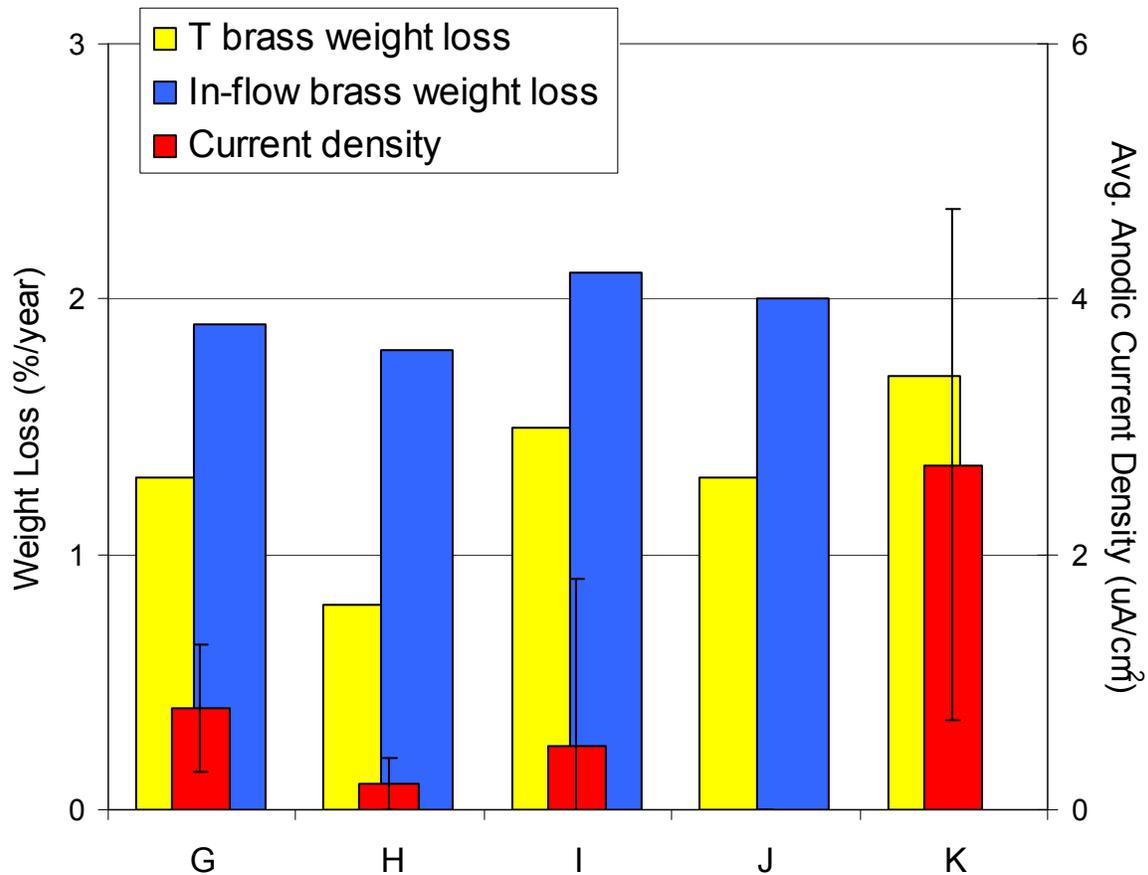


Figure 4.8: *T* and in-flow brass weight loss rates, and average current densities for tests in experiment 3. Current densities represent data from day 42 (i.e., after chlorine dosing was resumed) through the end of tests; error bars show 95% confidence intervals.

All tests produced a relatively smooth, dark grey scale, which was covered by at least some meringue (Figure 4.9). Test I produced meringue that covered a large portion of the *T* and in-flow brass surfaces, despite its shorter run time and lower chlorine residual. In other tests, meringue deposits were round and isolated, and tended to be larger and fewer on the *T*'s than on the in-flow surfaces. After removing the corrosion scales and cross-sectioning the brass samples, layer dezincification was revealed on all samples. Some also exhibited plug dezincification and/or pitting. According to XRF analyses, corrosion was most selective for zinc in tests G (high

velocity, differential flow), H (low velocity, differential flow) and J (high velocity, *T* and in-flow brass not connected), while significant lead leaching was observed in I (discussed further below), and more uniform corrosion (i.e., lower zinc depletion and copper enrichment) was apparent in K (Table 4.2).

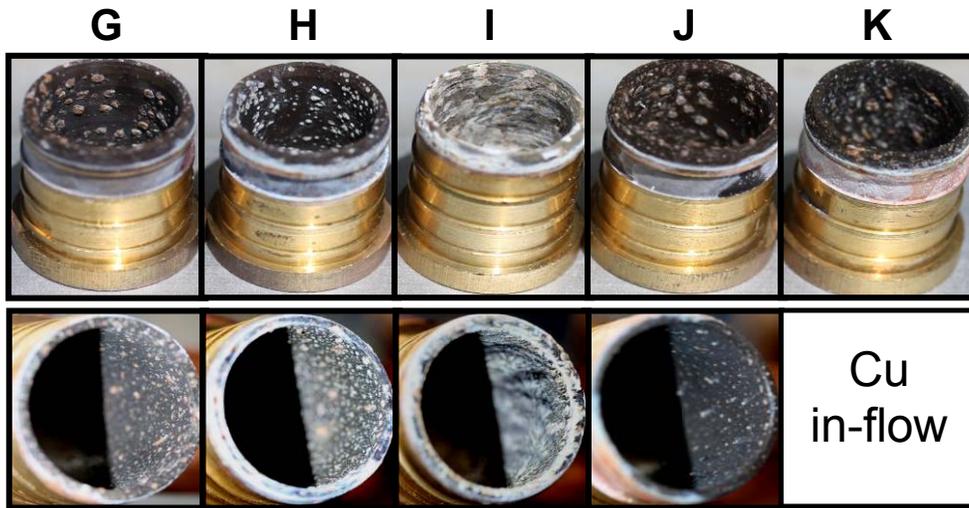


Figure 4.9: *T* (top) and in-flow (bottom) brass from all tests in experiment 3 (prior to scale removal).

