

Dezincification and Brass Lead Leaching in Premise Plumbing Systems: Effects of Alloy, Physical Conditions and Water Chemistry

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ABSTRACT

Brass components are widely used in drinking water distribution systems as valves, faucets and other fixtures. They can be corroded by “dezincification,” which is the selective leaching of zinc from the alloy. Dezincification in potable water systems has important practical consequences that include clogged water lines, premature system failure and leaks, and release of contaminants such as lead. Brass failures attributed to dezincification are known to occur at least occasionally all over the world, and have emerged as a significant problem in the U.S. recently due to the use of inexpensive high zinc brass fittings in cross-linked polyethylene (PEX) plumbing systems. As PEX systems gain popularity and leaded brass is recognized as an important source of lead in potable water systems, it is important to examine dezincification corrosion in more detail.

An in-depth literature review revealed that conventional wisdom about dezincification was no longer adequate in explaining failures observed in modern water systems. Little research has been conducted since the landmark work of Turner et al. nearly half a century ago. The potential role of chloramines, phosphate inhibitors, and modern understanding of water chemistry need evaluation. The role of physical factors including stirring, heating and galvanic connections are also potentially influential.

A mechanistic study of zinc solubility and corrosion of copper: zinc couples provided insight to factors that might mitigate and exacerbate zinc leaching from brass. Zinc solubility and corrosion was reduced by higher pH and bicarbonate, but was enhanced by higher chloride. Hardness ions including Mg^{+2} and Ca^{+2} had little effect.

Alloys with higher zinc content had a greater propensity for dezincification corrosion. Stirring and galvanic connections caused brass to leach more metals and have higher weight loss. Heating may contribute to corrosion scale accumulation.

A comprehensive examination of dezincification as a function of water chemistry used numerous techniques that include measurement of galvanic currents, metal leaching, and weight loss. In general, as would be predicted based on results of the study of solubility and corrosion of pure zinc, chloride emerged as an aggressive ion whereas bicarbonate was beneficial to brass corrosion. Hardness had little impact, and phosphates, silicates and Zn^{+2} inhibitors had a significant short-term benefit but little long-term benefit.

The relationship between dezincification corrosion, lead leaching from brass, and water chemistry was investigated in Chapter 5. Surprisingly, lead and zinc leaching from a range of brasses were found to be negatively correlated. Hence, use of brasses that minimize dezincification problems might increase lead leaching.

This thesis represents a comprehensive analysis of factors that are influential for dezincification and lead leaching from brass in premise water distribution systems through literature reviews, mechanistic investigations, bench-scale experiments, and case studies. Results can be used by water utilities, plumbing engineers, manufacturers and home owners to better prevent, recognize, and mitigate brass and dezincification corrosion problems.

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Authors' Preface

All five Chapters of this thesis are presented as separate manuscripts according to the specifications of Virginia Tech's journal article formatting. Chapter 1 is a literature review of brass dezincification in potable water systems. This work was undertaken as part of WRF project No. 4289 *Influence of Water Chemistry and Other Physical Factors on Copper Pitting and Brass Dezincification Corrosion in Premise Plumbing Systems*. The first author of this chapter Sarver discussed the basic electrochemical reactions driving dezincification and the effects of physical factors. Sarver made the whole article coherent and consistent. The author of this thesis Zhang summarized the manifestations of dezincification, and discussed the effects of alloy composition and water chemistry. Zhang contributed approximately one half of the writing for this chapter, and is appropriately listed as the second author of this article which is submitted to the journal *Corrosion Review* for publication.

The author of this thesis summarized the manifestations of dezincification, and discussed the effects of alloy composition and water chemistry. The author contributed approximately one half of the writing for this chapter, and is appropriately listed as the second author. The first author of this chapter Sarver discussed the basic electrochemical reactions driving dezincification and the effects of physical factors. Sarver also made the whole article coherent and consistent. This chapter is submitted to the journal *Corrosion Review* for publication.

All remaining chapters were prepared via collaboration between the author and his advisor Dr. Edwards, as is typical for a master's thesis. Chapter 3 discussed the effects of alloy composition and physical conditions on dezincification. This study was presented at the AWWA Annual Conference and Exposition in June of 2009 and part of it appears in the proceedings of that conference.

Chapter 4 addressed the impact of water chemistry parameters on dezincification corrosion. This work was presented at the AWWA Water Quality Technology Conference and Exposition in November of 2009 and a portion of it appears in the proceedings of that conference.

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Chapter 1 Review of Brass Dezincification Corrosion in Potable Water Systems

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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 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 synthesizes 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.

Keywords: dezincification, dealloying, brass, galvanic corrosion, potable water

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

(Triantafyllidou and Edwards 2007) (D. E. Kimbrough 2007) (D. Kimbrough 2001).

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 resurgence in use of high-zinc brass fittings 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 (Smith 2009).

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, synthesizes key research results, and develops hypotheses regarding underappreciated factors associated with modern plumbing practice and water chemistry.

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 1 - 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 (D. Nicholas 1994). 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.

The most commonly cited problem associated with dezincification is the formation of “meringue” deposits on brass components, which can physically block water flow (Figure 1 - 1, Figure 1 - 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 (Simmonds 1967) 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.

In addition to component failures and associated water damage, release of minor brass alloy constituents is also possible (Figure 1 - 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 (R. J. Oliphant 2007), and the literature suggests a relationship between the occurrence of dezincification and persistent lead leaching in many potable water systems (Triantafyllidou and Edwards 2007) (D. E. Kimbrough 2007) (D. Kimbrough 2001) (Lytle and Schock 1996) and in “green” buildings (Nguyen, et al. 2009). 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 (Maynard, Mast and Kwan 2008) (C. A. Risbridger 1952). Work by Triantafyllidou et al. (2007)

demonstrated that lead leaching could increase with time when dezincification was occurring in low alkalinity waters (Triantafyllidou and Edwards 2007), and this trend was confirmed by Maynard et al (Maynard, Mast and Kwan 2008). 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 (Jester 1985), Nicholas noted that if meringue was removed from a brass component plug-type red pits were often observed underneath (D. Nicholas 1994). 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 1 - 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, 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 1 - 1).

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 1 - 3).

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 (R. Oliphant 1978) (Selvaraj, et al. 2003) (Karpagavalli and Balasubramaniam 2007). When the zinc content is between about 30 to 40%, tensile strength and

machineability improve with higher zinc, but elongation ability is reduced (Selvaraj, et al. 2003). 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 (C. A. Risbridger 1952) (Selvaraj, et al. 2003). When the zinc content rises above 45%, the alloy tends to become very brittle which is problematic for use in plumbing systems (Selvaraj, et al. 2003).

Zinc content is also a key factor in determining the susceptibility of brass to dezincification (Figure 1 - 4). Brasses with zinc content below about 15% are generally considered resistant to dezincification (Oliphant and Schock 1996) (Davies 1993) (Kelly, Lebsanft and Venning 1980); 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 (Davies 1993).

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 (Davies 1993); a summary of key results is provided in Table 1 - 2. While some constituents may render alpha brass (and the alpha phase of duplex brass) relatively immune to dezincification (Simmonds 1967) (Davies 1993) (Heidersbach and Verink 1972), inhibiting the dezincification propensity of beta brass has proven more difficult (D. Nicholas 1994) (Heidersbach and Verink 1972). 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 (Karpagavalli and Balasubramaniam 2007).

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 observation 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 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 1 - 3 summarizes the effects of individual water constituents and/or parameters on brass dezincification reported in the literature.

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 (Oliphant and Schock 1996). "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 1 - 3), and having a pH of about 8.3 or greater, were prone to causing meringue build-up (M. E. Turner 1961). Using both laboratory and practical data, Turner empirically developed a diagram (Figure 1 - 5) to indicate water quality regimes in which dezincification problems will likely occur based solely on chloride and temporary hardness concentrations (M. E. Turner 1961). Turner's diagram has been adopted as a standard in predicting dezincification propensity based on water chemistry.

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 (Triantafyllidou and Edwards 2007) (Oliphant and Schock 1996). 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 (Triantafyllidou and Edwards 2007) (D. Kimbrough 2001) (Maynard, Mast and Kwan 2008), 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 (D. Nicholas 1994) (V. F. Lucey 1973).

pH, Temperature and Aeration

For meringue dezincification, Turner's field experience (M. E. Turner 1961) and further laboratory tests (M. Turner 1965) 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 (Simmonds 1967). 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 1 - 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 (D. Nicholas 1994) (Oliphant and Schock 1996). 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 (Jester 1985). 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 (D. Nicholas 1994).

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 (Oliphant and Schock 1996) (Davies 1993). 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 (Simmonds 1967) (V. F. Lucey 1973). Other researchers also observed that increased temperature accelerates dezincification rates (D. Nicholas 1994) (Oliphant and Schock 1996) (Abbas 1991). For example, research by Nicholas indicated that dezincification rates doubled when the temperature was increased from 20 to 70°C (D. Nicholas 1994).

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 formation was eliminated (M. Turner 1965). 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

(Kelly, Lebsanft and Venning 1980) (M. Turner 1965). Jinturkar et al. studied brass corrosion in sulfuric acid solutions and also found that increased dissolved oxygen enhances corrosion (Jinturkar, Guan and Han 1998). Ingleson et al. reported that free carbon dioxide promotes dezincification as well (Ingleson, Sage and Wilkinson 1949).

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 to accelerate dezincification of duplex brass (Table 1 - 3) (Ingleson, Sage and Wilkinson 1949). 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 (Risbridger, et al. 1951). 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 (D. Nicholas 1994).

Several studies have also looked at the effects of chloramination on dezincification (Table 1 - 3). Stuart, as cited by Nicholas (D. Nicholas 1994), observed that the penetration depth of dezincification increased linearly with chloramine concentration from 0.1-1.0 mg/L (Stuart 1988). 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 (G. C. Moore 1989). 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 (Moore and Beckwith 1982).

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 measurements (G. C. Moore 1989) 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 distribution 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 (Ingleson, Sage and Wilkinson 1949) (Risbridger, et al. 1951) (Larson, King and Henley 1956). 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 (Zhang, Love and Edwards 2009).

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 (Ingleson, Sage and Wilkinson 1949).

Edwards and Dudi found that chloramine typically increased lead leaching from brass samples versus the same water with free chlorine alone (Edwards and Dudi 2004). 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 1 - 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 (M. E. Turner 1961). Lucey's findings appear to show a synergistic effect between sulfate and chloride (V. F. Lucey 1973). 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 (M. E. Turner 1961). 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 (V. F. Lucey 1973). Oliphant's findings agreed with Lucey's with respect to the role of nitrate in reducing dezincification rates (R. Oliphant 1978).

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 (M. E. Turner 1961) (V. F. Lucey 1973). It is generally accepted that fluoride at or below 1 mg/L has negligible effects (D. Nicholas 1994) (R. Oliphant 1978).

Based on measured galvanic corrosion currents between copper cathodes and brass samples, Oliphant concluded that silica may temporarily inhibit dezincification (R. Oliphant 1978). 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 (Lehrman and Shuldener 1951). Furthermore, Oliphant reported that if the addition of silica is combined with approximately 1 mg/L zinc, stable and strong inhibitive effects were achieved (R. Oliphant 1978). 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 (M. E. Turner 1961). 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 1 - 3). Turner determined that 1 mg/L or less orthophosphate had no observable effects in a 30-day experiment as assessed by meringue formation (M. E. Turner 1961). 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 (V. F. Lucey 1973). 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 (Jester 1985). Indeed, Simmonds' field experience suggested that dezincification failures can also occur at the lower end of the typical conductivity spectrum for potable water

(Simmonds 1967). 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 (Tabor 1956).

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 (Kumar, et al. 2006). 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 (de Sanchez and Schiffrin 1982). In addition, scales laden with bacteria may also promote dezincification, as observed by Valcarce et al. (Valcarce, de Sanchez and Vazquez 2005). 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 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 1 - 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 1 - 6). To the extent that a meringue (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 1 - 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.

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 (Butler 1966) (Stratmann and Frankel 2003) (LaQue and Copson 1963). Seemingly in direct contrast with many textbooks are practical observations that brass corrosion (including dezincification corrosion) is often accelerated by water movement and flow (Kelly, Lebsanft and Venning 1980) (Bengough and May 1924). This discrepancy

is noted by Kelly et al. and is not inconsistent given considerations of separate of anodic and cathodic areas used in the different experimental set-ups (Kelly, Lebsanft and Venning 1980).

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 (V. F. Lucey 1973), 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 1 - 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 (Cigna and Gusmano 1976). 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 (V. F. Lucey 1965). Newman et al. agreed with the general effect of chloride but argued that it is the cuprous chloride anion (CuCl_2^-) which accelerates dezincification (Newman, Shahrabi and Sieradzki 1988).

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 (Nielsen and Rislund 1973). 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 (Kuppan 2000), 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 (Cigna and Gusmano 1976), 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 (Bengough and May 1924).

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 (Kelly, Lebsanft and Venning 1980). 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 (Kelly, Lebsanft and Venning 1980). 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 (Bengough and May 1924). 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 tends to increase with the flow velocity, and the acceleration is primarily due to entanglement of air in the flow. Houghton came to similar conclusions (Houghton 1931). 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 1 - 6 (Nowlan 1960).

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 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 (Sakamoto, Yamasaki and Matsumura 1995). They reported that flow-induced localized corrosion (or erosion corrosion), identified by the presence 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 (Moore and Beckwith 1982). 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 (Grzegorzewicz and Kuznicka 1998) and Efrid reported on critical shear stress for wall impingement of aluminum brass (22% Zn) (Efrid 1977). 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 (Langenegger and Callaghan 1972). 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 (R. Oliphant 1978) (V. F. Lucey 1973).

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 (Nielsen and Rislund 1973). 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 1 - 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 1 - 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.

In E, similar to case C in Figure 1 - 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 1 - 6, 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 (R. Oliphant 1978) (V. F. Lucey 1973). 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 (R. Oliphant 1978). 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 1 - 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 1 - 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.

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.

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

1. 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
2. Dezincification attack may manifest itself as either plug- or layer-type, and meringue deposits may form under circumstances of low zinc solubility
3. 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 in the alloy.
4. 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.
5. Meringue dezincification is favored by higher pH, temperature and aeration.
6. Increased free chlorine and chloramine may promote dezincification.
7. Most anions are believed to worsen dezincification, but nitrate and phosphate may slightly inhibit it in some cases.
8. 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,
9. 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.

10. 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
11. 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.
12. 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.

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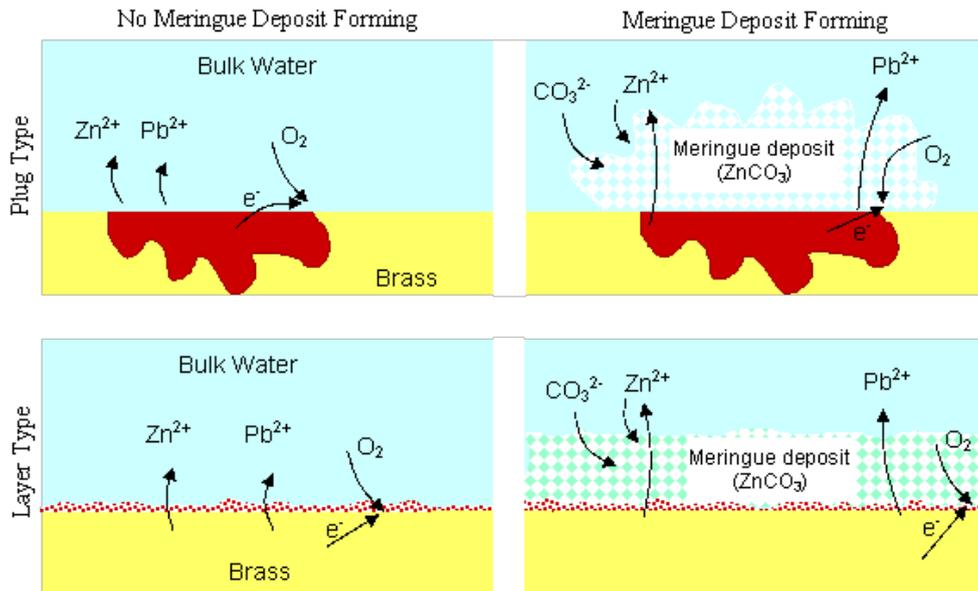


Figure 1 – 1 Dezincification can occur as either the plug (upper left) or layer (lower left) type, either of which may or may not lead to meringue deposition (right). Plug dezincification affects isolated areas of the brass and penetrates into the brass surface, whereas layer dezincification attacks the surface fairly uniformly.

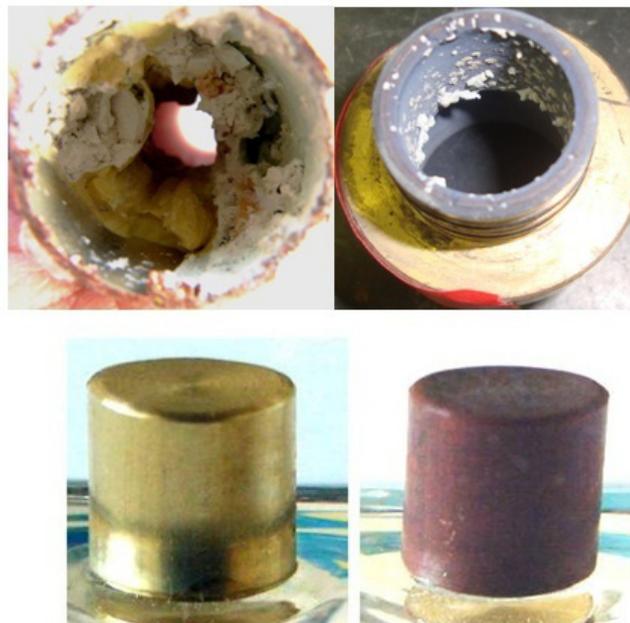


Figure 1 – 2 Meringue build-up inside a brass fitting can effectively block flow (upper left). After several months of plug dezincification, meringue build-up is evident on a brass fitting (upper right). As brass undergoes layer dezincification, its characteristic yellow surface (lower left) turns to a reddish color due to copper enrichment (lower right).

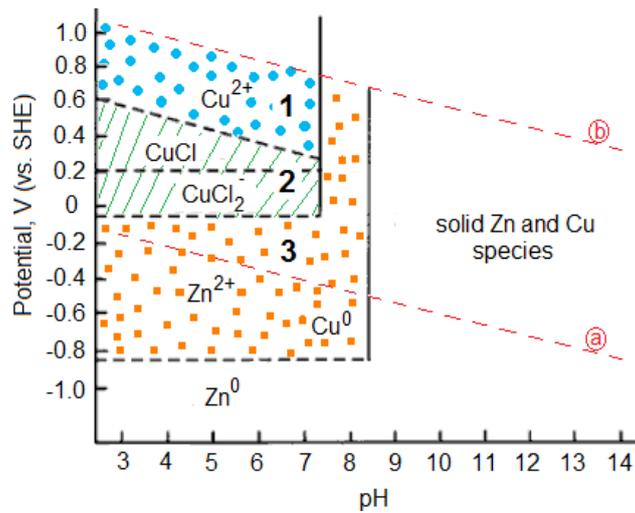


Figure 1 – 3 Illustrative potential-pH diagram for 70-30 brass in 0.1M chloride solution (adapted from Heidersbach & Verink 1972/18/). Region 1 represents uniform brass corrosion via copper and zinc dissolution with no copper re-deposition; 2 represents dezincification via copper and zinc dissolution 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

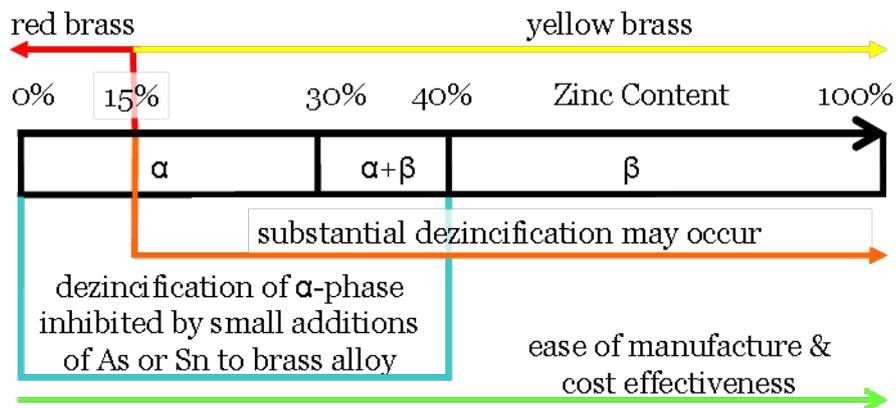
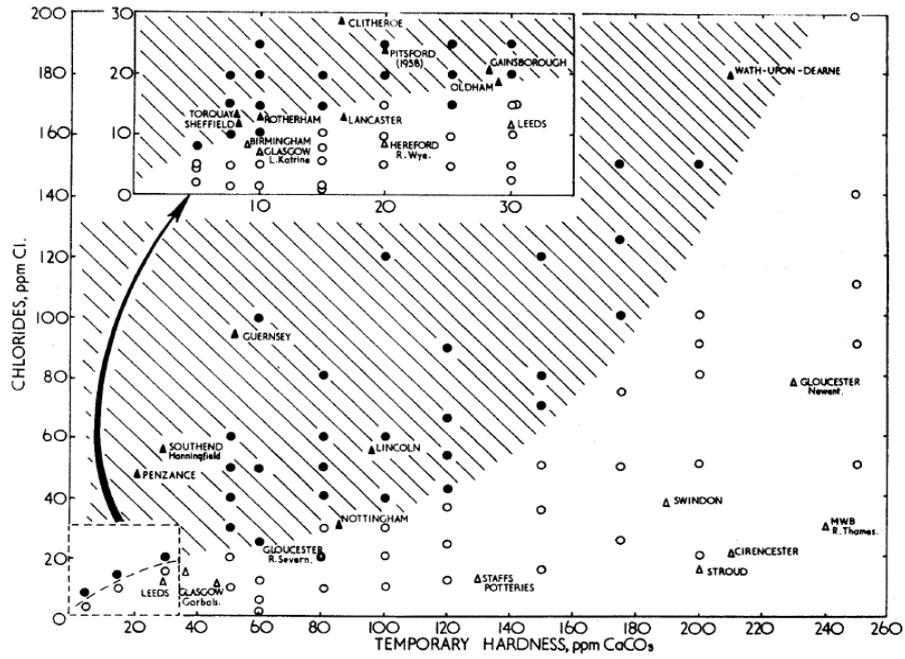


Figure 1 – 4 General trends for brass alloys as zinc content is varied.



- *Laboratory experiments in which meringue dezincification took place*
- *Laboratory experiments in which meringue dezincification did not take place*
- ▲ *Public water supplies known to produce meringue dezincification*
- △ *Public water supplies which are known not to produce meringue dezincification*

Figure 1 – 5 Turner’s Diagram for predicting meringue dezincification based on chloride and temporary hardness concentrations (taken from Turner, 1961/20/). Waters in the shaded area are considered likely to produce meringue dezincification at pH 8.3 or above.

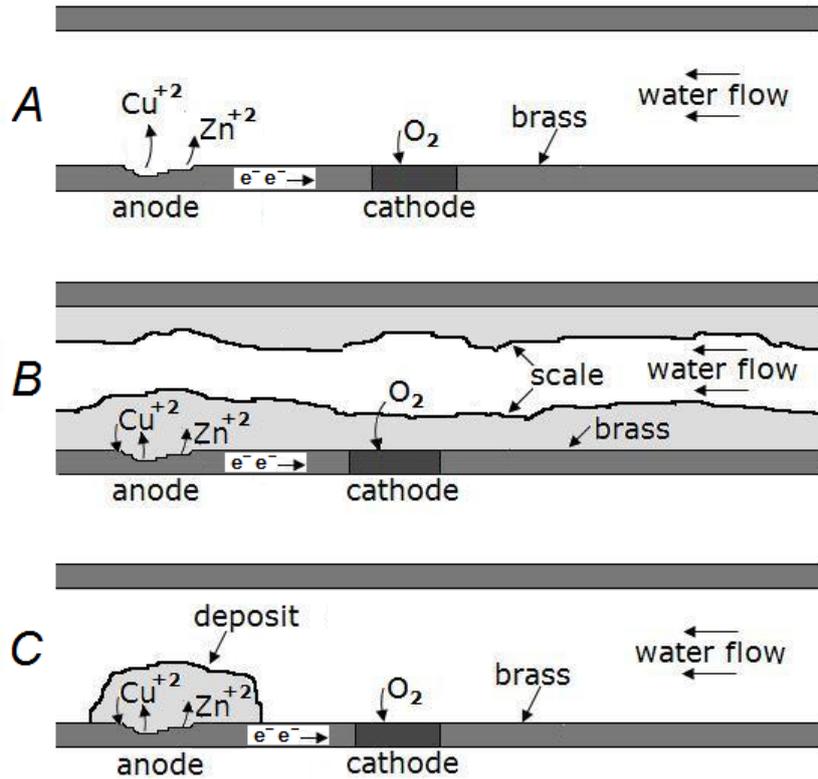


Figure 1 – 6 Potential manifestations of dezincification for a single piece of brass in potable water. On clean brass with or without flow, the anode and cathodes are located very near each other and corrosion proceeds uniformly (A). With time, deposits may grow and completely coat the brass surfaces (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.

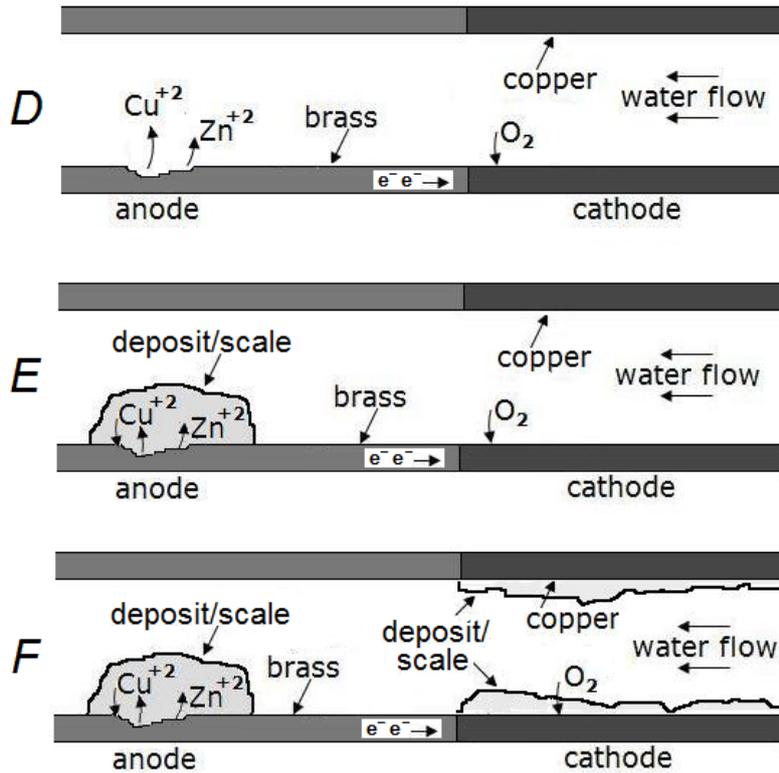


Figure 1 – 7 Potential manifestations of dezincification for a galvanic couple between brass and copper in potable water. *D* represents slow dezincification; *E* represents severe dezincification whereby a localized environment develops at the anode while the copper cathode is supplied with oxidant; and *F* represents dezincification as in *E*, only it is somewhat slowed by the loss of active surface area on the cathode.

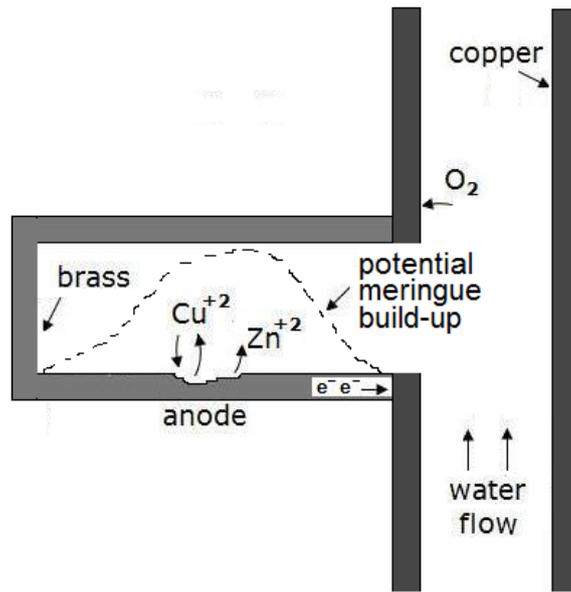


Figure 1 – 8 Hypothesized worst-case scenario for dezincification in the case of a galvanic couple between brass and copper in potable water. Due to its position in the system, the brass is removed from flow and a localized environment may quickly develop to promote dezincification and eventual meringue build-up.

Table 1 – 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
$\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$ $Cl_2 + 2e^- \rightarrow 2Cl^-$	0.814V (pH=7) 1.36V	Oxidant Reduction	Cathodic Surface
$Cu^0 \rightarrow Cu^{2+} + 2e^-$	-0.340V	Copper Oxidation	Dezincifying Surface
$Cu^{2+} + 2e^- \rightarrow Cu^0$	0.340V	Copper Deposition	Dezincifying Surface

Table 1 – 2 Observed effects of various alloy additives on brass dezincification propensity; partially summarized from Copper Development Association report (Davies 1993)

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 1% Sn	Karpagavalli et al. (2006)	Karpagavalli et al. (2006)
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	Weldon (1957)	CDA (1993)

	brass from 1.2 to 3.2% Sn		
	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)	Sullivan (1971)	CDA (1993)

	reduced dezincification rate of 60-40 brass		
	Gold and silver both inhibit brass dezincification	Kondrashin et al. (1989)	CDA (1993)

Table 1 – 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.
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 meringue dezincification.	Visual observation.
	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	Corrosion currents

			meringue dezincification.	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.
Orpho-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.

Chapter 2 Zinc Solubility and Zinc-Copper Galvanic Corrosion

Yaofu Zhang, Marc A. Edwards

Abstract

Zinc solubility and zinc-copper galvanic corrosion are significantly influenced by water chemistry parameters. The amount of soluble zinc decreases with higher pH, more bicarbonate, or less chloride. Zinc solubility is not significantly impacted by either phosphate or hardness alone. However, adding calcium or magnesium together with phosphate, facilitates precipitation or agglomeration of zinc-phosphate solids. Effects of bulk water chloride and alkalinity are magnified by galvanic corrosion, since these anionic constituents are concentrated near the zinc anode surface in a lower pH acidic environment.

Keywords: zinc solubility; Zinc-Copper galvanic corrosion, alkalinity, chloride, hardness, phosphate

Introduction

Brass is an alloy of zinc, copper and other minor constituents (e.g., lead, iron, tin) and its corrosion can lead to premature service failures (See Chapter 1) (Nicholas 1994) (Turner 1961) (Lucey 1973) (Oliphant and Schock, Copper Alloys and Solders 1996). Failures from dezincification have recently emerged as a significant problem in the U.S. (District 2007). Dezincification causes preferential zinc leaching, a porous/fragile structure that is prone to mechanical failure, and formation of a voluminous corrosion products termed “meringue” that can completely block water flow (R. J. Oliphant 2007) (Selvaraj, et al. 2003).

Water chemistry can play a strong role in controlling dezincification, although the precise mechanisms of action have not been elucidated. For example, the ratio of chloride to “temporary hardness” is believed to control meringue build-up via dezincification for brass that is galvanically connected to copper (Turner 1961). Temporary hardness refers to the concentration of hardness that is removed upon heating in a water heater, presumably due to precipitation of

CaCO_3 solids via a reaction of Ca^{+2} and HCO_3^- in water during heating. (Bicarbonate is the major component of alkalinity in drinking water. Alkalinity and bicarbonate are used interchangeably thereafter). Temporary hardness was once a routine measure for a water supply (Nielsen 1983), but it is rarely if ever measured in modern water systems. Because “temporary hardness” is a complex function of alkalinity and hardness, it is uncertain whether Turner was observing benefits for dezincification from hardness ions alone, alkalinity (bicarbonate) alone, or some complex combination of the two factors. The ambiguity is further compounded, because in laboratory experiments Turner (1961) almost always added a combination of Mg^{+2} or Ca^{+2} with bicarbonate, made visual observations about mercurine build-up, and never studied the isolated effect of hardness (Mg^{+2} or Ca^{+2}) or alkalinity.

Recent work has also provided mechanistic insight to the role of bicarbonate and chloride in galvanic corrosion between copper and less noble metals such as brass, lead or zinc (Edwards and Dudi 2004) (Triantafyllidou and Edwards 2007) (Dudi, et al. 2005). When copper is coupled to a less noble metal such as lead, the lead becomes the anode and is sacrificed, and the copper becomes the cathode and is protected. The pH can drop at the surface of the less noble metal to very low values, and anions such as Cl^- are drawn to its surface to balance electroneutrality. Because higher Cl^- and lower pH can increase the solubility of lead, protective scales are not readily formed, and very high rates of corrosion are maintained at the anode surface. Alkalinity is beneficial, in that it acts as a buffer, and tends to reduce the extent of the pH drop at the anode surface. Moreover, it was discovered that alkalinity could contribute to formation of a basic zinc carbonate $[\text{Zn}_5(\text{OH})_6(\text{CO}_3)_4]$ solid, that reduces zinc solubility (Paulson, Benjamin and Ferguson 1989) and could potentially form a protective scale on brass. These recent mechanistic insights are potentially relevant to understanding the adverse effects of Cl^- and benefits of alkalinity (or temporary hardness) in dezincification of brass as observed by Turner (1961).

This study will provide a fundamental perspective into the potential role of water chemistry in controlling zinc corrosion and zinc solubility, which in turn, has implications for zinc leaching from brass alloy. A series of jar tests were conducted to study the solubility of zinc as a function of pH, chloride, bicarbonate, hardness and phosphate. A second series of experiments examined the interplay between alkalinity and chloride in relation to galvanic corrosion of zinc connected to copper.

Material and Methods

Zinc Solubility Tests

Solubility jar tests were conducted in 500 ml HDPE containers at room temperature ($23 \pm 2^\circ\text{C}$). In each container, concentrations of target constituents were varied by additions from stock solutions into 300 ml nanopure water (Table 2 - 1). Solutions were adjusted with 0.01 M nitric acid and 0.01 M sodium hydroxide to the target pH values, and pH variation was less than 0.2 pH units. Soluble zinc was operationally defined as the portion of zinc that passes through a 0.45 μm pore size syringe filter. The amount of zinc, copper and chloride was quantified using a Thermo Electron X-Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) per Standard Method 3125-B (APHA 1998). Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume.

The test solution was vigorously shaken before sampling and two samples were collected thereafter including total metal (unfiltered) and soluble metal. The ratio of soluble zinc to the total zinc is used to calculate the percentage of soluble zinc.

Zinc-Copper Galvanic Tests

The role of galvanic connections was examined by connecting a copper pipe (7.6-cm long and 1.3-cm diameter) to a zinc wire (5-cm long and 1 mm diameter) (Figure 2 - 1). The copper pipe was laid horizontally at the bottom of a 2-liter plastic container, and the zinc wire was held vertically in a 1 ml pipette tip. The container was then filled with 2 liter test solution (Table 2 - 2). This arrangement and the opening of about 0.3 mm in the pipette tip created a Zinc-Copper galvanic cell with an isolated anode compartment in which changes in water chemistry near the zinc surface could be monitored. The test solution was pre-adjusted to the target pH 8.3 with 0.01 M nitric acid and 0.01 M potassium hydroxide. The pH stayed relatively constant at 8.3 ± 0.2 pH units during the experiment. Galvanic currents and voltages between the zinc wire in the anode compartment and the copper pipe were recorded with a Fluke 189 True RMS Multimeter, by disconnecting the copper wire between the two temporarily. A MI-406 Flat Membrane pH Microelectrode and a MI-402 Dip-type Reference

Microelectrode were used to measure the pH values in the bulk water and the anode compartment. At certain times 50 μL of supernatant was also taken from the anode compartment to be analyzed for zinc and chloride concentration by ICP-MS.

At the end of the 72 hour test, the entire solution of the anode compartment was collected to measure total, soluble and particulate contents. A portion of the water from the anode compartment was passed through a 0.45 μm filter to quantify soluble constituents. Solids collected on the filter were also acidified, digested in acid, and analyzed by ICP-MS.

Results and Discussion

Zinc Solubility Tests

Zinc solubility was significantly reduced by increasing the pH to 9.0 (Figure 2 - 2), and became slightly more soluble when pH was increased from 9 to 10. The trend matches well with the model ($6.15 \times 10^{-6} \text{ M Zn}^{2+}$ and $6.15 \times 10^{-6} \text{ M SO}_4^{2-}$) in the *meniq+* 4.0 software. To focus on the critical pH range for dezincification identified by Turner (pH 8 to pH 9), all the subsequent solubility tests were conducted at pH 8.3.

Soluble zinc decreased markedly when up to 100 mg/L of bicarbonate (concentration calculated as CaCO_3) was dosed (Figure 2 - 3). This is consistent with relatively recent research that suggests zinc basic carbonate $[\text{Zn}_5(\text{OH})_6(\text{CO}_3)_4]$ solid is an important control on zinc solubility (Paulson, Benjamin and Ferguson 1989).

The addition of 300 mg/L of chloride countered the reduction in zinc solubility due to bicarbonate (Figure 2 - 3). This is perplexing, because soluble zinc chloride complexes are not predicted to be significant at pH 8.3, so the mechanism by which chloride interferes with formation of $[\text{Zn}_5(\text{OH})_6(\text{CO}_3)_4]$ or other solids is not clear. Calcium hardness by itself had no effect on zinc solubility (Figure 2 - 4).

Interestingly, when phosphate was present, calcium hardness did have impacts on zinc solubility (Figure 2 - 4). Specifically, soluble zinc decreased with higher

calcium in the presence of phosphate. At 50 mg/L hardness and 1 mg/L phosphate as P, soluble zinc was only 20% versus 100% with phosphate but no hardness. Hence, phosphate and calcium appear to work synergistically to precipitate zinc. It is possible that the phosphate forms zinc-phosphate colloids, which agglomerate rapidly in the presence of the Ca^{+2} .

Soluble phosphate and calcium data were in agreement with this hypothesis. Soluble phosphate decreased with the soluble zinc as the calcium concentration went up. The molar ratio of zinc to phosphate in the solid was 1:0.7, roughly consistent with formation of a solid $\text{Zn}_3(\text{PO}_4)_2$. Calcium was not detectable in the precipitated solids, which is consistent with a role for Ca^{+2} in destabilizing colloids and causing particle agglomeration, but which is inconsistent with formation of a Ca-Zn-P containing precipitate.