All in-flow brass exhibited very shallow layer dezincification, as indicated by reddened, copper enriched surfaces; but the depth of dezincification could not be quantified. While no plug dezincification was observed on any of these samples, pitting was found on the in-flow brass from test H (low velocity) (e.g., Figure 4.10). The only other brass samples that appeared to have undergone pitting were the *T*'s from tests G (high velocity, differential flow) and K (galvanic connection to in-flow copper). ESEM-EDX analyses indicated that dezincification on the pitted surface shown in Figure 4.10 was more severe than on un-pitted surrounding surfaces that had undergone layer dezincification (Table 4.4).

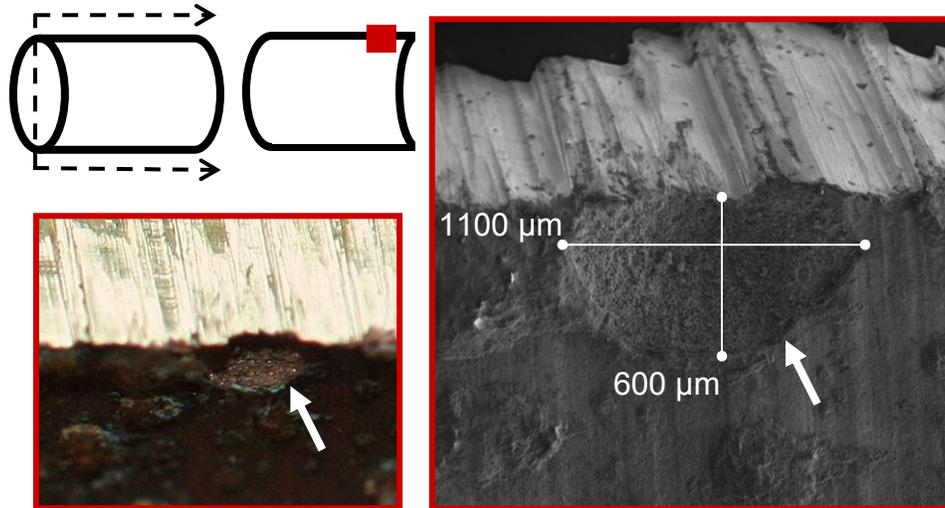


Figure 4.10: Photograph (lower left) and ESEM image (right) of pitting on in-flow brass from test H. Direction of sample cross-section (upper left) is shown and red box indicates location of imaging; white arrows indicate pit and dimensions are specified. This particular pit penetrated about 220 μm (i.e., roughly 15%) of the brass tube wall.

Table 4.4: Maximum depth of corrosion and metal enrichment/depletion (vs. un-exposed surfaces) on brass surfaces at specific corrosion sites as computed from ESEM-EDX data.

Test	Sample	Corrosion Type	Max. Depth [†] μm	Copper Enrichment		Zinc Depletion		Lead Enrichment	
				%	95% CI	%	95% CI	%	95% CI
G	<i>T</i>	<i>BP</i>	100	<i>ND</i>					
	<i>T</i>	<i>PD</i>	240						
H	<i>In.</i>	<i>BP</i>	220	28.7	2.6	79.3	0.7	318.1	7.4
	<i>In.</i>	<i>LD (shallow)</i>	<i>ND</i>	18.3	7.0	59.6	14.6	98.1	33.3
I	<i>T</i>	<i>LD (deep)</i>	260	<i>ND</i>					
	<i>T</i>	<i>PD</i>	170						
J	<i>T</i>	<i>LD (deep)</i>	160	<i>ND</i>					
	<i>T</i>	<i>PD</i>	340						
K	<i>T</i>	<i>BP</i>	150						
	<i>T</i>	<i>LD (deep)</i>	160	18.0	11.4	45.1	21.1	94.5	0.0

ND Not determined

T Brass located out-of-flow

In. Brass located in-flow

BP Brass pitting

LD Layer dezincification

PD Plug dezincification

[†]Observed on surfaces exposed by cross-sectioning; site of max. depth not necessarily site of ESEM-EDX analysis

Brass *T*'s from tests I, J, and K exhibited regions of layer dezincification (of varying size) that penetrated deep enough into the surface to view at low magnification (e.g., Figure 4.11). In tests G and H, the exposed brass surface was indeed enriched with copper (Table 4.2), however the depth of dezincification was too shallow to measure. Layer dezincification appeared to

penetrate deepest into the brass *T* from test I; the maximum depth observed on the cross-sectioned surfaces was approximately 260 μm . However, layer dezincification appeared to be the most uniform with respect to depth and coverage of the exposed brass surface on the brass *T* from test K, on which plug dezincification was not observed. Significant plugs were found on the *T*'s from tests G, I and J (high velocity, *T* and in-flow brass not connected) (e.g., Figure 4.12). ESEM-EDX data indicated that dezincification was more severe (i.e., corrosion was more selective for zinc) and lead leaching was less severe at sites of plug dezincification than at sites of layer dezincification (Table 4.4).

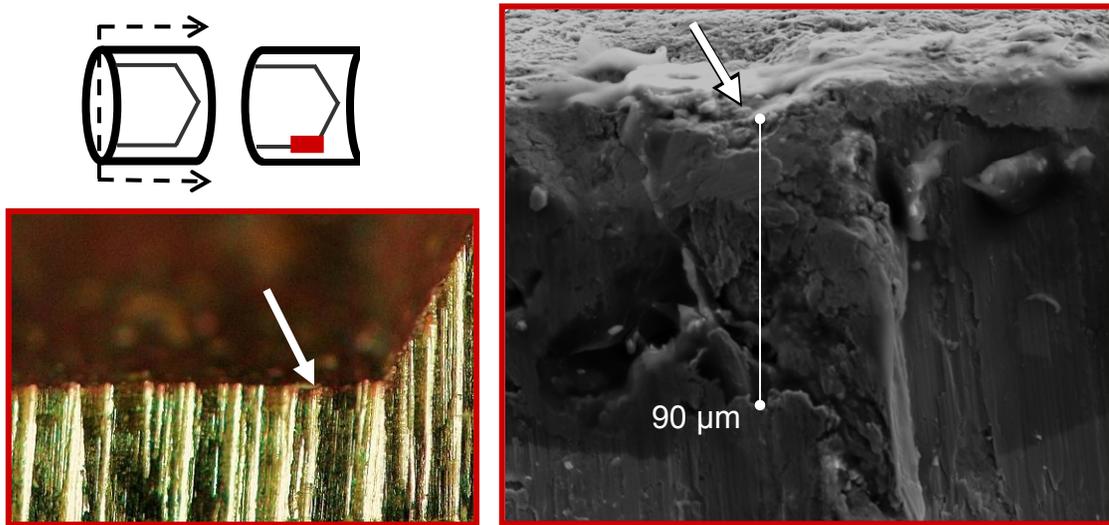


Figure 4.11: Photograph (lower left) and ESEM image (right) of deep layer dezincification on *T* brass from test K. Direction of sample cross-section (upper left) is shown and red box indicates location of imaging; white arrows indicate dezincification layer and depth at imaged point is specified.

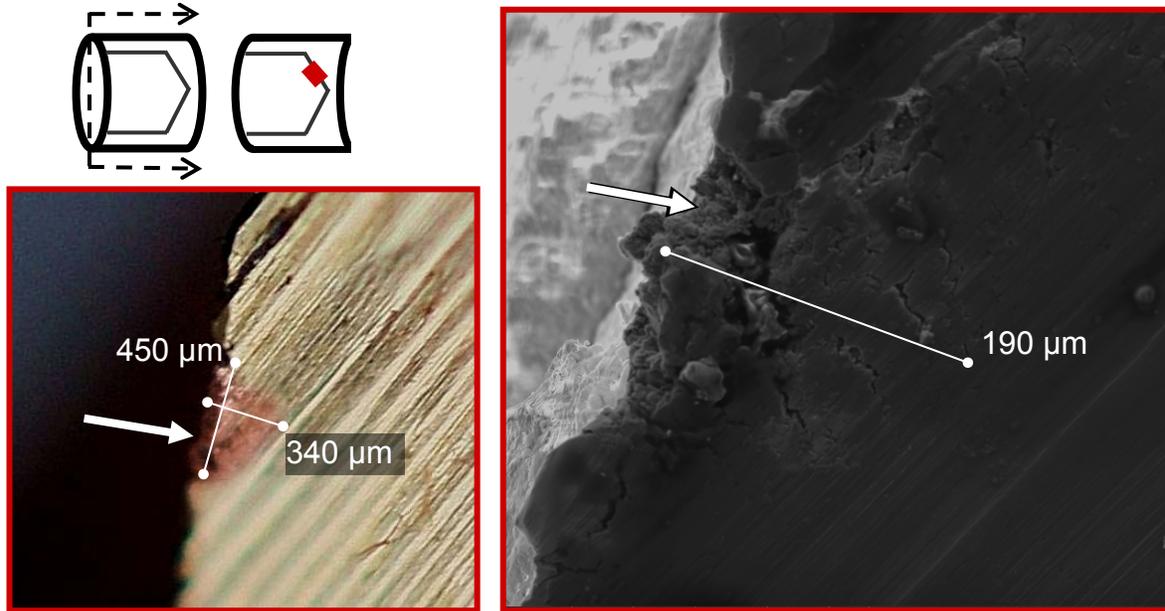


Figure 4.12: Photograph (lower left) and ESEM image (right) of plug dezincification on *T* brass from test J. Direction of sample cross-section (upper left) is shown and red box indicates location of imaging; white arrows indicate plug and dimensions are specified. Only a portion of the plug in the photograph is shown in the SEM image.

Metal concentrations in the bulk (not shown) and *T* (Figure 4.5) waters were quite variable over the entire test period. The high amounts of copper accumulated in the *T* water in test K were largely due to corrosion of the copper tube located in-flow in this test (i.e., similar to tests D and E in exp. 2); in this test, a very high fraction of copper (i.e., more than 12%) was also found in the corrosion scale on the *T* brass. The significant lead leaching in the heated test (I) was somewhat surprising, but was consistent with other data. Not only did the *T* water contain very high amounts of lead, but the exposed brass was also significantly depleted in lead content overall (as indicated by XRF data in Table 4.2). The lead fraction on the *T* and in-flow brass surfaces was computed to decrease during testing by approximately 44 and 33%, respectively; these values are higher than even zinc depletion values (19 and 29%, respectively) for this test. Furthermore, there was significant lead uptake to the corrosion scales. The *T* and in-flow scales contained 4.4 and 3.1% lead, respectively – which is higher than in any other test (Table 4.2).

These results do not appear to be merely an artifact of increased metal solubility with temperature. The lead to zinc mass ratio was significantly higher in test I than in test G (not heated) in both the *T* water and the solid corrosion scale (i.e., by factors of 3.8 and 3.3, respectively). Brass samples in tests G and H were also depleted in lead at the end of the testing, but to a much lesser extent.

While selectivity for zinc leaching was very high at specific sites of plug or layer dezincification produced in test I (as well as in other tests) (Table 4.4), lead leaching was not indicated by ESEM-EDX analyses at these sites. So while the most severe zinc leaching was localized, lead leaching appears to have been more generalized. Additionally, like in experiment 2, depletion of zinc on the exposed brass sample surfaces in experiment 3 was generally inversely related to depletion of lead (Figure 4.6). This is consistent with Zhang's [14] recent observations from original tests and reviews of metal leaching data from previous works (by other authors, e.g., [5]) on brass corrosion, and it suggests that the tendency for lead release from brass may not be mechanistically coupled with severe dezincification – although both can certainly occur on the same brass component.