The role of Mg^{+2} in zinc solubility was also tested to examine another divalent cation. Magnesium behaved in the same manner as calcium (Figure 2 - 4), in that it had no direct role in reducing zinc solubility, but its presence reduced zinc solubility in the presence of phosphate without becoming part of the solid. This is again consistent with Ca^{+2} and Mg^{+2} serving as a coagulant.

Zinc-Copper Galvanic Test

The primary components of brass are copper and zinc metal. The zinc and copper in brass form numerous galvanic cells, with copper as the cathode and zinc as the anode. In this test pure copper was galvanically connected to pure zinc, in order to examine how chloride and bicarbonate affect the galvanic cell and either mitigate or exacerbate corrosion.

The galvanic voltage represents the potential differences between the anode and the cathode, and is the driving force for corrosion of the zinc anode. Of the four test conditions (Table 2 - 2), the voltage was highest when chloride was highest and carbonate was lowest. The two conditions with lowest Cl^- had a driving force about 200 mV lower (Figure 2 - 5). The voltage for conditions with higher alkalinity tended to decrease with time, consistent with formation of a passivating layer due to precipitation of a Zn hydroxyl-carbonate solid $[\text{Zn}_5(\text{OH})_6(\text{CO}_3)_4]$.

The galvanic current represents the acceleration to zinc corrosion arising from

the connection to the copper cathode. Conditions with 200 mg/L chloride more than doubled the galvanic current of the 20 mg/L chloride conditions (Figure 2 - 6). Conditions with higher bicarbonate generally had decreasing galvanic currents with time; whereas conditions with low alkalinity had relatively constant currents. These trends are consistent with expectations based on the voltage measurements (Figure 2 - 5).

Measurements of water chemistry near the surface of the anode were highly enlightening. Higher bicarbonate prevented the pH from dropping, and higher chloride pushed the pH even lower presumably due to increased generation of Zn^{+2} which is a Lewis Acid. The pH at the anode surface was over 1 pH unit lower when chloride was high and alkalinity was low (Figure 2 - 7), which is expected to dramatically increase zinc solubility (Figure 2 - 1). While the anode had somewhat lower pHs at the other conditions, the pH drop was much less significant.

The water in the anode compartment had a significant buildup of white zinc solids (Figure 2 - 9). The zinc concentration in the supernatant was therefore a strong function of both zinc leaching and pH, and as expected, the condition with higher chloride and lower bicarbonate had much more zinc (Figure 2 - 8) and more white precipitates.

The trend for chloride concentrations in the anode supernatant were very interesting and somewhat counterintuitive (Figure 2 - 10). Within 1 hour, chloride migrated into the anode compartment and was concentrated, such that the Cl^- concentration shot up to the 500—900 mg/L range. The chloride level in the low chloride & low bicarbonate condition (20 mg/L chloride and 20 mg/L bicarbonate) was concentrated by 45 times. After the initial spike, the chloride concentration declined to values lower than was present in the bulk water. It was hypothesized that this decrease in chloride is due to formation of a zinc hydroxyl-chloride solid precipitate from the very high levels of zinc.

To test this hypothesis, the 1 ml solution in the anode compartment was filtered with a 0.45 μm filter. The white bulky solids were retained on the filter and later dissolved by 100 ml nanopure water. Contrary to expectations, hardly any chloride was found in the filter-soaking solution. Alternative mechanism would be needed to explain the behavior of chloride concentration.

At the end of 72 hours, total zinc and total chloride in the anode compartment were analyzed by acidifying and dissolving all the white solids. Confirming previous visual observation for solids, pH and electrochemical measurements, conditions with 20 mg/L of chloride (condition 1&2) leached far less zinc and accumulated far less chloride (Figure 11). Conditions with 200 mg/L of bicarbonate (condition 2&4) gathered less zinc and less chloride than their counterparts. Condition 3—higher chloride and lower bicarbonate—was by far the worse scenario in generating higher voltage, lower pH, more zinc and more precipitates.

Conclusion

1. Zinc solubility is significantly affected by pH, bicarbonate and chloride concentrations. Soluble zinc decreases as pH increases, as bicarbonate level increases, or when chloride decreases. This is a possible basis for benefits of alkalinity and detriments from chloride in dezincification of brass.
2. Hardness has no direct effect on zinc solubility. However, either calcium or magnesium ions can destabilize solids formed by zinc and phosphate.
3. The benefits of bicarbonate and detriments of chloride are exacerbated during galvanic corrosion of zinc when connected to copper. Bicarbonate reduced the extent of the pH drop by a buffering action, reduced the buildup of Cl⁻, and caused decreasing voltages and currents with time presumably due to formation of a protective scale on the zinc surface. Chloride ions tended to maintain higher galvanic voltages and currents, and contributed to greater pH drops at the zinc anode surface, factors that tend to sustain high levels of zinc leaching to the water and which can prevent passivation. While it is clear that Cl⁻ is also concentrated in the anode compartment, the trends of Cl⁻ concentration with time are not fully understood.

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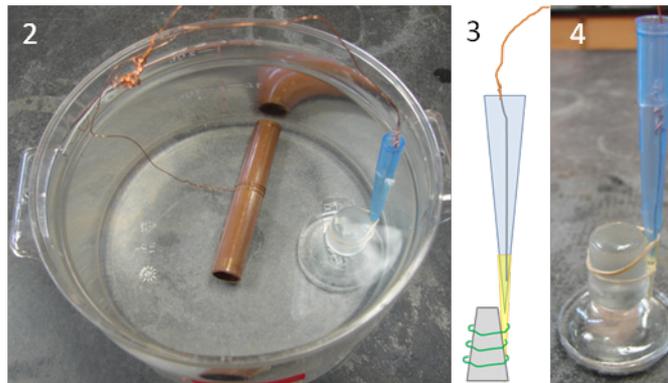
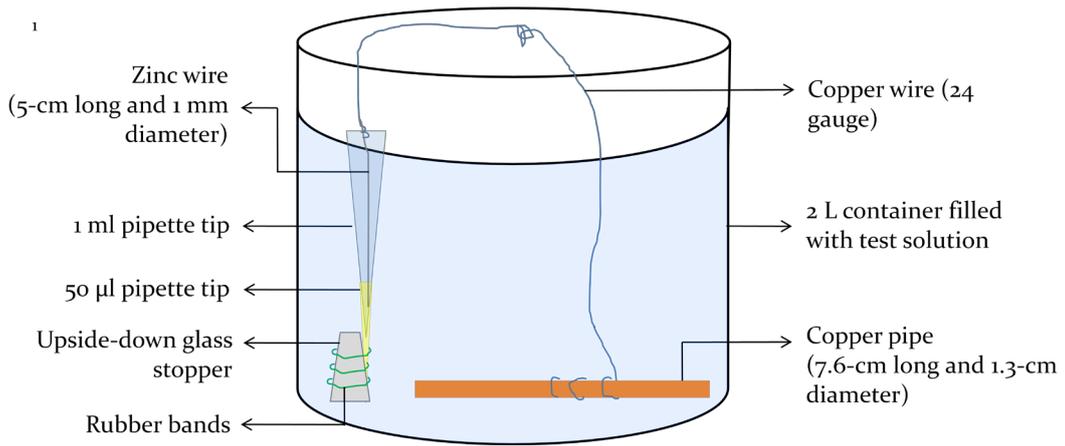


Figure 2 - 1 Experiment apparatus for the Zinc-Copper galvanic tests (Graph 1 on the top is the apparatus diagram; graph 2 on the lower left is the actual set-up; graph 3 and 4 are details of the anode compartment)

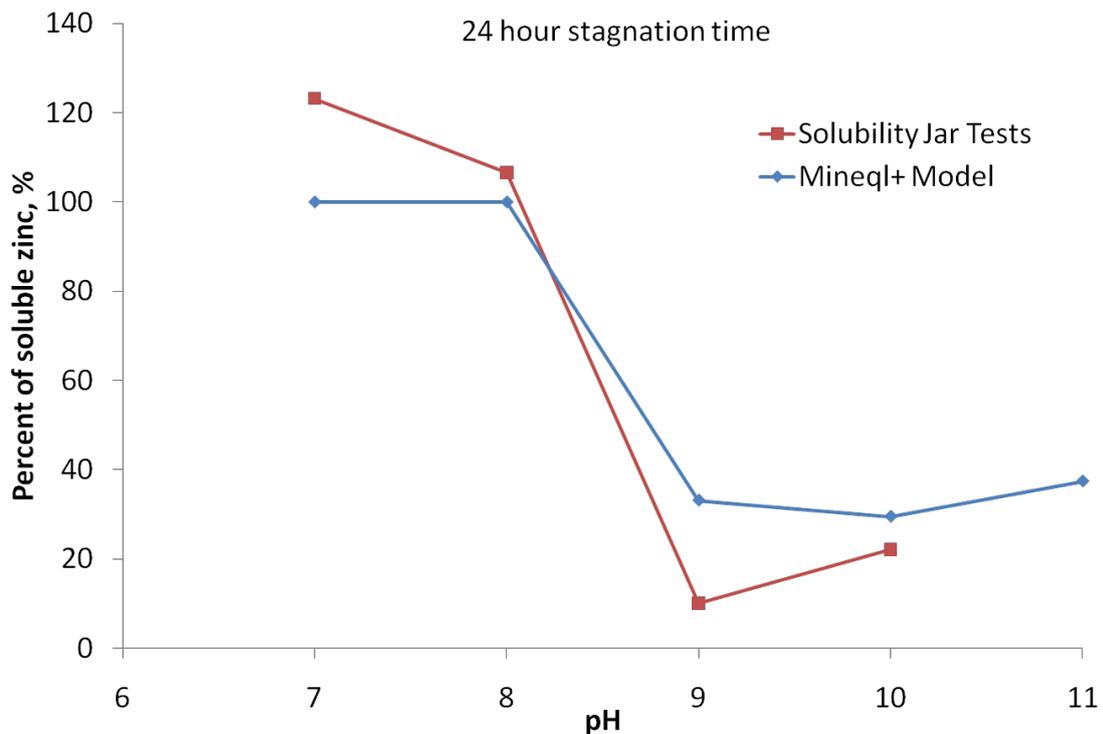


Figure 2 - 2 The effect of pH on zinc solubility

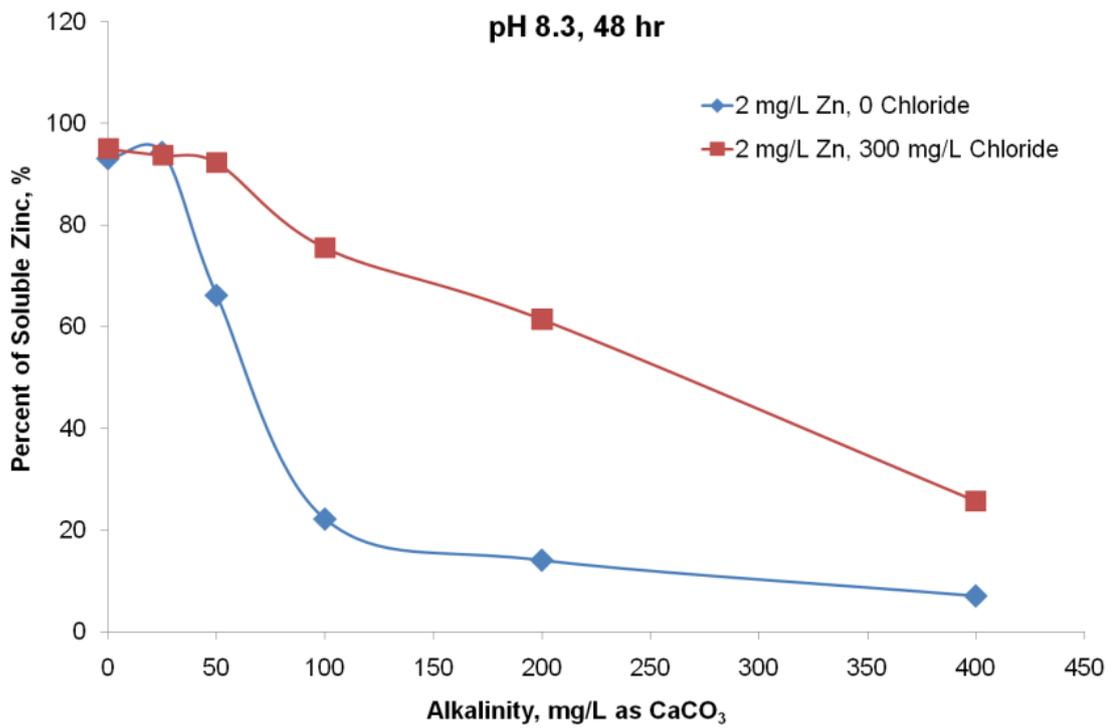


Figure 2 – 3 The effects of increasing bicarbonate on zinc solubility at no and 30 mg/L chloride

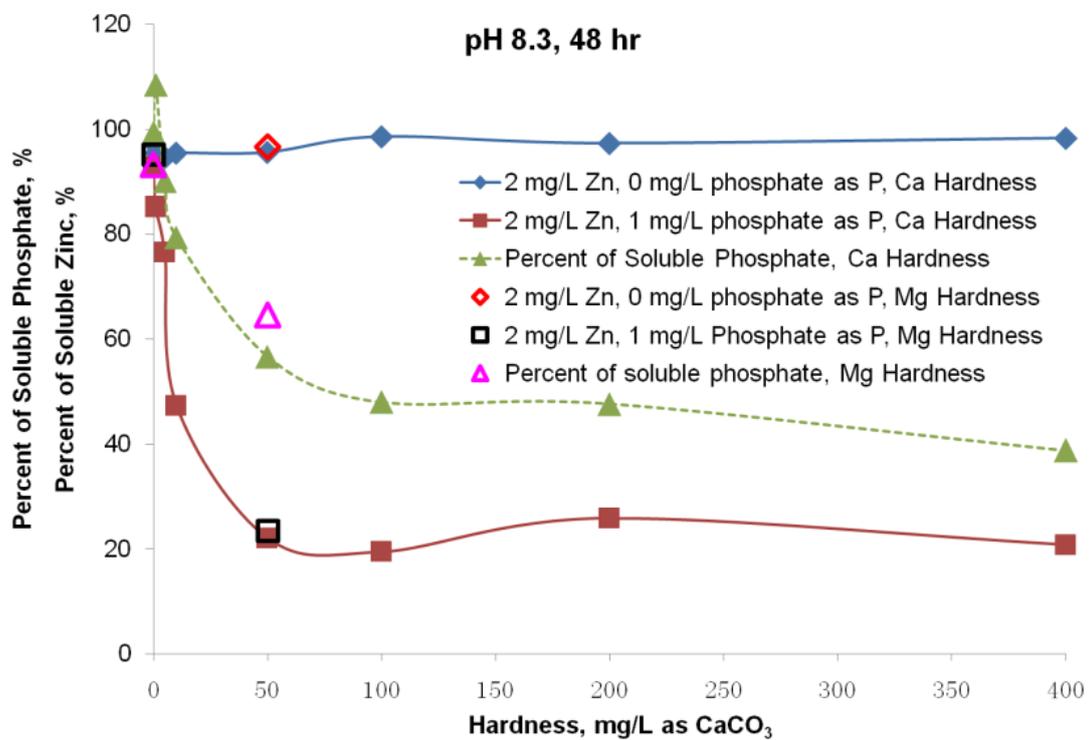


Figure 2 – 4 The effects of hardness on zinc solubility

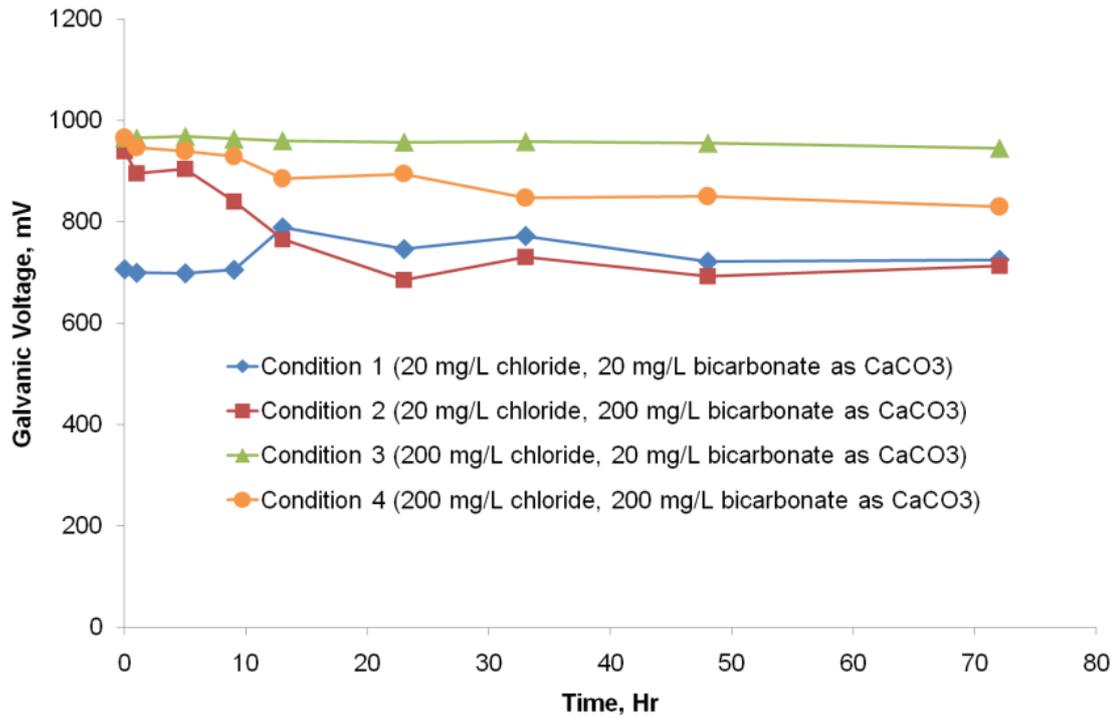


Figure 2 – 5 Galvanic voltages between the zinc wire (anode) and the copper pipe (cathode)

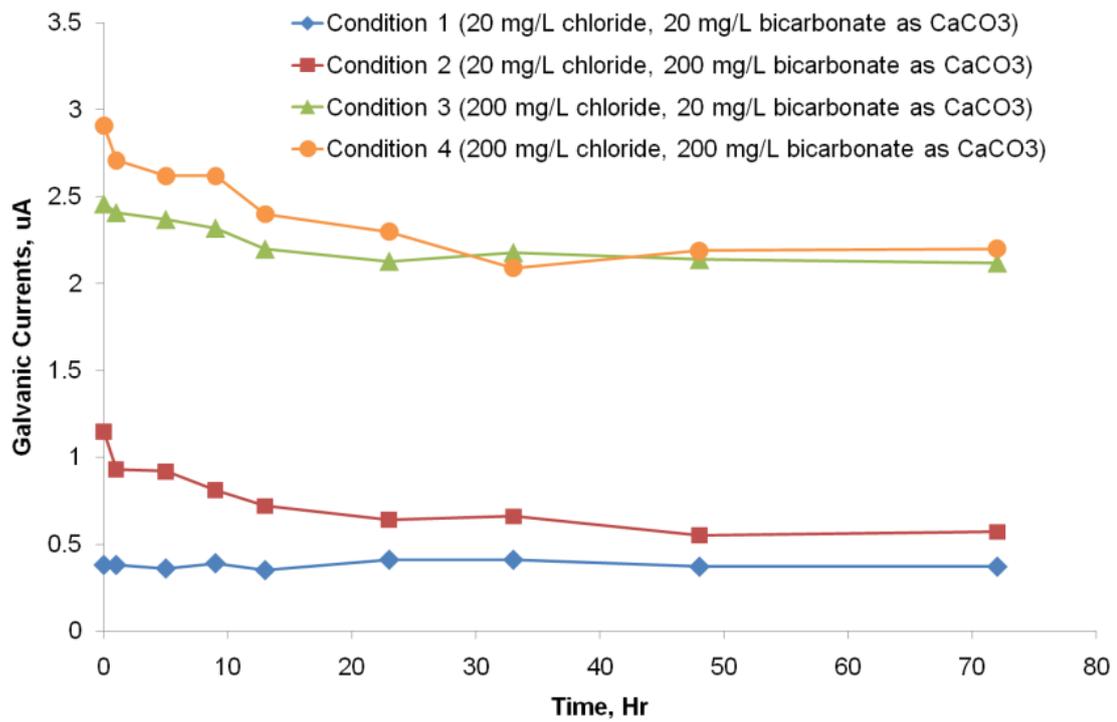


Figure 2 – 6 Galvanic currents between the zinc wire (anode) and the copper pipe (cathode)