DISCUSSION

Effects of Flow

As hypothesized, the action of flowing water to deliver oxidant (i.e., free chlorine) to a cathode surface did indeed influence corrosion on a remote (i.e., removed from flow) brass anode. Kelly et al. [25] first demonstrated this effect by varying flow velocity of oxygenated water past one brass sample (in an analogous but smaller-scale version of the test apparatus in exp. 3) and noting the effects on the corrosion current of a second brass sample, which was in electrical contact with the first but removed from flow. In that work, increasing flow velocity

(i.e., increasing oxidant delivery rate) tended to increase corrosion current. In the present work, oxidant delivery rate was varied by varying bulk oxidant concentration (i.e., test A, exp. 1), as well as flow velocity (i.e., tests G and H, exp. 3); and, in both cases, it was confirmed that increasing oxidant delivery rate to the cathodic metal surface can result in increased corrosion of anodic brass located out-of-flow. In experiment 3, not only did average corrosion current on the remote brass (i.e., the *T*) increase with flow velocity, but so did the rate of weight loss; the *T* weight loss in test G (high velocity) was nearly 40% higher than in H (low velocity).

Influences of flow velocity on mode of corrosion were subtle. Apart from the facts that plug dezincification was observed in Test G but not in H, and that meringue deposits were visually different between the two (e.g., smaller, whiter deposits in test H than in G or other tests as shown in Figure 4.9), brass samples from the high and low velocity test conditions appeared very similar. Additionally, computed zinc depletion and copper enrichment values were nearly identical between tests G and H. This suggests that only the corrosion rate changed with velocity, not the corrosion mechanism(s). By comparing results (e.g., metal depletion/enrichment) of the *T* and in-flow brass samples from test J (which were not affected by electrical connection to any other metal), it appears that the corrosion mechanisms were even similar between stagnant and flowing conditions. Again, the predominant influence was on corrosion rate, which was higher for the in-flow brass than for the *T*.

With respect to differential flow, results from tests B (differential flow) and C (uniform flow) (exp. 1) indicated that, when connected to a noble cathode (e.g., copper) being supplied with oxidant, brass corrosion may be accelerated if the brass located out-of-flow as compared to being located in-flow. Results from tests G (differential flow) and J (*T* and in-flow brass not connected) (exp. 3) are somewhat contradictory in that electrical connection between the brass

samples located in- (cathode) and out-of-flow (anode) did not appear to have much effect on the overall corrosion rate of either sample (i.e., weight losses were similar in both tests). This may be due to differences in the types of corrosion that occurred. For example, dezincification appeared to be enhanced by the electrical connection between brass samples. Specifically, zinc depletion on the in-flow brass surface from test G was about 15% greater than its counterpart in test J; and the ratio of zinc to copper in the corrosion scales in test G were also much higher.

Effects of Plumbing Materials

In comparing plastic to copper plumbing tube materials, experimental observations generally confirmed initial hypotheses. Plastic (i.e., relatively inert) tubing tended to keep chlorine levels high, and therefore allowed brass to be exposed to higher chlorine than was the case in systems with copper tubes. Although this did not result in higher corrosion rates here, in more realistic systems where chlorine concentrations in bulk water are not maintained and consequently chloride does not build-up, relatively high corrosion rates and mercuric build-up (as was demonstrated here) may be expected. This may explain why PEX plumbing systems are associated with so many recent brass failure epidemics [e.g., 10,36], which are prompting attention from the standpoints of both alloy certification [i.e., 37] and regulation [e.g., 38]. Additionally, background levels of copper ions from copper tubing tended to limit copper dissolution from brass, resulting in highly selective dezincification.

Finally, galvanic connections between copper tubing and brass were indeed found to be highly influential on both the rate and type of corrosion that occurred on brass in this work. Tests with galvanic connections (i.e., D and K) had the highest weight loss rates of all brass *T*'s – 20 and 31% higher than their counterparts in tests E and G. Moreover, the galvanic connection between brass and copper made corrosion less selective for zinc in experiments 2 and 3. This

was a somewhat unexpected result, as it was originally thought that the galvanic current may worsen dezincification, but it is logical given the overall highly anodic behavior of brass when connected to copper. The unique, very uniform layer of dezincification corrosion in test K (which was relatively less selective for zinc than plug dezincification or pitting) was likely the result of the consistently high corrosion currents measured on brass in this test (e.g., Figure 4.7). On the other hand, the brass pitting which occurred in this test was likely due to water chemistry alone, given that pitting was also found in tests G and H (no galvanic connection). Pit depths were relatively shallow in test K as compared to G and H, which is consistent with the observations that brass corrosion was more uniform in the case of a galvanic connection to copper.

Effects of Temperature

The most significant effects of increased temperature on brass corrosion were observed in the meringue formation and lead release in test I (exp. 3). The increased meringue build-up seen in this test is consistent with prior observations that meringue dezincification problems are often worse in hot water plumbing lines than in cold [e.g., 28,32]. Additionally, weight losses of the brass samples in test I were slightly higher than their counterparts in test G (ambient temperature), which is also consistent with findings of other researchers [e.g., 3].

Lead release was considerably higher at higher temperature, and this could not be simply attributed to increased total metal leaching or increased solubility; instead, lead appeared to be more selectively leached by heated water. This result was not anticipated, especially considering that the average chlorine residual (which was expected to promote corrosion) was substantially lower for test I than for other tests, and that the test duration itself was relatively short. The literature surrounding effects of water temperature on brass lead leaching is scarce, and while

some field reports indicate that hot water may increase lead concentrations [e.g., 33], other laboratory tests show that temperature may have no effect or may even decrease lead release [39]. Given the limitations of the current work (e.g., testing of a single brass alloy, lack of replication) and heterogeneities (e.g., pooling) associated with lead distribution in brass devices, further research on this topic is certainly warranted.