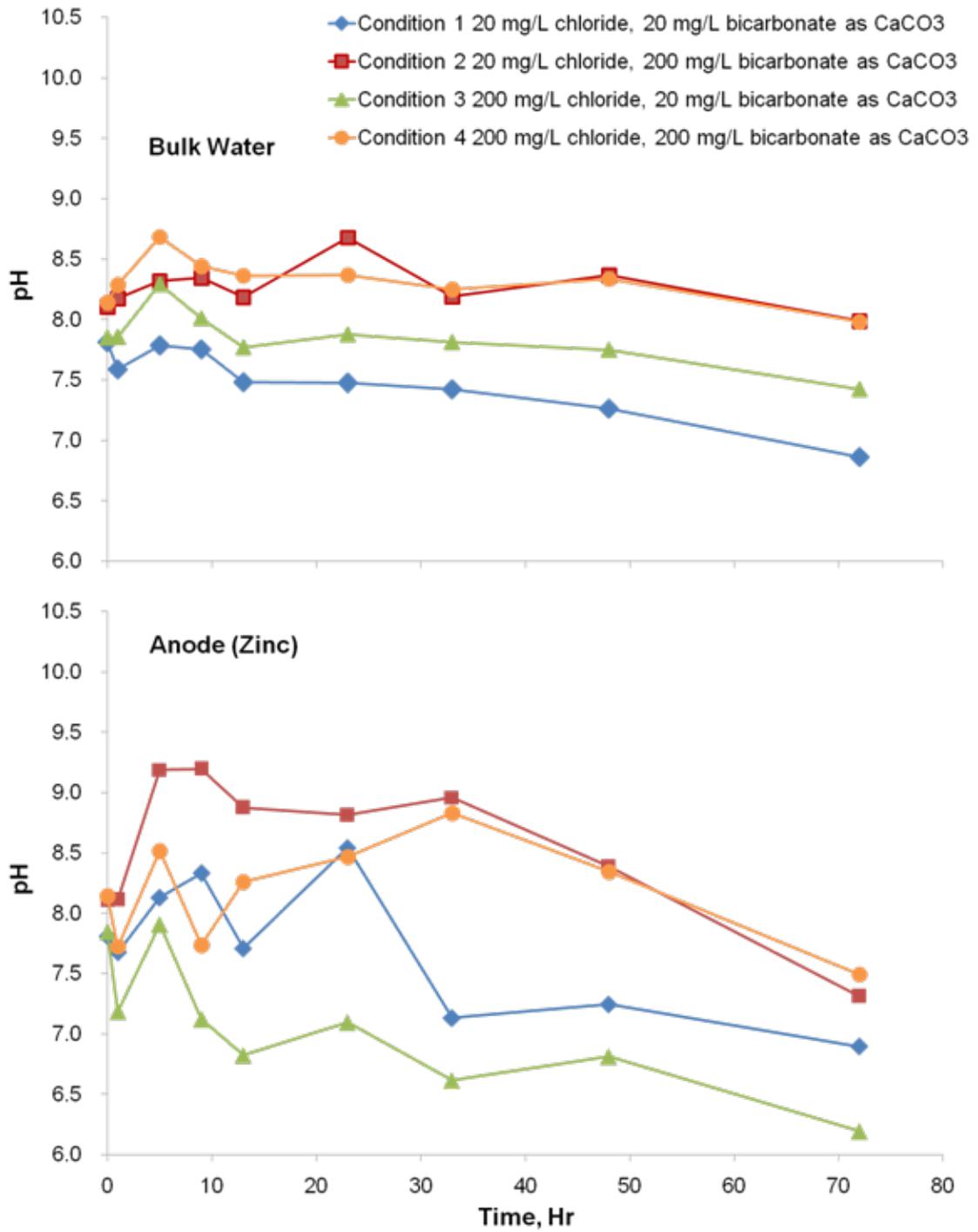


Figure 2 - 7 pHs of the bulk water and the anode compartment

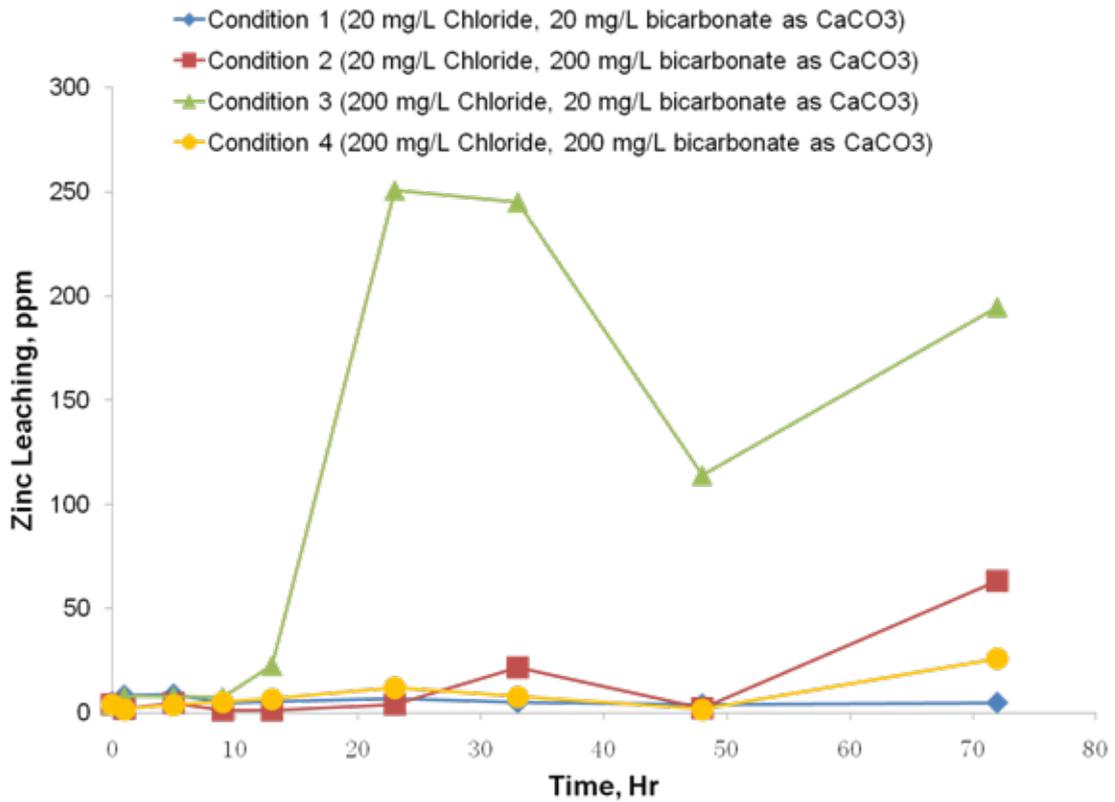


Figure 2 – 8 Zinc concentrations in the anode compartment supernatant

Condition 1. 20 mg/L chloride, 20 mg/L bicarbonate as CaCO_3

Condition 2. 20 mg/L chloride, 200 mg/L bicarbonate as CaCO_3

Condition 3. 200 mg/L chloride, 20 mg/L bicarbonate as CaCO_3

Condition 4. 200 mg/L chloride, 200 mg/L bicarbonate as CaCO_3

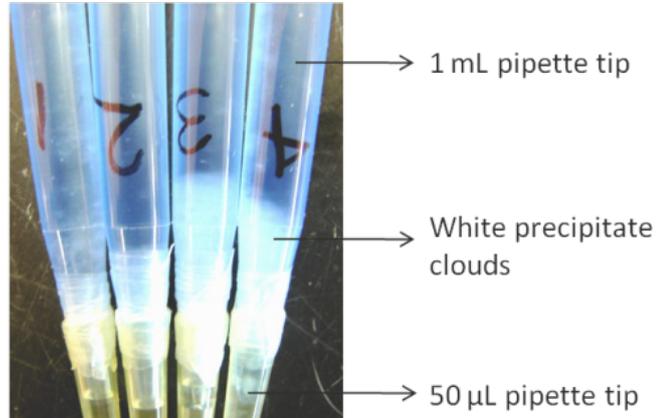


Figure 2 – 9 White precipitate clouds at the bottom of each anode compartment after 72 hours

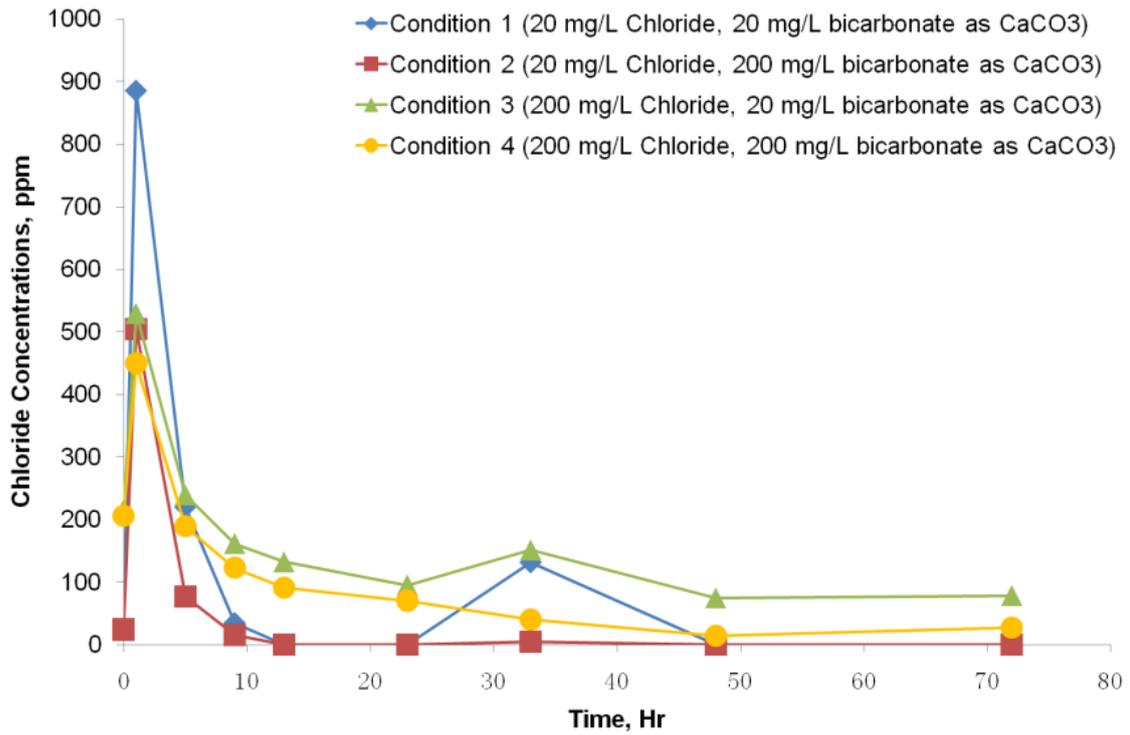


Figure 2 - 10 Chloride concentrations in the anode compartment supernatant

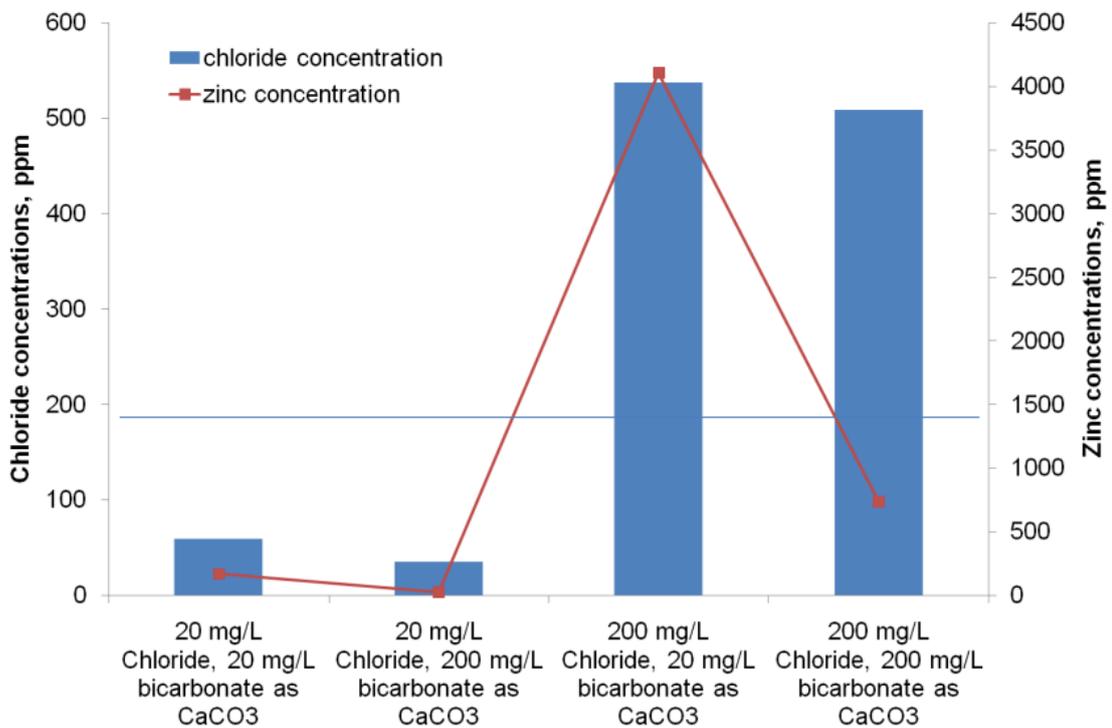


Figure 2 - 11 Total zinc and total chloride in the anode compartment after 72 hours

Table 2 – 1 Test conditions for the solubility jar tests

Group 1*. The effects of pH				
pH adjustment	7	8	9	10
Base solution	400 µg/L zinc (Zn ²⁺) added as ZnSO ₄ ·7H ₂ O			

Group 2*. The effects of bicarbonate						
Bicarbonate adjustment, mg/L bicarbonate as CaCO ₃	0	25	50	100	200	400
Base solution	2 mg/L zinc (Zn ²⁺), added as ZnSO ₄ ·7H ₂ O pH 8.3, adjusted accordingly Bicarbonate added as NaHCO ₃					

Group 3*. The effects of bicarbonate together with chloride						
Bicarbonate adjustment, mg/L bicarbonate as CaCO ₃	0	25	50	100	200	400
Base solution	2 mg/L zinc (Zn ²⁺) added as ZnSO ₄ ·7H ₂ O pH 8.3 adjusted accordingly 270 mg/L chloride (Cl ⁻) added as NaCl Bicarbonate added as NaHCO ₃					

Group 4*. The effect of calcium hardness								
Calcium hardness adjustment, mg/L hardness as CaCO ₃	0	1	5	10	50	100	200	400
Base solutions	2 mg/L zinc (Zn ²⁺) added as ZnSO ₄ ·7H ₂ O pH 8.3 adjusted accordingly Calcium hardness added as CaCl ₂ ·2H ₂ O							

Group 5*. The effect of hardness together with phosphate								
Calcium hardness adjustment, mg/L hardness as CaCO ₃	0	1	5	10	50	100	200	400
Base solutions	2 mg/L zinc (Zn ²⁺) added as ZnSO ₄ ·7H ₂ O pH 8.3 adjusted accordingly 3 mg/L phosphate (PO ₄ ³⁻) added as Na ₃ PO ₄ ·12H ₂ O Calcium hardness added as CaCl ₂ ·2H ₂ O							

Group 6*. The effects of magnesium hardness			
Magnesium hardness adjustment, mg/L hardness as CaCO ₃	50	50	0
Phosphate adjustment, mg/L as PO ₄ ³⁻	0	1	1
Base solutions	2 mg/L zinc (Zn ²⁺) added as ZnSO ₄ ·7H ₂ O pH 8.3 adjusted accordingly Magnesium hardness added as MgCl ₂		

*All solutions start with 300 ml of deionized water; all the pHs were adjusted with 0.01 M HNO₃ and 0.01 M KOH.

Table 2 – 2 Test conditions for the Zinc-Copper galvanic tests

Test Conditions	Chloride ¹ , mg/L as Cl ⁻	Bicarbonate, mg/L as CaCO ₃	Volume and pH ²
1	20	20	2 L and pH 8.3
2	20	200	2 L and pH 8.3
3	200	20	2 L and pH 8.3
4	200	200	2 L and pH 8.3

* Stock solution NaCl is 57400 mg/L as Cl⁻, and stock solution NaHCO₃ is 38300 mg/L as CaCO₃

Chapter 3 The Effects of Brass Composition and Physical Conditions on Dezincification

Abstract

Brass failure has been reported in several systems across the United States in using high-zinc brass fittings. Even within a given home exposed to the same water chemistry, the extent of attack on identical brass fittings varied markedly from location to location. Factors that might influence dezincification rates of brass in homes were examined. Alloy zinc content and physical exposure conditions including galvanic connections, mixing and temperature significantly impact the rate of corrosion and weight loss.

Keywords: brass dezincification; zinc content; galvanic connections.

Introduction

Dezincification is a corrosion process in which zinc is selectively leached from brass alloys (Cu-Zn-other minor constituent). Dezincification can leave brass with a reddish coppery color and a porous/fragile structure. In potable water systems, dezincification can contribute to premature brass fitting failure and associated water damages. In other cases dezincification can lead to formation of voluminous off-white colored corrosion products (often termed “meringue”) – which can completely block water flow through the device (Simmonds 1967) (Turner 1961). Lead leaching is also an emerging issue that has been associated with dezincification (Maynard, Mast and Kwan 2008) (R. J. Oliphant 2007) (Triantafyllidou and Edwards 2007) (Dudi, et al. 2005) (Edwards and Dudi 2004), contributing elevated lead to potable water in some systems (Kimbrough 2007) and even brand new buildings (Nguyen, et al. 2009). Dezincification might play a role in sustaining high lead leaching rates from a given alloy (Triantafyllidou and Edwards 2007).

Factors influencing dezincification can be classified into three categories: the alloy itself, the water chemistry and other physical factors including stirring,

heating and galvanic connections. The issue of alloy composition was once believed to have been “solved” by using brass containing less than 15% weight percent, and through development of certain dezincification resistant alloys that contained up to 30% zinc and addition of arsenic or tin (Davies 1993). The threshold of 15% zinc content for the onset of significant dezincification problems has been a useful guide based on practical experiences (Oliphant and Schock 1996) (Oliphant and Schock 1996) (Kelly, Lebsanft and Venning 1980) (Davies 1993). In all cases examined to date with serious product failure from dezincification, zinc contents in the alloy have always been over 15% by weight.

Even if an alloy with very high zinc is used, we have observed that other factors such as water chemistry and the location of the product in a premise plumbing system can determine whether failure occurs. Physical factors are believed to play a key role. For example, more meringue build-up has been observed in hot water systems (Turner 1961) (Oliphant and Schock 1996). Higher flow rates and galvanic connections between brass and copper are widely believed to determine rates of failure (Kelly, Lebsanft and Venning 1980), although there is little or no hard data in the peer reviewed literature on this subject. This work is aimed at examining the effects of physical factors including stirring, heating and galvanic connections on dezincification rates, as determined by metals leaching and weight loss in well-controlled laboratory experiment.

Materials and Methods

Effects of Alloy Composition

Seven different types of brass (Figure 3 -1, Table 3 - 1) fittings were machined into rings or half rings of weight \approx 1 gram. The composition of brass was measured using an Innov-X ALPHA X-ray fluorescence (XRF). Test waters were gathered from communities known to have series dezincification failures (Real Water, Table 3 - 2). Three brass rings were suspended in each jar container to obtain composite measurements of metal leaching and triplicate weight loss (Figure 3 - 2).

The brass was exposed at room temperature ($22^{\circ} \pm 2^{\circ} \text{C}$) without stirring unless stated otherwise. Chlorine was maintained at $1.1 \pm 0.2 \text{ mg/L}$ as Cl_2 using sodium hypochlorite (NaOCl) and pH was maintained at 7.80 ± 0.2 using small amounts

of nitric acid (HNO₃) to lower pH or sodium hydroxide (NaOH) to raise pH. The water in each container was completely changed every week unless otherwise specified. Samples for metal leaching were collected routinely from the container after stirring and the contents were analyzed for metals using a Thermo Electron X-Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) per Standard Method 3125-B (APHA 1998).

Before the experiments each cut brass ring was lightly sanded and washed 3 times with pure water. After drying in a desiccator for two hours, the brass rings were precisely weighed with +/- 0.1 mg accuracy. After the experiment, the rings were dried and weighed again, both before and after a light polishing step using a Dremel tool equipped with a soft cloth polishing pad. Experiments, experience and testing demonstrated that this polishing pad removes the vast majority of loose scale and rust on the brass ring, but does not remove intact metal. “Weight loss” of the brass metal is determined by difference between the initial and final weight of the sample and is the best overall estimate of the extent of corrosion.

Effect of Physical Exposure Conditions: Stirring, Heating and Galvanic Connections

Water temperature (i.e., hot versus cold), water movement (i.e., stirred or unstirred), and possible galvanic connections between brass and copper are expected to be important factors relative to dezincification. Three brass ring samples were tested for each of the following conditions using water known to cause dezincification problems (Real water, Table 3 - 2):

- 1) Room temperature, unstirred, unconnected to copper (Control);
- 2) Heated temperature (48 ± 2 °C), unstirred, unconnected to copper;
- 3) Heated temperature (48 ± 2 °C) , stirred, unconnected to copper;
- 4) Room Temperature, unstirred, connected to copper;

Total metal leaching and weight loss of each ring were measured. General experimental conditions in terms of pH adjustment, chlorine level, experiment duration, water change frequency were as described for work with different brass alloys in this Chapter. A temperature of 48°C typical for U.S. water heaters was maintained using a Thermolyne heating plate with magnetic stir bar attachments. For the stirred samples the contents of the container were mixed at

500 rpm using a 5 cm magnetic stir bar. A galvanic connection was established between copper and brass by drilling an appropriately sized hole through a 3/4" copper coupling, and firmly inserting the brass to make physical contact (Figure 3 - 3).

A complementary pipe test was also conducted to quantify trends in galvanic corrosion currents passing between brass and copper. Cylindrical brass samples (Free cutting brass C36000, Table 3 - 1) were connected to copper pipes as per the schematic in Figure 3 - 4. Control samples were run with polyvinyl chloride (PVC) pipes in place of the copper. The copper pipes were filled with synthesized tap waters (synthetic water, Table 3 - 2). The water in the pipes was changed with dump and fill protocol three times a week. The pH of the water was adjusted using 0.01 M nitric acid and 0.01 M sodium hydroxide and the final nitrate concentration did not exceed 0.6 mg/L. The galvanic currents between copper and brass were measured 30 minutes before and after every water change using a Fluke 189 True RMS Multimeter. Water samples were collected and then analyzed by ICP-MS for metal leaching. Brass samples were weighed before and after the experiments to obtain the weight loss. This test was also run in triplicate.

Results and Discussion

Effect of Alloy Composition

Results of a typical experiment conducted for 2700 hour duration, with the first 750 hours without any water change, illustrate the concentration of zinc leached to the water (= Final Zinc - Initial Zinc) at the indicated time (Figure 3 - 5). Arrows indicate the time of each water change.

After each water change zinc concentration tended to increase in the water at a linear rate and was highest immediately before a water change (Figure 3 - 5). For simplicity in summarizing key experimental trends, only the zinc and copper concentrations immediately before water changes are plotted after the first 750 hours for each type of brass). The type of brass significantly impacted the extent of dezincification and metal leaching to the water (Figure 3 - 5). The highest zinc levels were consistently leached by Sample A duplex brass, which are roughly ten times that leached by the brass with the lowest propensity to leach

zinc (e.g. Sample G DZR). Depending on zinc content, components of brass have different crystal structures. Below about 30% zinc content, brass alloy is present as a single alpha phase and are classified into phases like alpha, beta and gamma (See Chapter 1 for characteristics of each phase). Duplex brass refers to brass alloys that contains both alpha and beta phases. The zinc content of the alloy is correlated with zinc in the water (Figure 3 - 6), although there is also a significant variation in leaching of nearly 100% for five alloys with between 35.4% and 36.5% zinc. This variation indicates that trace alloy composition (e.g, Tin, Fe, Ni in samples) and other manufacturing techniques can also play a significant role in controlling zinc leaching.

An attempt was also made to examine the relationship between zinc content in the alloy and zinc in the water using raw data presented by Lytle & Shock's (1996). Six types of brass were tested by these authors for 150 days, and the zinc data was not previously synthesized. Zinc leaching was strongly correlated ($R^2 = 0.995$) to zinc content of the alloy in that work (Figure 3 - 7).

In the water tested, copper leaching (Top, Figure 3 - 8) tends to passivate (decrease with time) to a greater extent than did leaching of zinc. The net result is that the ratio of Zn:Cu leaching changes with time. In order to better capture the selective nature of zinc leaching and therefore the extent of dezincification, a "Dezincification Index" was defined that is calculated as follows:

$$\text{Dezincification Index} = \frac{(\text{Zinc/Copper})_{\text{leached into the water}}}{(\text{Zinc/Copper})_{\text{present in the alloy}}}$$

in which zinc and copper leached to the water are measured in ppb, and zinc and copper in the alloy are based on percent weight. If the Dezincification Index is larger than 1, zinc is selectively released, and the greater the magnitude of the index the worse the dezincification. Zinc was selectively leached from all brasses (Figure 3 - 9), but to a much less degree for alloy C and G. The Dezincification Index for C and G also decreased with time, which is a favorable trend for long-term performance considering a desired service life of multiple decades. The duplex brasses were dezincified much more severely, and in the worst case the index was as high as 70. This alloy with the highest Dezincification Index was known to have very high rates of failure in the field.

The overall metal dissolution rate is the cumulative leaching of Zn, Cu and Pb to the water each week. The concentration of total metal leached to the water at the

end of each week stayed roughly constant during the 16 weeks of experiments (Bottom, Figure 3 - 8). The seven alloys can be generally put into three groups. Sample A, B and F duplex brass leached almost the same amount of metals as each other. The fourth duplex brass sample D had less metal leaching. The third group includes sample C alpha brass, E DZR and G DZR. Sample A released twice as much metal as did the third group.

The measurement of total weight loss during experiments, which included the weight of metal leached to the water plus the metal that corroded and which was stuck to the pipe as scale, showed similar trends to that observed for overall metal dissolution (Figure 3 - 10). The ranking by weight loss after polishing is highest for sample A, F, B, D duplex brass. Sample C alpha brass had the least overall weight loss.

If there were no experimental error and corroded metal was all leached to the water, the cumulative total metal leaching to the water should be equal to the weight loss (Figure 3 - 11). These two parameters are in very good agreement, indicating very good experimental precision and relatively little error. In fact, there is very little difference between results with and without scale removal, which illustrates that in this case very little of the brass that was corroded was retained on brass surface as scales. The relatively low brass surface area to water volume ratio in this experiment might tend to reduce mercuric buildup relative to that which would occur in homes.

Effect of Physical Exposure Conditions: Stirring, Heating and Galvanic Connections

Stirring and galvanic connections tend to increase metal leaching (Figure 3 - 12). Stirring increased total metal leaching by approximately 50% compared with the unstirred condition. They are statistically different ($p = 4.2 \times 10^{-8}$, $\alpha = 0.05$). The “Heated & Stirred” water dissolved 391 ppb zinc on average, while the “Heated” water dissolved 257 ppb. Brass components subject to higher flow are therefore likely to have worse dezincification than samples exposed to lower flow.

In terms of metal leaching, heating did not make much difference ($p = 0.11$, $\alpha = 0.05$) (Figure 3 - 12). The weight loss was actually slightly lower than the control condition (Figure 3 - 14). This at first appeared to contradict field observation

that more pipe blockage occurs in hot water systems (Turner 1961) (Jester 1985), however, more disuniform scale also accumulated on the brass in the heated water (Figure 3 - 13). The amount of scales was confirmed by the weight loss increases after polishing, 19% and 5% respectively for the heated and the control conditions (Figure 3 - 14). This observation could help explain why more “meringue” were seen in hot water systems.

Galvanic connections had significantly higher metal leaching initially (Figure 3 - 12), which probably paved the way for higher weight loss in the end (Figure 3 - 14), despite the fact that the dramatic effect of galvanic connections on zinc leaching disappeared after the initial 750 hours or so. During week 7 to 12, the galvanic condition even leached less zinc than the control, before rising again at week 14. Galvanic connections also increased total metal leaching by over 200% at all times (Figure 3 - 12), although a significant portion of that represents copper from the pipe and not leaching from brass. Overall, galvanic connection appeared to make dezincification worse, especially at the beginning. The hypothesis was that galvanic connection created such a strong battery in the initial stage, which either dissolved all the easily accessible zinc on brass surface, or dulled the surface to keep extreme corrosion in check.

The effects of galvanic connections between brass and copper are consistent with the considerable galvanic currents measured in sister tests (Figure 3 - 15). Current density represents the increase in corrosion rate per unit of brass surface area due to the galvanic connection. The galvanically connected brass leached more than 2 times more zinc than the PVC connected brass (Figure 3 - 15), which confirmed the harmful effect of galvanic connection.

Conclusion and Summary

Brass composition and local physical exposure conditions significantly impacted overall dezincification. Alloys with higher zinc content have a greater propensity for dezincification corrosion, although other factors also clearly play a role. When brass was galvanically connected to copper, brass leached more metals into the water and had higher weight loss. Stirring increased dezincification, which suggests that higher flow rates may contribute to more rapid failures of brass in parts of home plumbing with higher flow rates. Heating and exposure to hot water did not significantly change an alloy’s tendency to corrode in terms of

metal leaching. However, weight losses revealed that heating may contribute to “meringue” accumulation.

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Figure 3 – 1 Brass fittings used
(From left to right, Sample A Duplex Brass, Sample B Duplex Brass, Sample C Alpha Brass, Sample D Duplex Brass, Sample E Dezincification Resistant Brass (DZR), Sample F Duplex Brass and Sample G DZR)

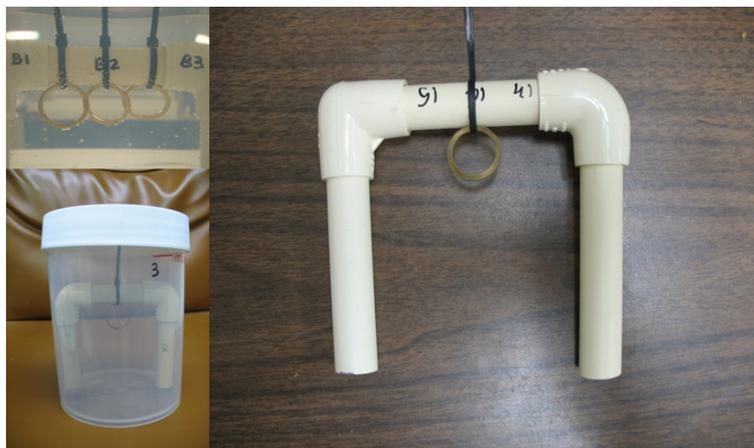


Figure 3 – 2 Brass ring tied to PVC pipes with cable ties



Figure 3 – 3 Brass ring held by the copper coupling

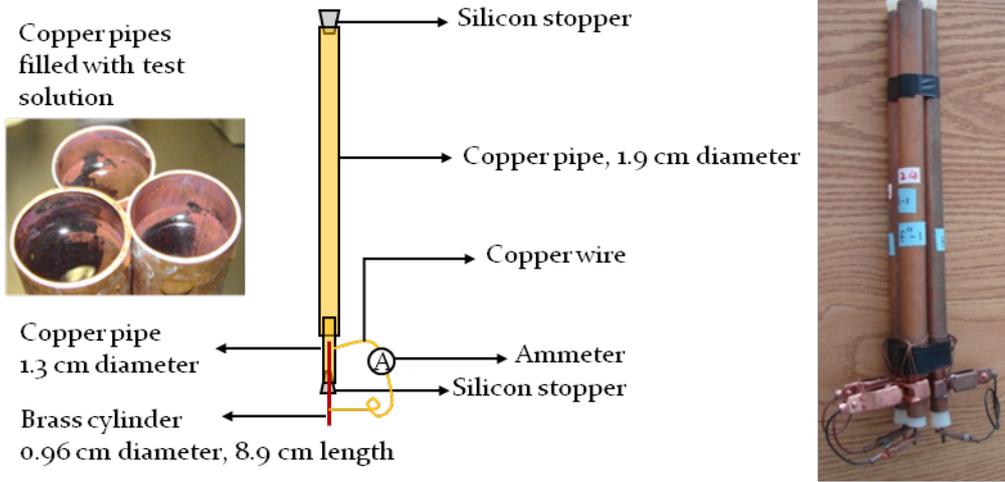


Figure 3 - 4 Experiment Apparatus (surface area over volume = 0.047 cm²/ml)

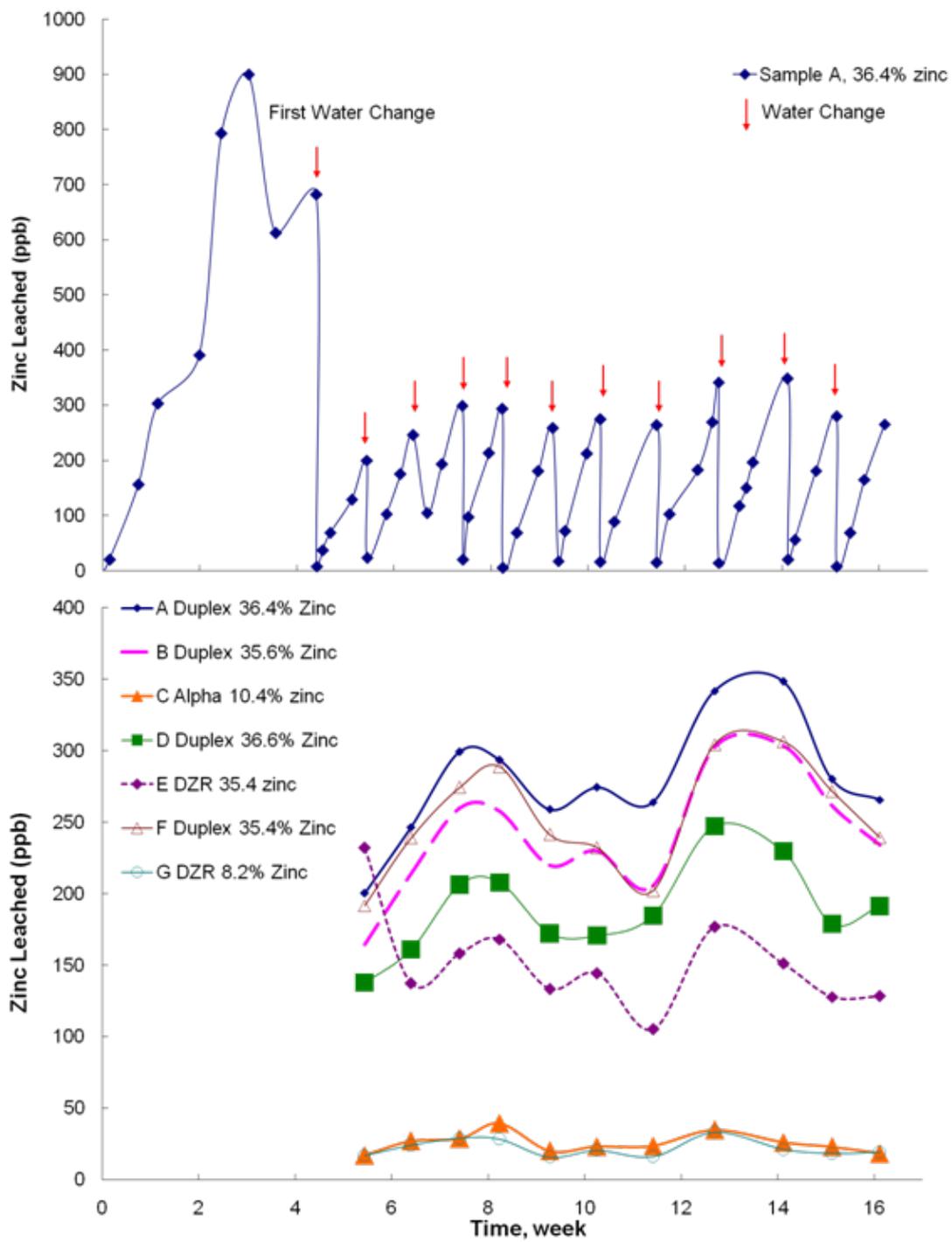


Figure 3 – 5 Zinc leached to the water by sample A throughout the experiment (Top); zinc in water before each weekly water change for all brass samples from week 5 to week 15 (Bottom)