CONCLUSIONS

- Increased flow velocity of chlorinated water tends to accelerate brass dezincification and/or uniform corrosion rates via increased delivery of oxidant to cathodic surfaces; however, at the velocities tested, the type of brass corrosion is not significantly affected.
- Differential flow conditions could accelerate corrosion of brass surfaces that are removed from flow but are in electrical contact with brass or a more noble metal (e.g., copper) located in-flow.
- Galvanic connections between copper and brass tend to increase overall brass corrosion rates, while making corrosion less selective for zinc. In these tests, the galvanic connection was found to increase brass corrosion rate, reduce meringue build-up, and render brass corrosion less selective for zinc.
- Plastic plumbing tubes do not significantly consume chlorine, and therefore allow brass devices to be exposed to higher chlorine residuals than do copper tubes.
- Aside from potential galvanic effects, copper plumbing tubes may also inhibit copper leaching from brass devices, thereby making brass corrosion more selective for zinc.
- Increased water temperature might significantly increase lead leaching from brass, while reducing selectivity of corrosion for zinc and promoting meringue build-up.

- In addition to other brass corrosion types, pitting may occur in waters with high chlorine residuals.

While the pipe-loops used here were designed to closely simulate conditions that may be present in specific plumbing installations, further work may be needed to understand how flow conditions, plumbing materials, and temperature may affect brass corrosion in systems with different water chemistries or other brass alloys.

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CHAPTER 5: REVISITING BRASS DEZINCIFICATION PERFORMANCE TESTING: EXPOSURE TO REAL POTABLE WATER VS. ISO 6509

Emily Sarver, Yaofu Zhang and Marc Edwards

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ABSTRACT

Brass dezincification is a re-emerging issue in potable water systems and NSF/ANSI Standard 14 has recently been revised to require that all NSF-14 listed brass valves and fittings are dezincification resistant. In order to comply, brasses must be tested per ISO 6509 and cannot exhibit a corrosion depth greater than 200 μm . The ISO test involves short-term exposure to a very aggressive heated cupric chloride solution, which is unlike realistic exposure conditions. Using seven different brasses, including duplex and DZR types, testing was conducted to compare results of the ISO test with those of longer-term testing using real potable water. In terms of dezincification corrosion, results of the two test methods were in good agreement. But, with respect to other corrosion mechanisms (i.e., uniform corrosion and lead leaching), results were inconsistent.

BACKGROUND INFORMATION

Brass is a major component in both copper and plastic plumbing systems, used for intricate in-line devices (e.g., valves) and terminal fixtures (e.g., faucets). Brass is easily machined, relatively inexpensive and is typically corrosion-resistant,¹ but it may be susceptible to de-alloying under some conditions (e.g., when some alloys are exposed to aggressive water).² Most notably, dezincification (i.e., selective zinc leaching) can occur, which results in reddening of brass as the surface is enriched with copper (e.g., Figure 5.1). Dezincification can lead to premature plumbing failures via leaks at junctions or mechanical weakening of brass, and/or reduced flow due to build-up of corrosion products called “meringue.” On top of repairing or replacing plumbing materials, homeowners with dezincification problems can face water damage and mold growth.³ Recent outbreaks of such failures in the US have resulted in legal actions.⁴



Figure 5.1: Dezincified interior (left) and meringue build-up (right) within brass plumbing components.

Duplex brasses with high zinc content (i.e., >30%), often called “yellow” brasses, are particularly prone to dezincification, but alpha brasses with moderate zinc content (i.e., 15-30%) may also be susceptible. While low-zinc (i.e., “red”) and dezincification resistant (i.e., “DZR”) brasses are widely available for use in plumbing, they are not always utilized in the US and some other countries – presumably due to their higher costs. Following recent dezincification-related problems, the NSF/ANSI Standard 14 (NSF 14),⁵ which applies to plastic piping systems and

related components, was revised in 2009 to require that all NSF 14-listed brass valves and fittings (>15 % Zn by weight) are resistant to dezincification. Shortly thereafter, California became the first state to mandate that brass components used with PEX systems meet the revised NSF 14.⁶ In various other countries (e.g., Sweden, Australia), use of dezincification resistant brass alloys for potable water applications has been required for many years;³ but, in the US, regulation has been limited to alloys in underground service lines, not premise plumbing.⁷

To comply with NSF 14, brasses must be tested according to ISO 6509,⁸ an accelerated “jar” test in which brass samples are subjected to an aggressive heated cupric chloride solution for 24 hours. After testing, brasses must exhibit a maximum corrosion depth no greater than 200 µm. ISO 6509 is derived from an accelerated test method developed and refined by the Swedish Corrosion Institute in the 1970’s, which also conducted some practical testing around that time to evaluate how well the test’s results may represent more realistic conditions.⁹ It was generally concluded that results of the ISO test were in satisfactory agreement with those of field and laboratory tests; one duplex (un-inhibited) brass was highly susceptible to dezincification in the ISO and practical tests, while four inhibited duplex (i.e., DZR) brasses performed favorably. But in the intervening decades, additional confirmation testing has not been conducted.

The fact that ISO 6509 results depend on a single metric (i.e., corrosion depth) presents an important limitation of the compliance criteria: it assumes relatively uniform corrosion, yet heterogeneities in dezincification (e.g., plug-type dezincification) are well known.² Also, it has not been reported how the selectivity of corrosion for zinc (or other alloy constituents like lead) may differ between the ISO test and more realistic exposures in potable water. Considering the above, and that much has changed in brass manufacturing, potable water qualities, and plumbing

installations, the topic of brass dezincification performance testing was revisited. Herein, work is presented comparing results of long-term jar tests using real potable water to those of ISO 6509.