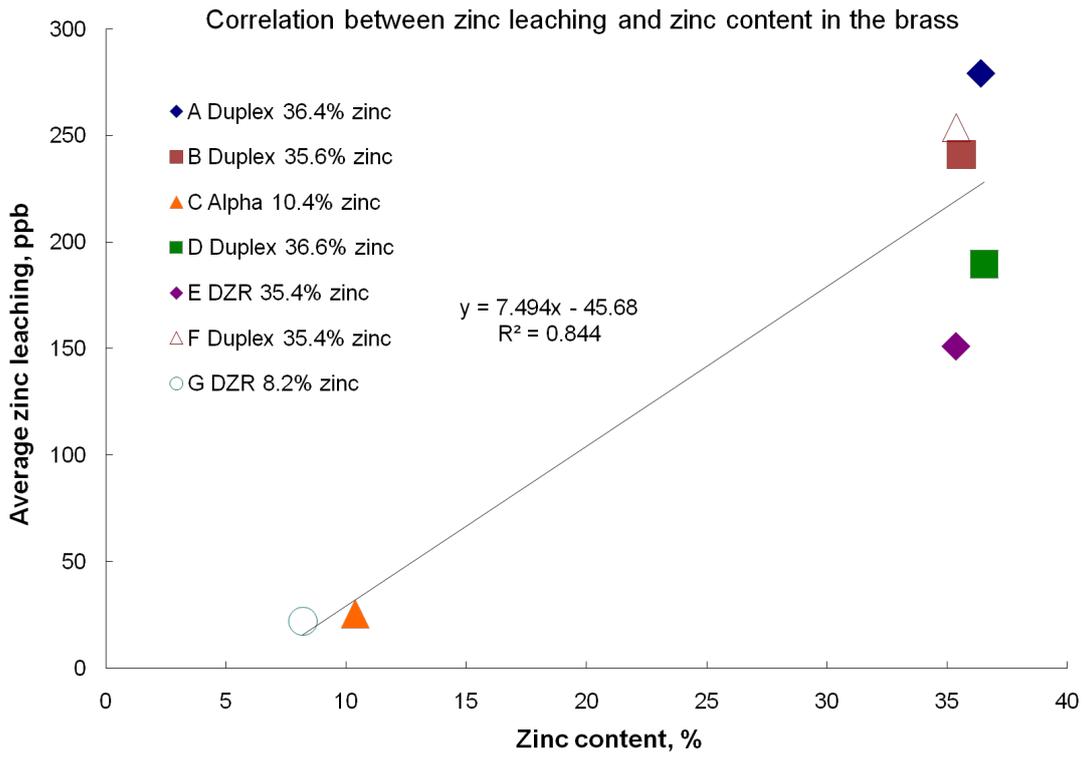


Figure 3 — 6 Correlation between zinc leaching and zinc content in the alloys (Zinc leaching values are the average of 21 weeks)

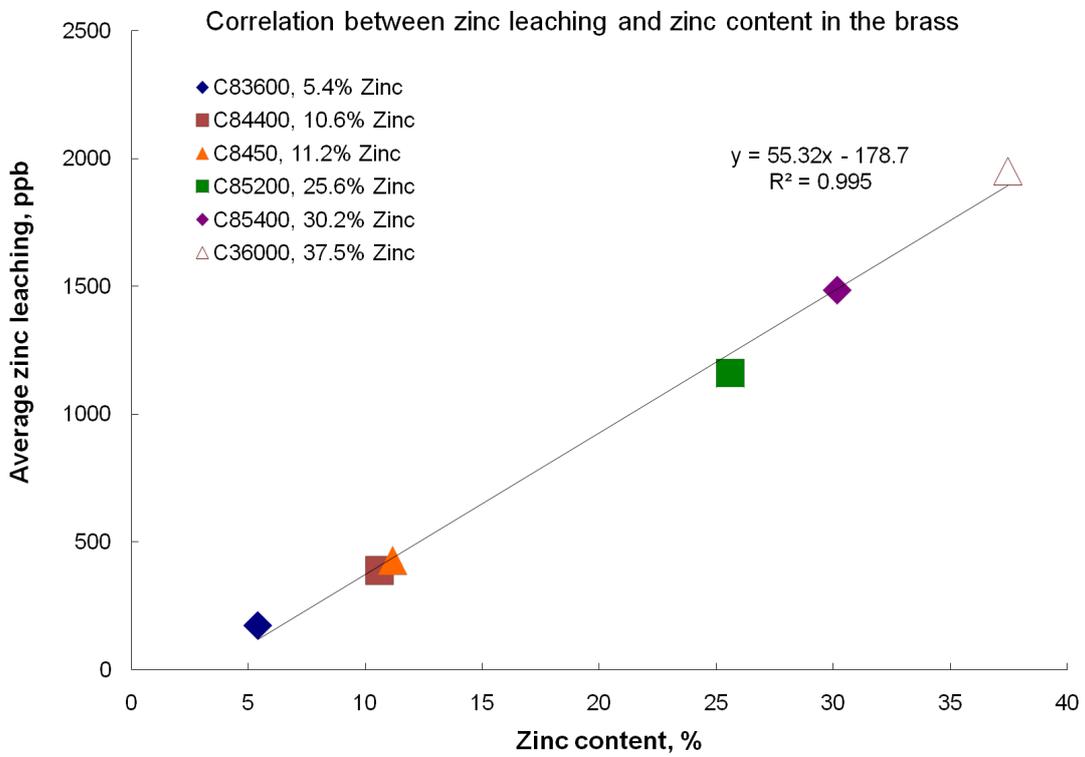


Figure 3 - 7 Correlation between zinc leaching and zinc content in the alloys (Lytle and Schock 1996) (Zinc leaching values are the average of 150 days across all test conditions)

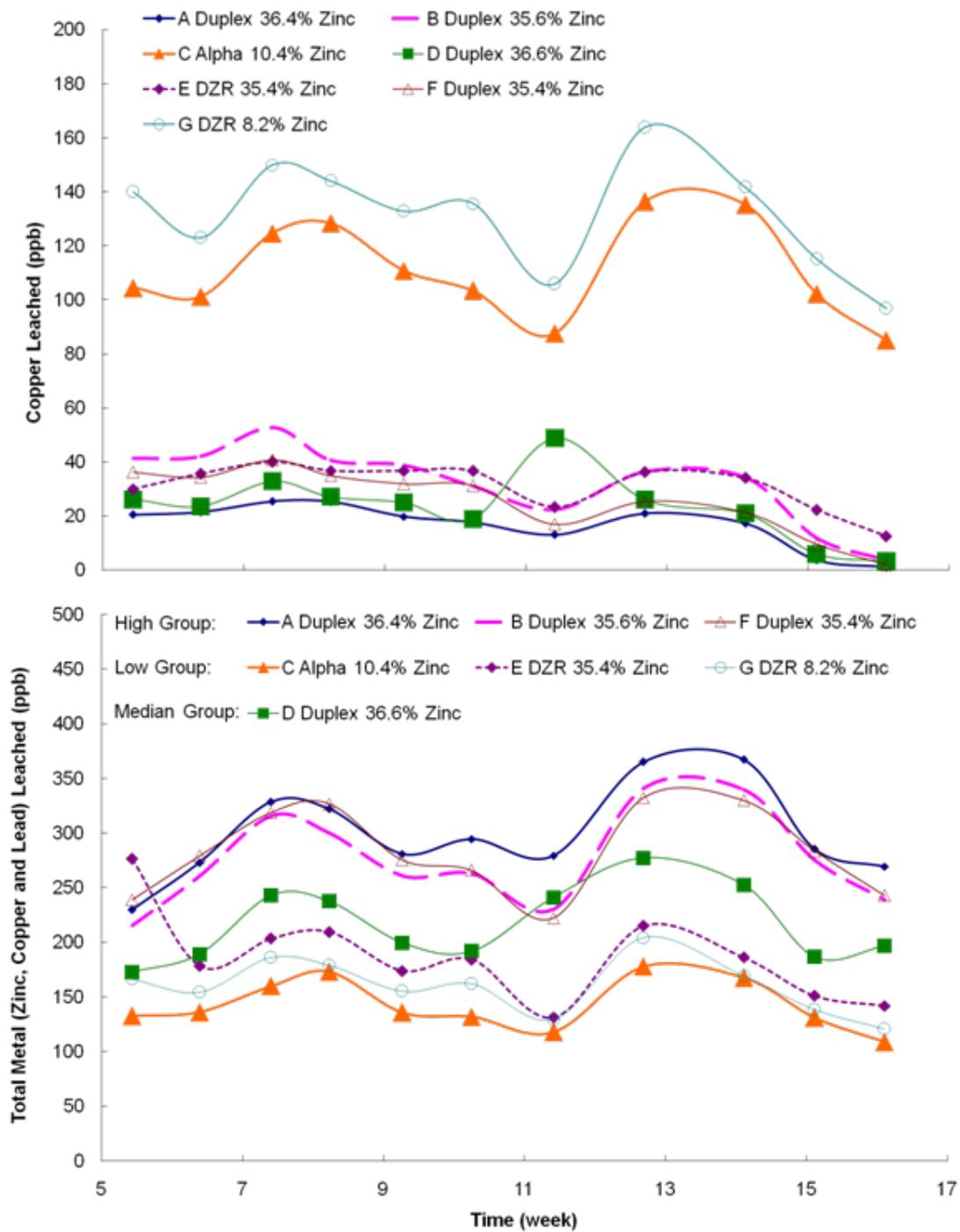


Figure 3 – 8 Copper and total metal leached to the water before each weekly water change

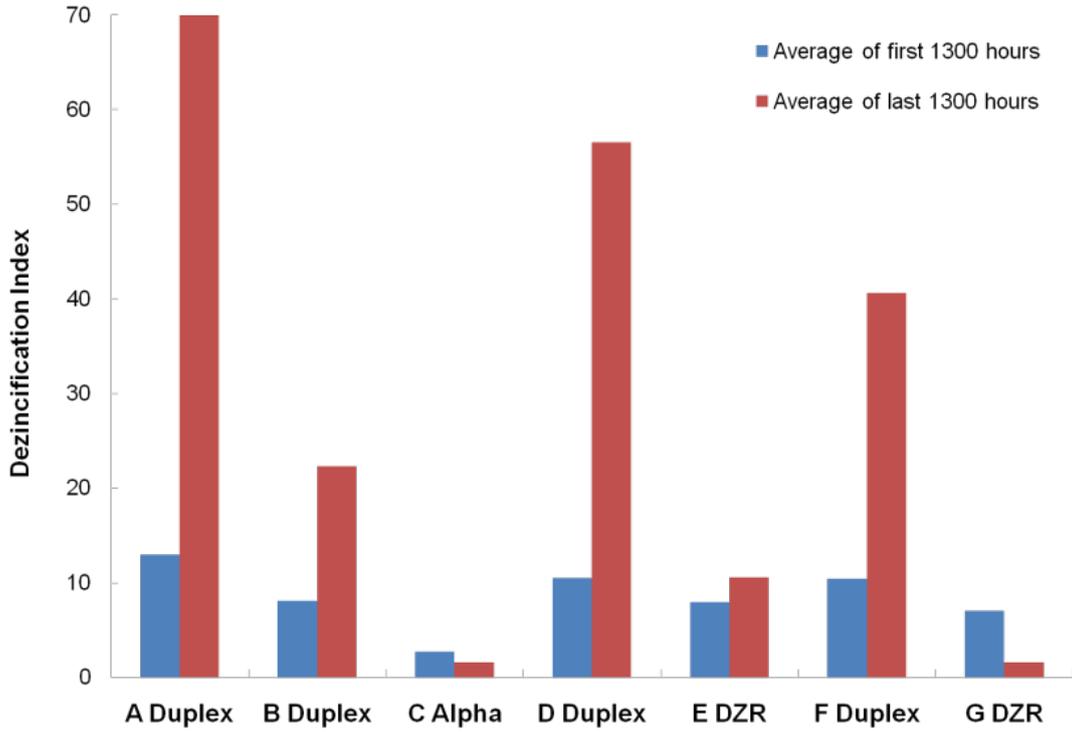


Figure 3 – 9 Dezincification Index for brass samples

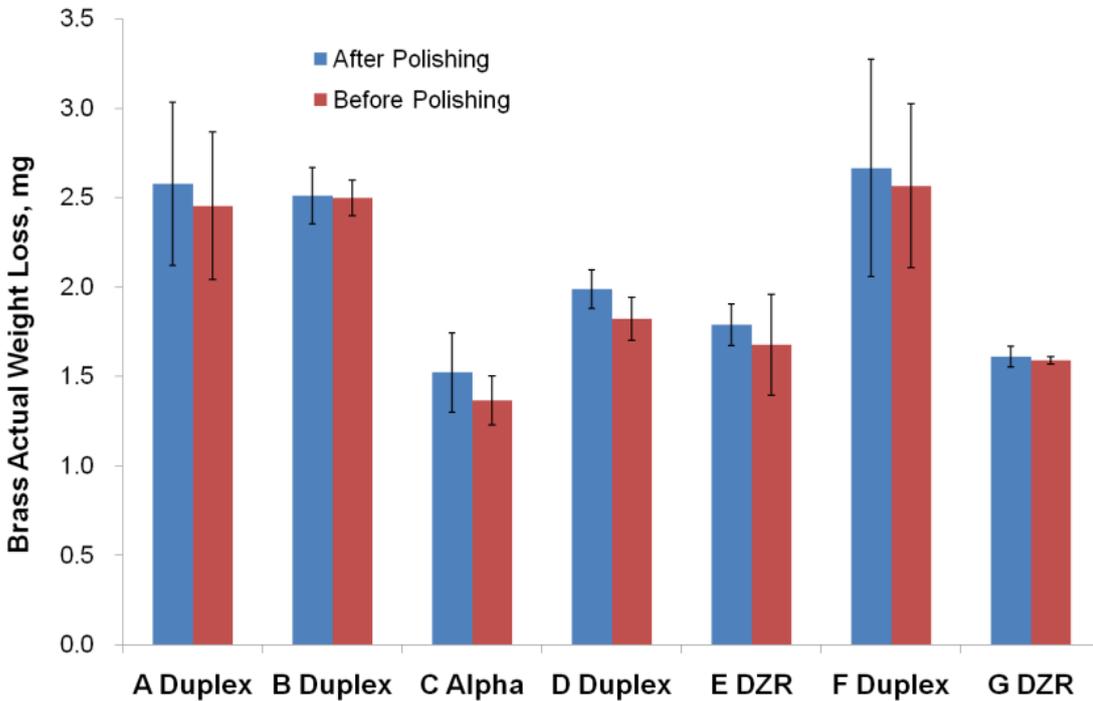


Figure 3 – 10 Weight loss of brass rings

(Weight loss values are the average of three brass rings. All the error bars in this chapter indicate 95% confidence interval unless specified otherwise.)

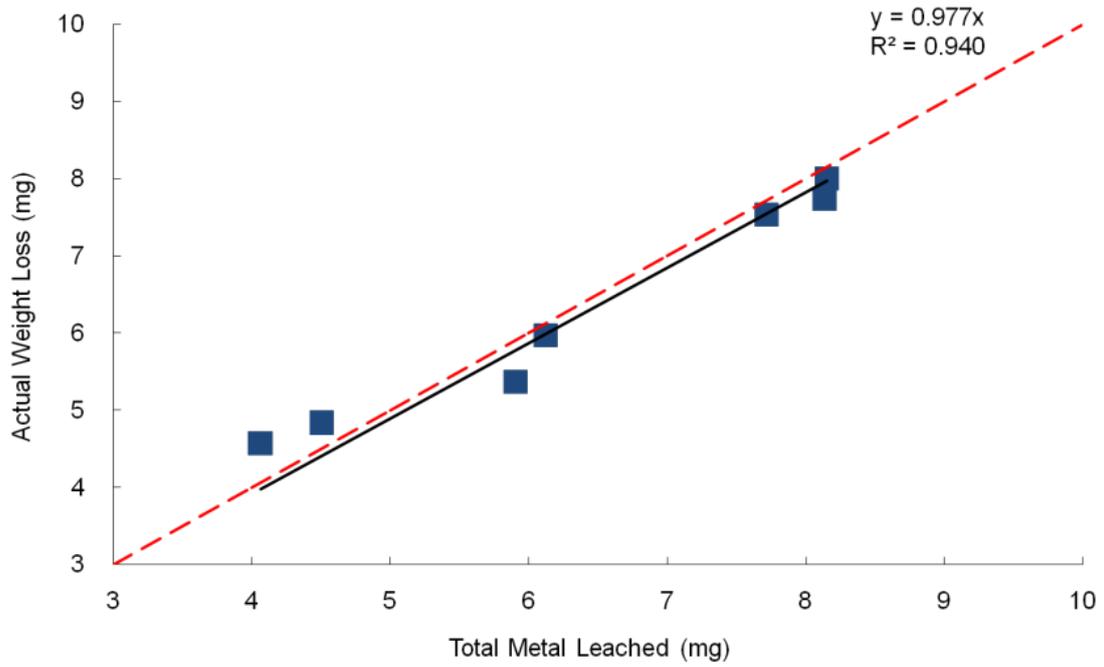


Figure 3 – 11 Correlation between actual weight loss (after polishing) and total metal leached (For every alloy type, there are three brass rings. Actual weight loss values are the sum of weight losses on each brass ring)

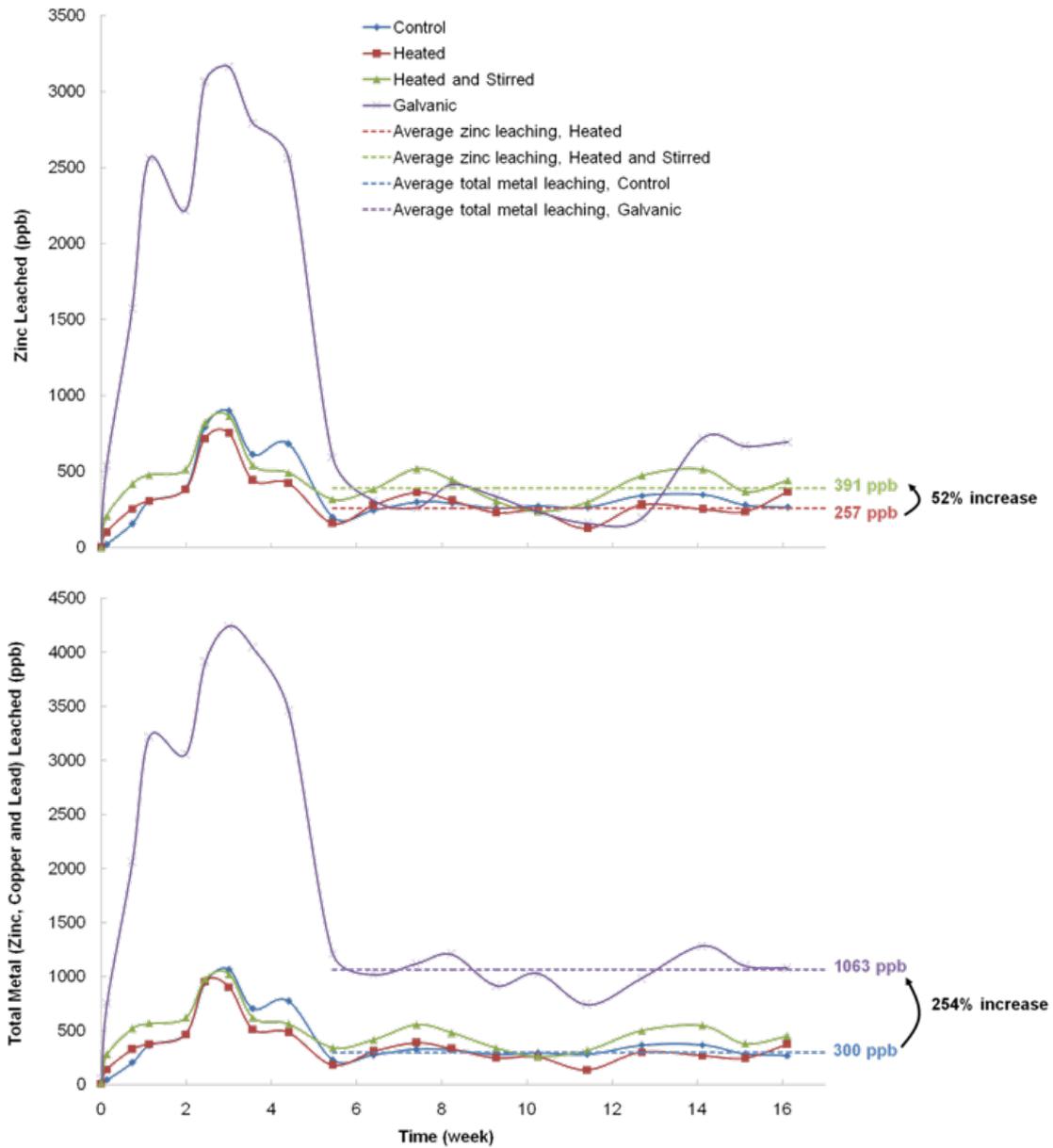


Figure 3 – 12 Zinc and total metal leached for different physical exposure conditions (Average values are calculated using data after the first 750 hours)