TEST METHODS

The susceptibility of seven different brasses (Table 5.1) was assessed based on weight loss and metal leaching in the real water exposure test, and corrosion depth and metal leaching in the ISO 6509 test. The composition of each brass was determined using a handheld X-ray fluorescence (XRF) instrument (Innov-X Systems, model Alpha 8000).

Table 5.1: Composition of tested brass alloys (as measured by XRF).

Brass	Mass %					
	Zn	Cu	Pb	Sn	Fe	Ni
A (duplex)	36.6	60.2	2.9	0.1	0.1	0.1
B (duplex)	36.4	59.2	3.3	1.2	0.6	0.4
C (duplex)	35.6	61.2	2.9	0.1	0.1	0.1
D (duplex)	35.4	60.9	3.3	0.1	0.1	0.1
E (DZR)	35.4	62.5	1.6	0.1	0.1	0.1
F (DZR)	8.2	89.3	1.7	0.3	0.1	0.5
G (alpha)	10.4	87.6	1.9	<i>ND</i>	<i>ND</i>	<i>ND</i>

ND Not detected

Real Water Exposure Test

Each of the seven brass alloys were purchased as new plumbing devices (e.g., couplings). Given their varying shapes and sizes, the brasses were machined into rings to provide similar surface areas (i.e., 400-500 mm²) and weights (i.e., ~ 1 gram) for testing. After being cut, brass rings were lightly polished, rinsed with de-ionized water, dried in a dessicator, and then weighed (to an accuracy of ± 0.1 mg). Then, three rings of each brass type were suspended in glass jars (i.e., one jar for each brass type), which were filled with the test water (Table 5.2) and closed. The test lasted a total of 16 weeks; water was not changed for the first four weeks, but was changed weekly thereafter using a dump-and-fill protocol.

Table 5.2: Water quality used real water exposure test.

pH	Alkalinity (as CaCO ₃)	Free Cl ₂	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Zn ²⁺	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	SiO ₂
mg/L											
7.8	119	1.1	75	26	93	5	0.19	96	252	0.15	7.6

pH (7.8 ± 0.2) and free chlorine residual (1.1 ± 0.2 mg/L) were maintained at least every 72 hours. Nitric acid and sodium hydroxide were used to adjust pH, and chlorine was added as reagent-grade sodium hypochlorite. Temperature was controlled by ambient conditions and stayed between 20-24 °C. Water samples from each jar (i.e., composite samples from triplicate brass rings) were collected periodically (i.e., 3-4 times per week) to quantify metal leaching. Water was stirred before taking samples, and soluble metal concentrations were determined using a Thermo Electron X-Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). Selectivity for zinc leaching was quantified as follows:

$$Selectivity\ for\ Zn = \frac{(Zn/Cu)_{leaching}}{(Zn/Cu)_{\%in\ alloy}}$$

At the end of the test, brass samples were allowed to dry before loose scale and rust were removed using a Dremel tool with a soft cloth polishing pad. The samples were then weighed again to determine the total weight loss (i.e., difference between pre-test and final weight).

ISO 6509 Test

The second test was conducted following the standard procedure outlined in ISO 6509. Each of the seven brasses was tested in triplicate, and the only major modifications to the prescribed procedure were that: 1) all three samples from each brass type were machined from similar locations on the device, such that each had identical thickness; and 2) temperature was maintained via a controlled oven, instead of an oil or water bath as specified in the standard.

Following testing, each sample was cross-sectioned such that corrosion depth could be measured on two unique planes (using a Boreal stereomicroscope). Additionally, zinc and lead leaching were determined via ICP-MS from samples of test solution (to which a single piece of brass had been subjected) taken at the end of the 24 hour test. Due to the very high copper concentration in the test solution (i.e., ~ 5 g/L), neither copper nor total metal leaching could be determined with confidence; thus, the selectivity of corrosion for zinc could not be quantified.

EXPERIMENTAL RESULTS

Results from the two test methods were in relative agreement with respect to dezincification corrosion, and demonstrated that the duplex (un-inhibited) brasses were, by far, more prone to dezincification than the alpha or DZR brasses (Figure 5.2). According to the NSF 14 criteria, the duplex (i.e., A-D) brasses failed the ISO 6509 test because all samples exhibited maximum dezincification depths of 200 μm or greater; the deepest (i.e., ~ 600 μm) was measured on a brass C sample (Table 5.3). The alpha brass (G) exhibited limited areas of more shallow corrosion, with maximum observable depth being about 190 μm . Exposed surfaces of the DZR brasses (E and F) appeared dull and very dark reddish-brown, indicating they had been corroded, although the corrosion depth was too shallow to quantify at even 100x magnification.

Overall, as corrosion depth (Figure 5.3) and zinc leaching (Table 5.3) increased in the ISO test, weight loss, zinc leaching and total metal leaching (i.e., sum of zinc, copper and lead) increased in the real water test. It should be noted that, while the DZR brasses exhibited no measurable corrosion depth in the ISO test, they did lose a significant amount of weight (i.e., at least 60% as much as each duplex brass) in the real water test due to more uniform corrosion (i.e., more copper leaching). This underscores a primary discrepancy in the two test methods, which could be important in screening brass alloys for use in potable waters where corrosion

other than dezincification is problematic. With respect to zinc selectivity, results of the real water test were found to be in good agreement with corrosion depths in the ISO test (Table 5.3).

Metric		Ranking						
		← most susceptible				least susceptible →		
Real Water Test	Weight loss	D	B	C	A	E	F	G
	Total metal leaching	B	D	C	A	E	F	G
	Zinc leaching	B	D	C	A	E	G	F
	Selectivity of zinc leaching	B	A	D	C	E	F	G
ISO 6509 Test	Corrosion depth	C	B	D	A	G	E, F	
	Zinc leaching	A	D	C	B	E	G	F

Figure 5.2: Ranked susceptibility of tested brasses based on different metrics. The duplex brasses (A-D) were consistently more susceptible to dezincification (or other corrosion) than were the alpha and DZR brasses.

Table 5.3: Summary of selected results.

Brass	<i>Real Water Exposure Test</i>								<i>ISO 6509 Test</i>					
	Weight Loss		Average Metal Leaching Per Sampling Event						Max. Corrosion Depth		Average Metal Leaching			
	(%)	95% CI	Zn (µg/L)	95% CI	Pb (µg/L)	95% CI	Cu (µg/L)	95% CI	(µm)	95% CI	Zn (mg/L)	95% CI	Pb (mg/L)	95% CI
A	1.99	0.11	189.9	18.6	3.9	1.4	23.5	7.2	298	88	350.0	109.1	19.2	6.4
B	2.58	0.41	279.3	24.7	3.4	1.3	16.9	4.7	425	175	294.8	43.9	82.7	129.5
C	2.51	0.16	241.2	24.5	3.1	1.4	32.3	8.5	511	93	331.6	43.9	31.0	24.8
D	2.67	0.61	253.8	22.8	3.7	1.6	25.9	7.2	397	88	334.2	124.1	18.6	6.3
E	1.79	0.12	151.2	19.8	4.0	2.3	31.3	5.0	0	-	118.2	3.6	10.0	8.9
F	1.61	0.06	22.1	3.5	6.7	0.8	131.8	11.7	0	-	21.5	5.3	2.6	0.7
G	1.52	0.22	25.7	4.0	6.5	1.0	110.9	10.6	98	108	26.1	1.7	5.0	0.4

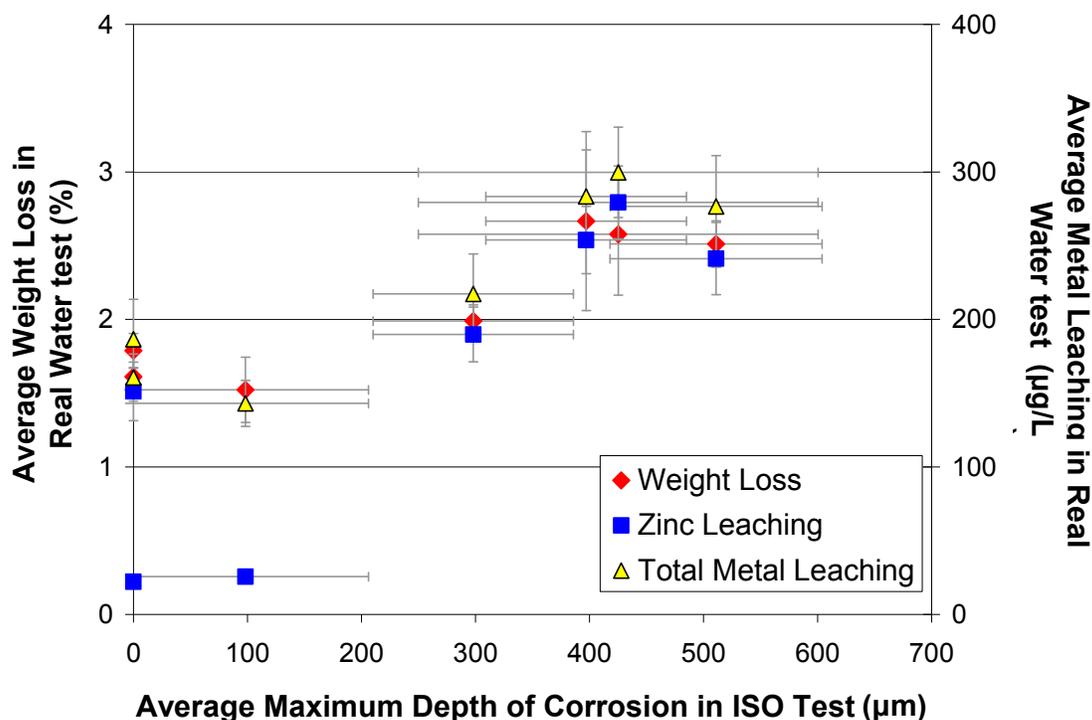


Figure 5.3: Weight loss and metal leaching in the real water exposure test vs. maximum depth of corrosion in the ISO 6509 test. Average values were computed from triplicate samples and error bars represent 95% confidence intervals.

Interestingly, opposite trends were observed in lead release between the two test methods (Figure 5.4). Lead and zinc leaching were inversely related in the real water test, consistent with some prior findings that DZR brasses tend to release relatively high amounts of lead due to intergranular corrosive attack in potable water.¹⁰ However, lead and zinc leaching were positively related in the ISO test, suggesting that different corrosion mechanisms may have occurred. This was supported by the fact that the exposed brass surfaces also appeared visually different between the two tests. Non-uniform meringue and other corrosion products slowly formed on the duplex brass samples exposed to real water (pH of ~ 8), which likely resulted in under-deposit corrosion (i.e., driven by a differential concentration cell) that was highly selective for zinc; whereas the alpha and DZR brasses generally formed thin and uniform scales, allowing the alloy constituents (including lead) to be leached more uniformly. In contrast, corrosion products did

not form on any brasses in the ISO testing due to the low pH (i.e., 3-4) of the test solution. Indeed, most samples in the ISO test underwent highly uniform layer dezincification, while only a few were observed to exhibit more heterogeneous attack (e.g., Figure 5.5), which could not be attributed to “edge” or “crevice” effects or imperfections on the initial brass surfaces.