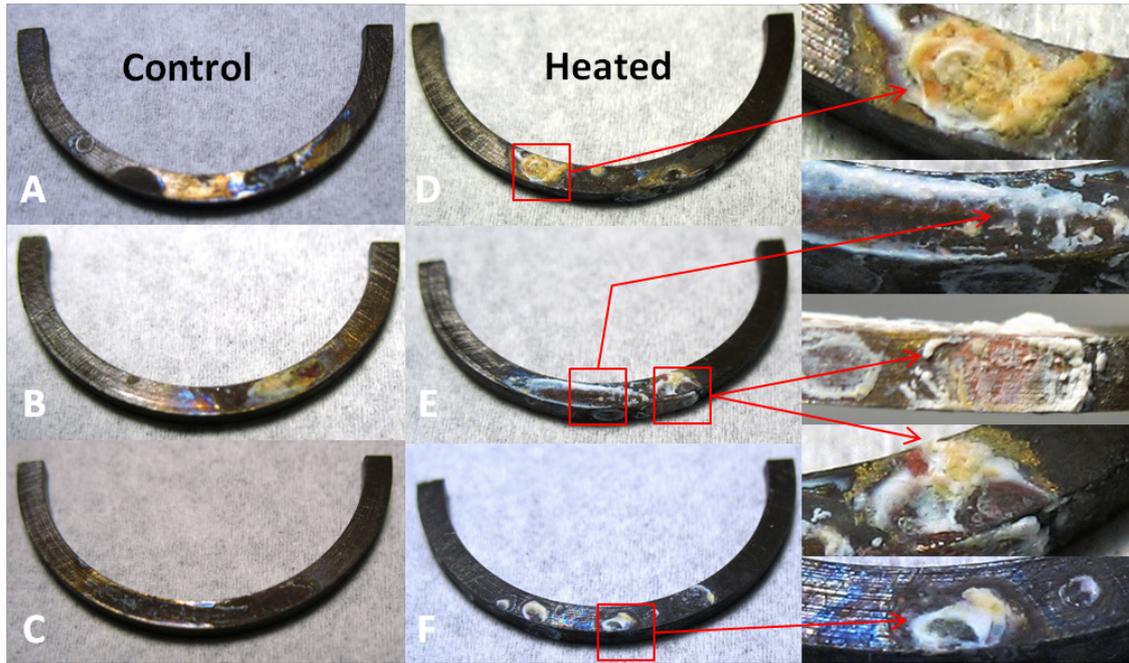


Figure 3 – 13 Surface images of brass samples at the end of 16 weeks
(Brass A, B, C and D, E, F are triplicates in the Control and the Heated water respectively)

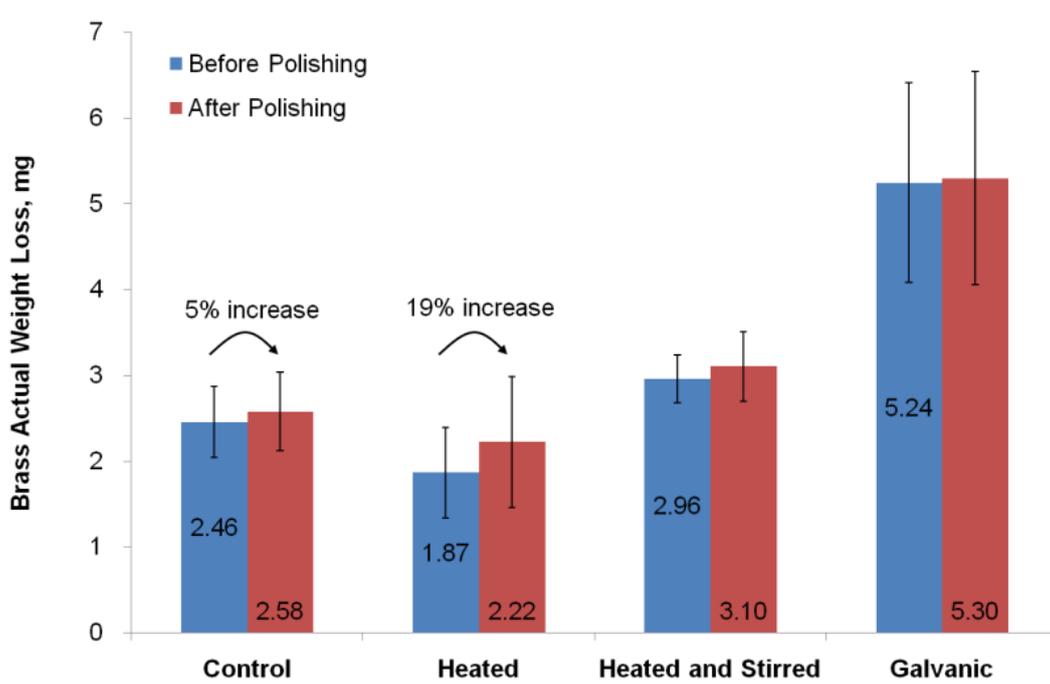


Figure 3 – 14 Brass weight losses for different physical exposure conditions
(Weight loss values are the average of three brass rings)

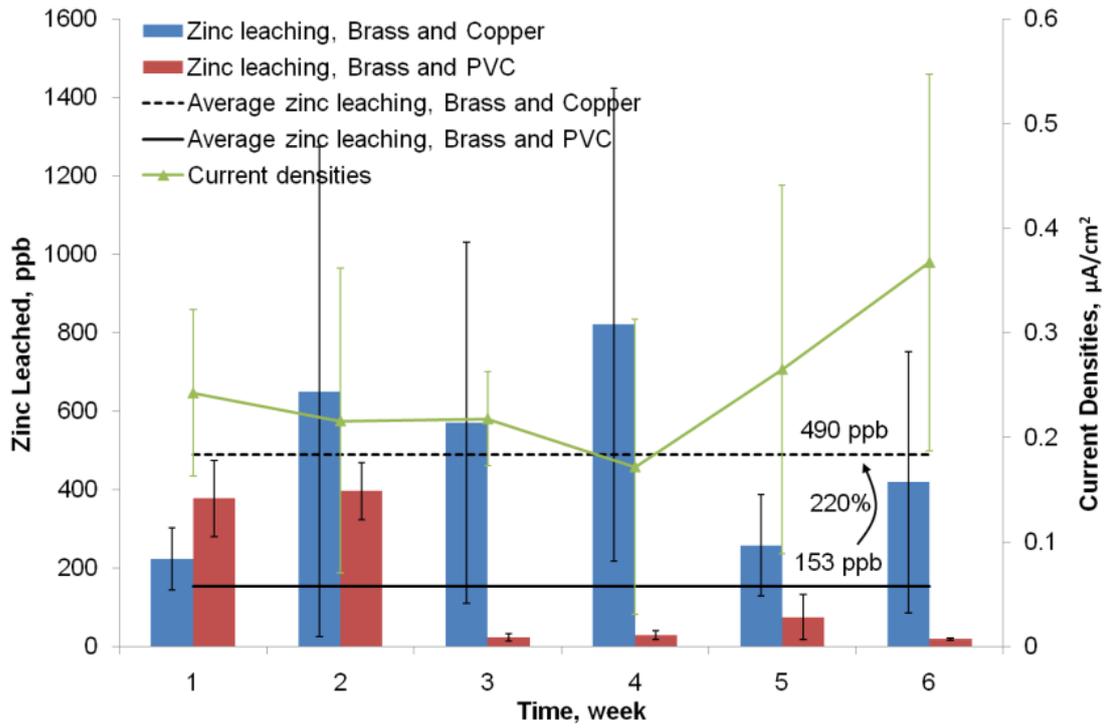


Figure 3 – 15 Galvanic currents between the copper pipe and the brass rod

Table 3 – 1 Composition of brass samples

	A	B	C	D	E	F	G	C36000
Brass Type	Duplex	Duplex	Alpha	Duplex	DZR	Duplex	DZR	Free Cutting
Zn Content, %	36.4	35.6	10.37	36.55	35.37	35.38	8.2	37.6
Cu Content, %	59.2	61.2	87.62	60.15	62.5	60.92	89.3	60.5
Pb Content, %	3.26	2.86	1.94	2.89	1.58	3.33	1.69	2.73
Sn Content, %	1.2	0.1	ND*	0.1	0.1	0.1	0.3	0.16
Ni Content, %	0.4	0.1	ND	0.1	0.1	0.1	0.5	ND
Fe Content, %	0.6	0.1	ND	0.1	0.1	0.1	0.1	ND

Table 3 – 2 Composition of test water

	pH	Alkalinity as CaCO ₃ , mg/L	[Ca ²⁺] ppm	[Mg ²⁺] ppm	[Na ⁺] ppm	[K ⁺] ppm	[Zn ²⁺] ppb	[Cl ⁻] ppm	[SO ₄ ²⁻] ppm	[PO ₄ ³⁻] ppb	[SiO ₂] ppm
Real Water*	8	119	75	25.6	93	4.8	191	96	252	147	7.6
Synthetic water	8.3	40	31	20	30	2	0	121	34	0	0

* This water was known to cause serious dezincification failures with brass A

Appendix: Method Development Tests (QA/QC)

BACKGROUND

This section describes the pre-testing of experimental techniques that could determine the impacts of water chemistry and other factors on dezincification rates using short-term bench scale protocols. Dezincification refers to the preferential dissolution of zinc from brass alloys. Dezincification can contribute to many possible problems including:

- 1) Formation of a rust layer, or scale, that looks like “meringue”) and which can block water flow through the pipe;
- 2) Reduced strength due to excessive corrosion and premature failure of the fitting;
- 3) Accelerated leaching of lead to water in association with the zinc.

Most research that has been conducted on dezincification in potable water was associated with pipe blockage due to meringue buildup in the fitting.

The rate at which dezincification problems arise in brass used in homes depends on three key factors that include:

- 1) The dezincification propensity of the metal alloy used to make the device
- 2) The dezincification propensity of the water supply as determined by pH, use of corrosion inhibitors, chlorine or other disinfectant, and other natural constituents in the water supply
- 3) Physical factors that can vary from home to home, such as use of softeners, hot water recirculation systems, water velocity, frequency of flow, and water heater temperature set point

A review of the research literature reveals that very little work has been completely which examines the individual role of each above factors in dezincification as it occurs in waters representative of modern water treatment. This work is aimed at developing a test method that can be used to examine each of the above factors, and to develop conclusions about their relative importance with statistical confidence.

MATERIALS AND METHODS

One type of duplex brass were obtained (Figure 1) and machined into rings with a width of 0.15 cm and a diameter of 2 cm. The brass rings were held to PVC pipes using plastic cable ties, placed in one-liter Nalgene PC jars and submerged in a water of interest (Figure 2). Many tests utilized water collected in from household taps known to have dezincification failures and then shipped to Virginia Tech in 5 gallon plastic jugs.

Brass samples were subject to 6 different exposure conditions that include:

- 1) Room temperature, stirred water and triplicate (i.e., three) rings in one jar;
- 2) Heated temperature, stirred water and triplicates of rings in one jar;
- 3) Room temperature, unstirred water and triplicates of rings in one jar;
- 4) Room temperature, stirred water and one ring in one jar;

- 5) Heated temperature, stirred water and one ring in one jar;
- 6) Room temperature, unstirred water and one ring in one jar.

Room temperature is $22 \pm 2^\circ\text{C}$. The samples exposed to heated water were maintained at 48°C , which is a typical temperature for hot water in households. The cold water was heated using Thermolyne magnetic heating plates. The samples exposed to stirred waters were mixed at 500 rpm using a magnetic 5 cm stir bar. For the triplicate exposure of rings, none of the suspended rings were allowed to touch each other. Henceforth, jars with only 1 brass ring are reference to as “Single samples” whereas those with 3 brass rings per jar are referred to “triplicate samples.”

Chlorine was added to a level of 1.1 mg/L with sodium hypochlorite (NaClO). The value of pH is adjusted to 7.80 with using small amounts of nitric acid (HNO_3) to lower pH or sodium hydroxide (NaOH) to raise pH. Chlorine levels and pH are maintained at the target value daily and the water is completely changed every week unless otherwise specified. Water samples are collected through out the tests after stirring the contents of the container and metal concentrations leached to the water from the brass rings were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The test water collected from consumers’ homes was found to consistently contain between 180-200 ppb zinc, as well as trace levels of copper (≈ 20 ppb) and lead (≈ 2 ppb). These levels of zinc are consistent with available data on zinc reported in the 2007 Water Quality Summary leaving the treatment plant. Thus, zinc, copper or lead leached to the water from the brass ring(s) during the experiment, are determined by difference between the measured metal at a given time, and the initial amount of metal in the water.

Before the experiments, each ring was lightly sanded and washed 3 times with nanopure water. After drying in the desiccator for two hours, each brass ring is precisely weighed. After the experiment, the rings are dried and weighed again, both before and after a light polishing step using a Dremel tool with a soft polishing pad, which has been shown to remove loose scale on the brass ring but which does not remove intact metal. “Weight loss” is determined by difference between the initial and final weight of the sample.

In this first phase of testing, the entire experiment was completed twice, at a time one week apart, to determine the overall reproducibility of the method and the conclusions drawn. As in any water supply, the water changed very slightly in between the two tests, which could also contribute to differences between tests.

METHOD DEVELOPMENT AND EVALUATION OF REPRODUCIBILITY

Zinc Leaching. The measurement of zinc leached to the water during the first two weeks of the test followed the same pattern in each of the two experiments. The highest initial rates of zinc leaching occurred for the water with triplicate samples and stirring (either hot or cold water), and the rate of release for these conditions gradually slowed as zinc levels built up in the water. In contrast, rates of zinc leaching were roughly linear in the case of single samples per jar.

The trends shown for water sample 1 are highly reproducible when compared to water sample 2 (Figure 3). Given that test 1 and test 2 used two different batches of water, slight differences between waters can be expected, and can account for some of the minor differences observed between the two tests. But the overall trends and rankings of dezincification propensity are consistent.

Weight Loss. Weight loss data for samples between the two tests were also consistent (Figure 4). There is more weight loss for single samples under the stirred condition at room temperature, than for triplicate samples for the same condition, presumably because the very high concentrations of zinc in the test water with three brass rings tends to reduce dezincification propensity (Figure 3). That is, if there is more zinc in the water, the water has a lower tendency to leach zinc for this condition. For the other samples, there was little difference between weight loss obtained using triplicate versus single ring exposure. In addition,

Relationship between Metal Leaching and Weight Loss. In this preliminary test of very short duration, a comparison was made between the total zinc, copper and lead that leached to the water during the testing (determined via ICP-MS), versus the total weight loss of the brass ring (Figure 5). In nearly all cases, there was somewhat more weight loss measured than could be accounted for due to metal leaching to the water. However, accounting for possible errors in weighing the sample which are estimated at ± 0.3 mg, the data are actually in very good agreement. Future testing must use a test duration longer than 2 weeks, in order to obtain higher weight losses above 2 mg per brass sample, in order to obtain better agreement between these two measures.

SUMMARY AND CONSIDERATION OF TEST PARAMETERS AND APPROACH

The goal of this part of the work was to rationally select a base set of conditions for future testing that would give results of high statistical confidence with the minimal human effort and expense. Consideration of the results (Table 1) indicates that triplicate samples, a 3-month test duration, room temperature, no stirring and once weekly water changes will achieve the desired results.

Table 1. Summary of key trends to be considered in designing a standard test protocol

Factor	Conclusion
Single vs. Triplicate	Use of triplicate samples per jar did sometimes lower the rate of dezincification somewhat, but not the relative trends.
Test duration	Two weeks gives reasonable results, but a longer test duration of just over 3 months is expected to dramatically improve the strength of key conclusions.
Heat	Higher temperature did not dramatically increase the rate of dezincification. This might be due to more rapid loss of chlorine at higher temperature.
Stirring	In a 2 week test, stirring did increase the rate of dezincification by up to 50-100%, but rapid corrosion also observed without stirring.
Water changes	While the rate of dezincification sometimes decreased markedly in the week between water changes, sufficient weight loss would accrue in a 3+ month test to give highly significant results.