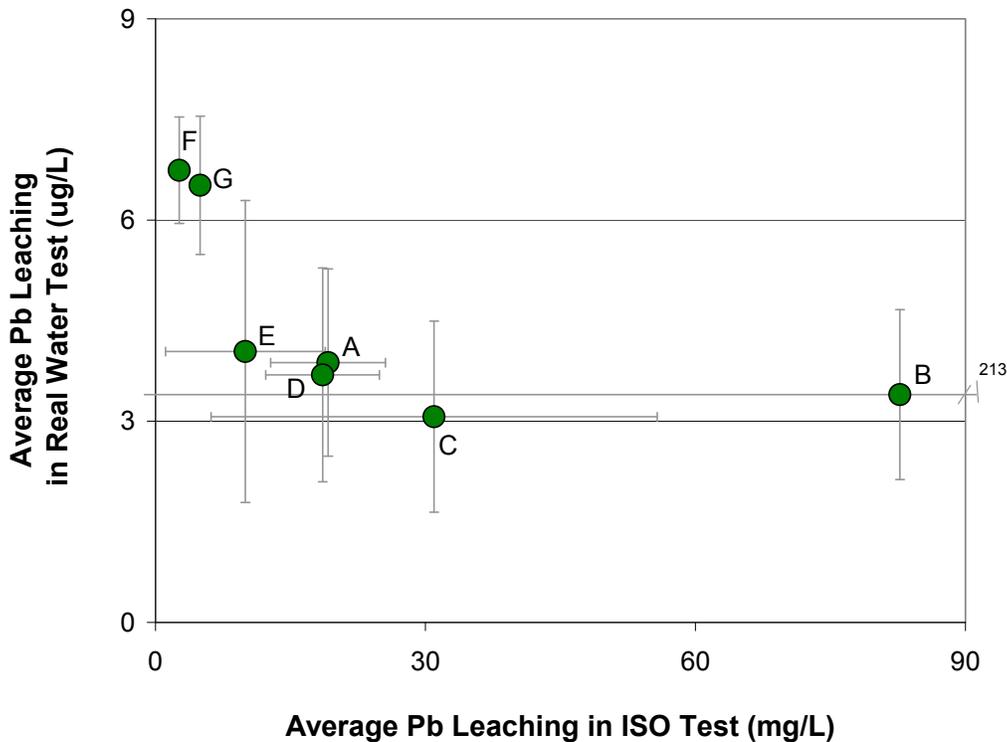


Figure 5.4: Lead leaching in real water exposure test vs. that in ISO 6509. Average values were computed from triplicate samples and error bars represent 95% confidence intervals.

Additionally, on one brass B sample it appears that an area of high lead content was attacked and dezincification was reduced. Lead leaching from this sample was over 10x higher than the other B samples in the ISO test (i.e., 235 vs. 15 and 20 mg/L) – accounting for the outlying data point in Figure 5.4 – but the maximum corrosion depth was only about half that of the others (i.e., 248 vs. 495 and 533 μm). Variations were also present between triplicate results for other brasses in both tests, but to a much lesser extent (e.g., weight losses of D samples in the real water test varied by $\sim 50\%$). These results highlight the fact that heterogeneities in brass

devices due to metallurgy and/or manufacturing may complicate standardized testing of dezincification (or other corrosion problems), as well as compromise field performance.

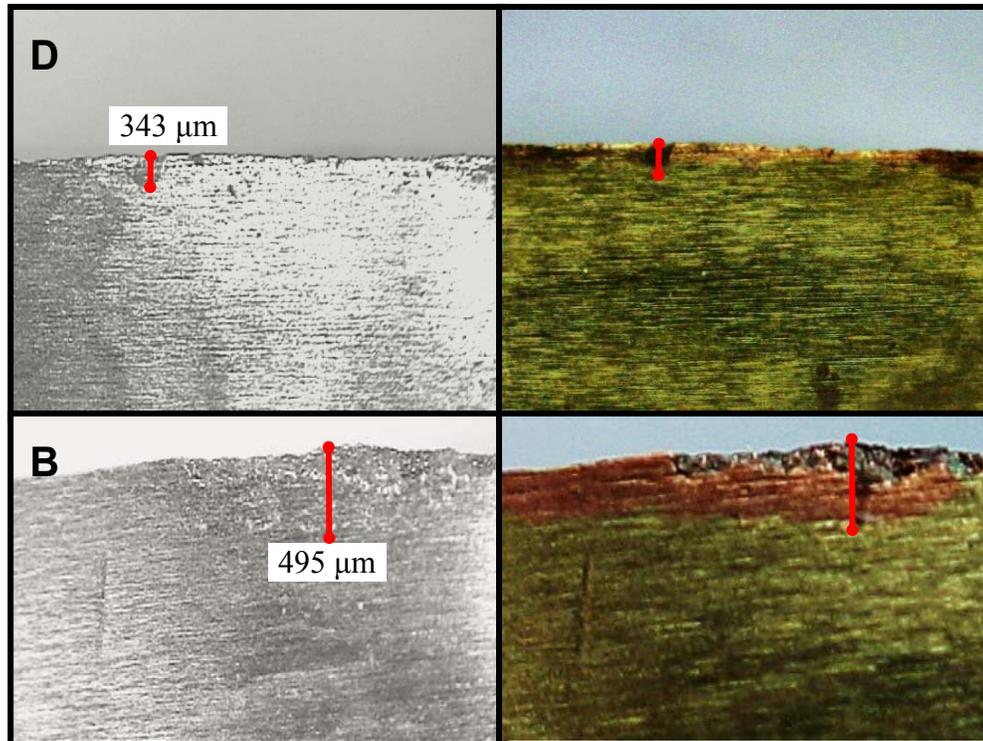


Figure 5.5: Stereomicroscope images (left) and photographs (right) of layer (top) and plug (bottom) dezincification on brasses D and B, respectively.

CONCLUSIONS

Brass dezincification is a re-emerging problem in US plumbing systems, and is being partly addressed by NSF 14, which requires alloys in plastic pipe systems to be tested per ISO 6509 and meet performance criteria. In terms of the explicit test objectives (i.e., to evaluate dezincification susceptibility), the ISO test produced results that were in good agreement with longer-term testing using real potable water for seven different brasses, which complements prior findings regarding usefulness of the test by Holm et al.⁹ However, the ISO test conditions do not replicate brass corrosion as it practically occurs, as evidenced by differences in lead leaching and

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