Figure 1 Sample brass fittings

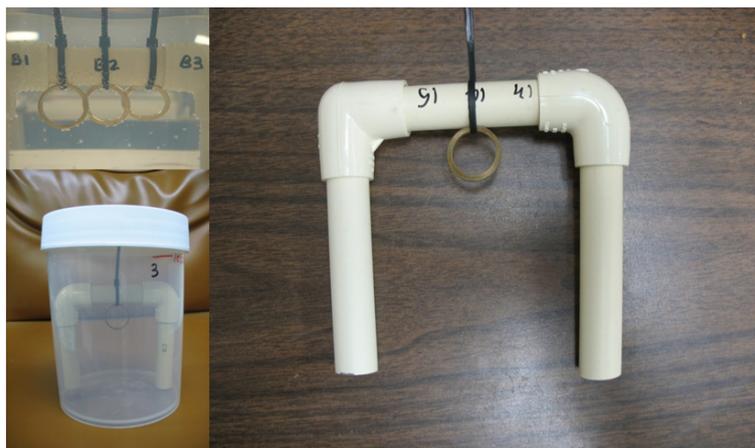


Figure 2. Brass ring tied to PVC pipes with cable ties

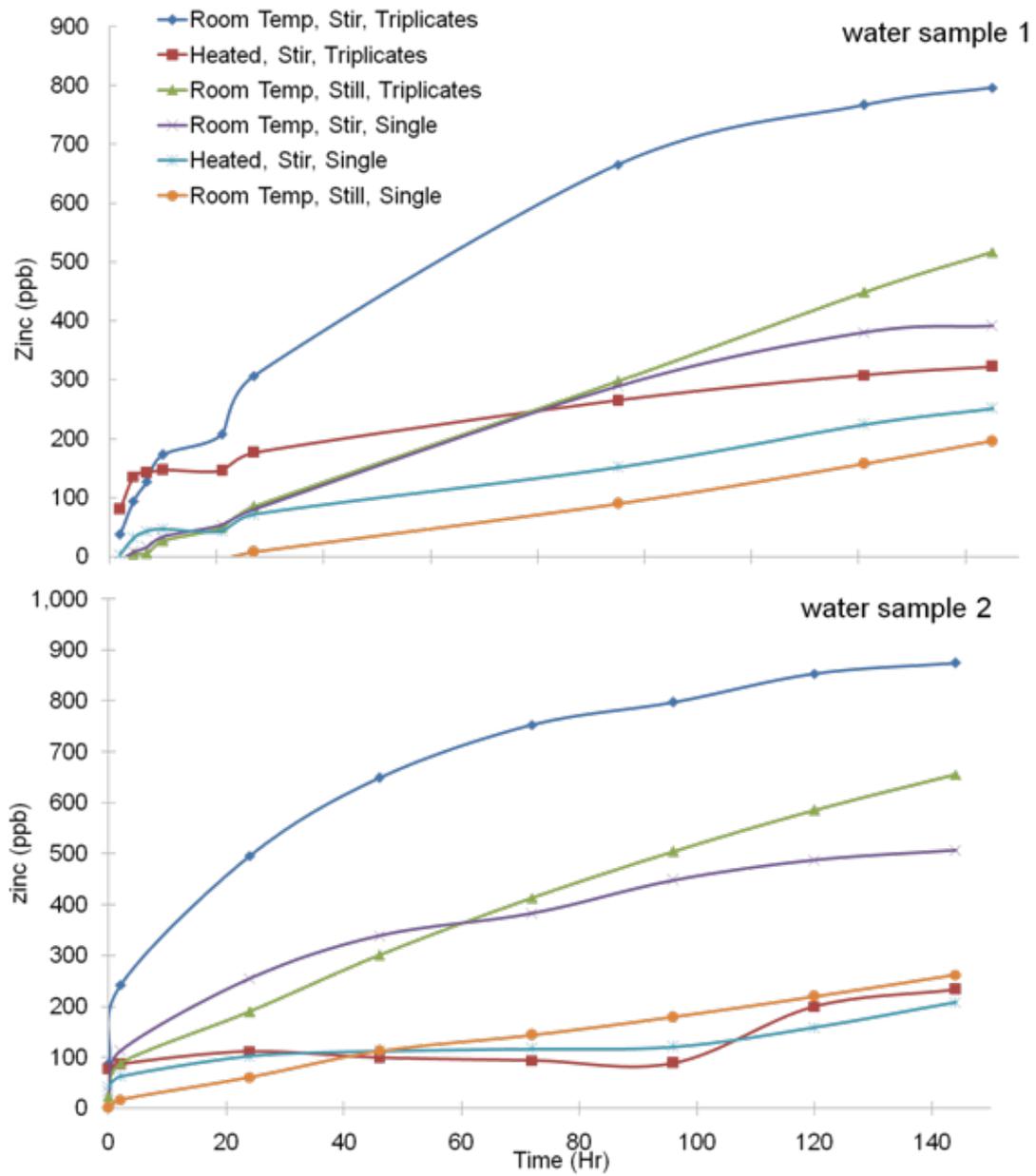


Figure 3. Zinc leached in the water in the second week of experiments

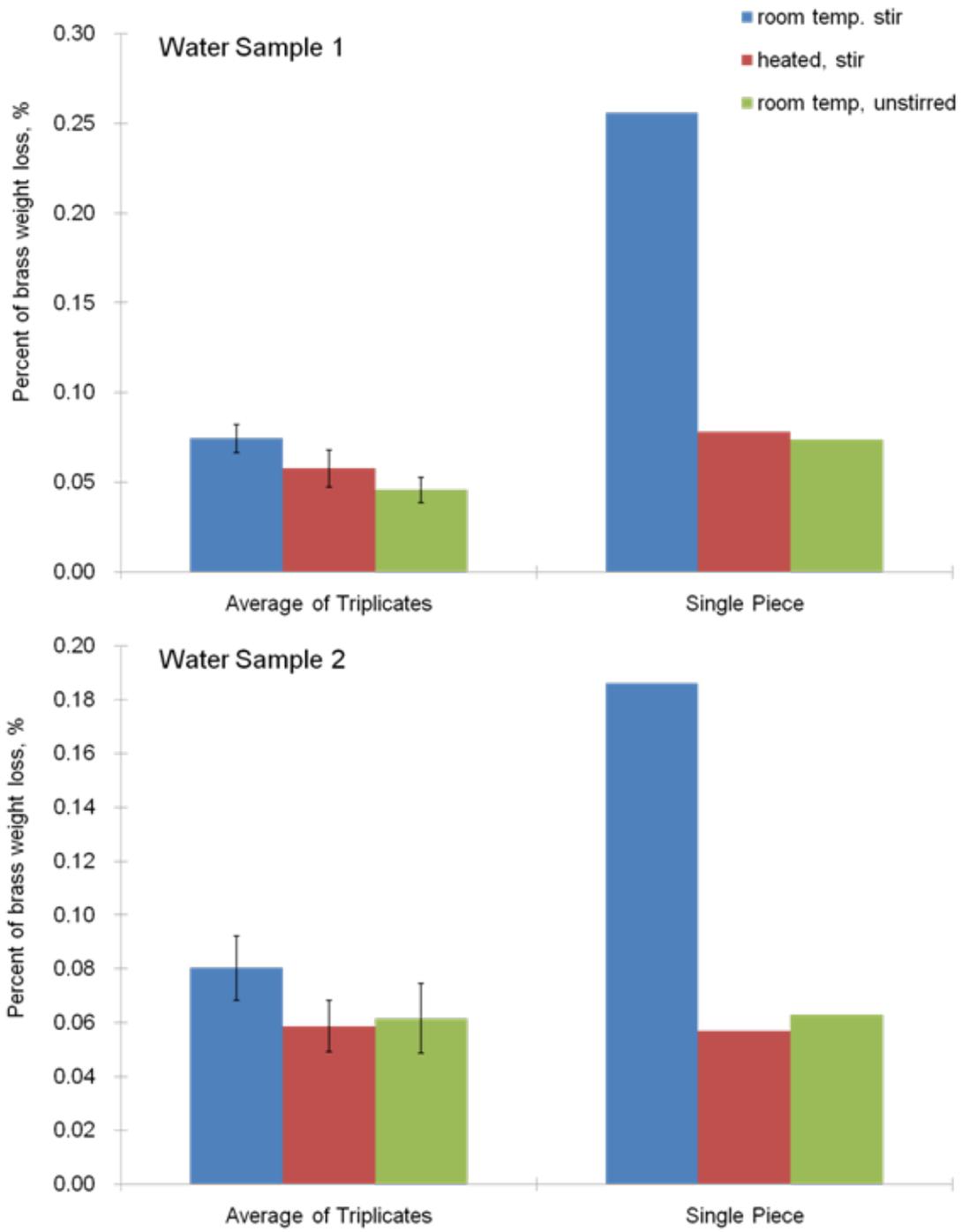


Figure 4. Brass rings weight loss after polishing (Error bars indicate 95% confidence interval)

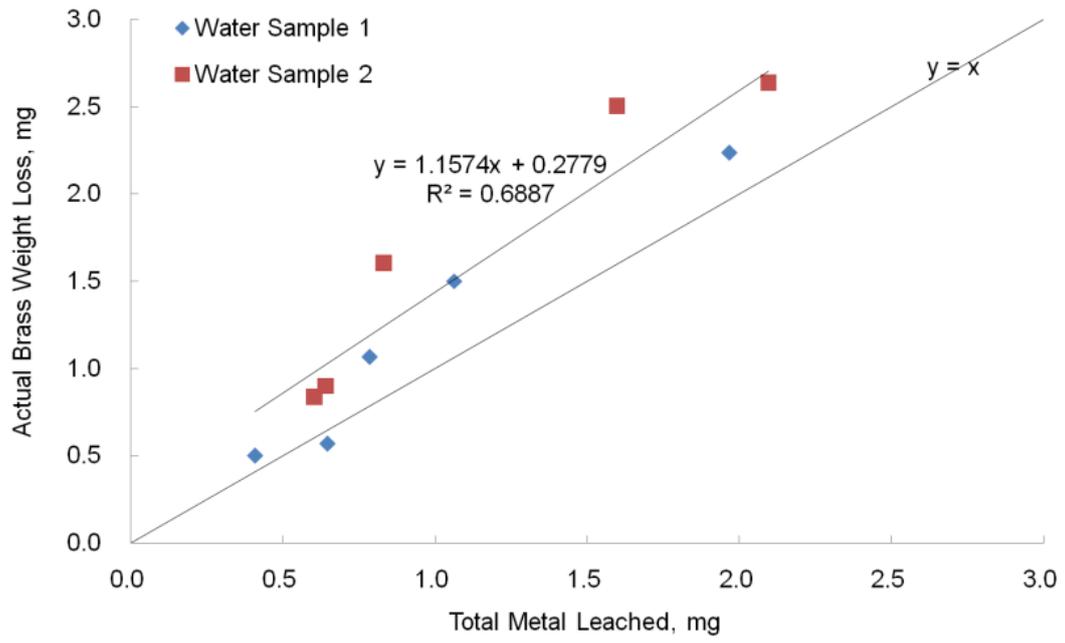


Figure 5. The correlation between actual brass and predicted weight loss

Chapter 4: The Effects of Water Chemistry Parameters over Dezincification

Abstract

Water chemistry impacted dezincification propensity of brass galvanically connected to copper. Both zinc and copper were leached rapidly at low pH; however, selective leaching of zinc (dezincification) is highest around pH 8.3. Chloride was highly aggressive in causing dezincification and sulfate was less aggressive. Orthophosphate and silica showed promise in mitigating dezincification based on short term testing, but benefits of these inhibitors gradually disappeared over a period of five months. The conventional theory of ‘meringue’ dezincification suggests that waters low in temporary hardness will have higher dezincification propensity. This work isolated individual effects of hardness and alkalinity, and demonstrated that hardness itself has little effect, but that higher alkalinity dramatically decreases dezincification. This is practically important because it suggests that water softeners would have little impact on the dezincification propensity of water.

Keywords: brass dezincification; chloride and alkalinity; corrosion inhibitors

Introduction

Brass components can be corroded by “dezincification” which is the selective leaching of zinc. Dezincification in potable water systems has important practical consequences that include clogged water lines, premature system failure and leaks, and release of contaminants such as lead (R. J. Oliphant, Causes of Copper Corrosion in Plumbing Systems 2007) (Maynard, Mast and Kwan 2008). Brass failures attributed to dezincification are known to occur at least occasionally all over the world (Campbell 1973), and have emerged as a significant problem in the U.S. recently due to the use of inexpensive high zinc brass fittings in cross-linked polyethylene (PEX) plumbing systems. As PEX systems gain popularity in potable water systems (Reuters 2009), it is important

to better understand the effects of water chemistry on dezincification to prevent future failures.

Only limited research linking dezincification to potable water chemistry has been conducted since the landmark work of Turner et al. nearly a half century ago. By exposing brass samples to Sheffield (UK) water for 30 days at 90°C, Turner discovered that the ratio of chloride to “temporary hardness” is key to predicting “meringue” accumulation (Turner 1961). But the Turner diagram and conventional wisdom were based only on visual observations and field experience from a limited geographical region. Turner’s conclusions are generally consistent with other references (Table 4 - 1), but the archaic measure of “temporary hardness” leaves complete ambiguity as to whether benefits are due to hardness, due to alkalinity, or a combination of the two (See Chapter 1). Furthermore, since the time of Turner’s work, the technology and practices of water treatment industry has changed dramatically. For example, little research has been done to elucidate possible effects of phosphate inhibitor dosing, or use of chloramines, on dezincification propensity. This study will be the first comprehensive examination of dezincification as a function of water chemistry using numerous techniques that include measurement of galvanic currents, metal leaching, and weight loss in relatively long term testing.

Material and Methods

Because brass is corroded more severely when galvanically connected to copper as per the approach of Turner (1961) and results of Chapter 3, cylindrical brass samples (Table 4 - 2) from free cutting brass C36000 were connected to copper pipes for these experiments via a simulated joint with copper (see Chapter 3). This apparatus allows quantification of trends in galvanic current via a physically separated brass anode and copper pipe cathode, with a cathode: anode surface area ratio of 32:1.9. The galvanic currents flowing between copper and brass were measured 30 minutes before and after every water change using a Fluke 189 True RMS Multimeter.

The copper pipes were filled with synthesized tap waters (Table 4 - 3 Test water) to mechanistically isolate key water chemistry factors influencing dezincification. The water in the pipes was changed using a dump and fill protocol three times a week (M, W, F). The pH of the water was adjusted using

0.01 M nitric acid and 0.01 M sodium hydroxide. Water samples were collected and then analyzed by Thermo Electron X-Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) for metal leaching per Standard Method 3125-B (APHA 1998). Brass samples were weighed before and after the experiments to obtain the weight loss and all conditions were run in triplicate.

Results and Discussion

In the control water tested in this work, there was good temporal agreement between the galvanic currents and metal leaching (Figure 4 - 1). Total metal leaching was relatively stable after the 90th day, although zinc leaching was increasing slowly from day 30 to 150 days. By definition, during dezincification zinc is preferentially leached from the alloy versus copper. To define the magnitude of the selective leaching, the “Dezincification Index” is calculated as per Chapter 3. On this basis the control condition is undergoing severe dezincification (Figure 4 - 1). The Dezincification Index was roughly stable after about 90 days.

The Effects of pH

The magnitude of zinc leaching and galvanic current density decrease as the pH increases (Figure 4 - 2). The zinc leached into the water at pH 6 is 210 times of the zinc leached at pH 10, whereas the galvanic current density at pH 6 is only 14 times higher than at pH 10. However, as reflected in the Dezincification Index (Figure 4 - 2), zinc was most preferentially leached around pH 8.0. Thus, from this perspective dezincification was worst at pH 8.0, consistent with previously identified empirical values (Simmonds, Dezincification of Water Supply Fittings 1967).

The Effects of Chloride and Sulfate

Chloride and sulfate are common anions in water that often strongly influence corrosion processes. Their concentrations are highly variable depending on the source of the drinking water, type of coagulant, localized use of road salt and other factors. Chloride and sulfate are believed especially important for certain types of galvanic corrosion (Triantafyllidou and Edwards 2007). Higher levels of

chloride and sulfate make dezincification corrosion worse (Figure 4 - 3, 4 - 4). The comparison between the Dezincification Index is most dramatic. Increasing the chloride level by 125% tripled the dezincification, whereas increasing the sulfate level by 400% doubled the Dezincification Index.

Measurements of brass weight loss and current densities confirmed the trends with the Dezincification Index for chloride. Increasing the chloride by 125% doubled weight loss and current densities. However, sulfate hardly made any difference for weight loss and galvanic currents. Overall, slightly higher chloride makes corrosion much worse, while much more sulfate makes corrosion slightly worse if at all.

These results are consistent with those of Turner who found that chloride was more aggressive than sulfate in causing dezincification corrosion (Turner 1961). As illustrated in the mechanistic studies conducted elsewhere in this thesis (See Chapter 2), adverse effects of chloride arise from the concentrated chloride near the surface of the brass anode which increases zinc solubility, decreases pH, and cause higher sustained galvanic currents. As a result, water with high chloride dissolves more zinc and sustains galvanic currents for longer periods of time.

The higher chloride and the higher sulfate conditions also produce very different brass surfaces from the control condition. There were many large white patches for the higher chloride condition consistent with “meringue” type deposits and results of Chapter 2. The sulfate condition has a smoother surface which was relatively free of meringue type deposits.

The Effects of Alkalinity

Similar to chloride and sulfate, the role of alkalinity in dezincification is very important. Higher alkalinity protects brass from dezincification while lower alkalinity makes water more aggressive (Figure 4 - 5). The Dezincification Index of the lower alkalinity water is 12 times that for the higher alkalinity water. Throughout the 150-day experiment, higher alkalinity also reduced the galvanic currents to levels lower than for the control condition (Figure 4 - 6). Water with higher alkalinity (200 mg/L versus 20 mg/L alkalinity as CaCO₃) reduced zinc leaching by over 5 times (Figure 4 - 5).

The surfaces of brass samples at the end of 21 weeks are consistent with

alkalinity's beneficial effect (Figure 4 - 7). A thin layer of light blue scale (presumably malachite) covered the brass surface in the high alkalinity water. In comparison the brass sample in the same water but at low alkalinity water had nearly no visually observable coating. The brass also gained weight after 21 weeks of exposure in high alkalinity water (Figure 4 - 8). Brass exposed to water containing 40 mg/L alkalinity lost 15 mg – 2.5% of its initial weight. Increasing alkalinity to 150 mg/L reduced weight loss to negligible.

Earlier mechanistic studies illustrated that alkalinity has multiple benefits relative to corrosion of zinc connected to a copper cathode (See Chapter 2). Alkalinity anions reduced the buildup of Cl^- at the zinc anode surface, the extra buffering tends to maintain higher pH, and alkalinity reduces the solubility of zinc through formation of zinc carbonates which can passivate surfaces. The blue scales and lower zinc leaching in water with more bicarbonate confirmed alkalinity's benefits.

Results of mechanistic studies also showed that higher alkalinity reduced the amount of white voluminous “meringue”, which helped differentiate the light blue compact coating from the loose bulky problematic scales. The protective role of basic carbonates of copper and zinc to decrease zinc solubility has also been described by other researchers (Paulson, Benjamin and Ferguson 1989) (Symes and Kester 1984).

The Effects of Ortho-Phosphate

Currently, about 50% of U.S. utilities use some form of phosphate corrosion inhibitor (McNeill and Edwards 2002). The effects of phosphate are not as straight forward as parameters discussed previously, in that there were differences in the long-term and short-term behavior. Overall, adding orthophosphate inhibited corrosion for quite some time and then the inhibitive effect gradually disappeared (Figure 4 - 9). After 21 weeks of experiments, the surface of brass remained smooth compared to other tested conditions (Figure 4 - 10). Dosing of orthophosphate decreased the Dezincification Index at all times after 25 days.

In terms of zinc leaching, the condition with added orthophosphate reached the lowest value around the 25th day and stayed there for the next 60 days (Figure 4 - 9, top). During this period, the control condition leached 25 times more zinc

than the orthophosphate condition. However, the zinc leaching and Dezincification Index for the orthophosphate condition gradually increased and eventually nearly matched the control condition by the 140th days (Figure 4 -9, top). The galvanic currents also significantly increased after 100 days (Figure 4 -9, bottom) compared with the lowest value 0.028 $\mu\text{A}/\text{cm}^2$ from day 40 to day 80, although they were still much lower than the control condition. All of these trends create concern about the long-term effects of phosphate as an inhibitor of brass corrosion.

Re-analysis of copper and zinc leaching data from prior research also confirmed this trend. Although the authors were mainly targeting the lead leaching problem and did not discuss the effects of orthophosphate in dezincification (Lytle and Schock 1996), the inhibitive effect of dosing 1.5 mg/L orthophosphate as PO_4^{3-} started to disappear after 100 days (Figure 4 - 11). Consistent with results of this work, our calculation of Dezincification Index in that work indicated that it too rose with time.

It is unclear why the inhibitive effects of orthophosphate gradually disappear with time. It was believed that a zinc phosphate and copper phosphate film is formed over the alloy surface to inhibit dezincification (Ashour and Ateya 1995). Solubility jar tests in this thesis also revealed that phosphate would precipitate zinc, especially when calcium/magnesium is present (See Chapter 2). Further research will be needed to determine why the protective effect dissipates with time.

The Effects of Silicate

Both natural and artificially added silicate might inhibit brass corrosion and dezincification (Figure 4 - 12). From day 40 to 90, silicate provided substantive inhibition against dezincification. However, both the zinc leaching and the Dezincification Index increased and eventually surpassed the values seen in the control condition in the next 50 days. These effects were observed at both lower (20 mg/L silicate as SiO_2) and higher (40 mg/L silicate as SiO_2) levels of silicate. The trends with galvanic current densities were similar, although the currents for the silicate conditions were still much lower the control.

The Effects of Zinc

If zinc leaching was controlled by solubility and equilibrium with zinc ions in the water, and not by corrosion kinetics, it would be reasonable to believe that adding zinc to the water as an inhibitor would reduce zinc leaching and dezincification. Recent survey's found that 34 % of utilities added inhibitors that contained Zn^{+2} (McNeill and Edwards 2002). However, in this work, dosing of zinc did not inhibit zinc leaching, and may have made it worse. Although the visual appearances of brass samples with and without zinc were similar (Figure 4 - 13), the condition with added zinc had greater non-uniformity of deposits. In addition, the zinc leaching and the weight loss data reveal that adding zinc did significantly decrease these manifestations of brass corrosion (Figure 4 - 14 and 15). Thus, zinc leaching to water is not reduced by the presence (or dosing of) zinc to the water supply, and zinc addition (up to 0.6 mg/L zinc as Zn^{2+}) does not inhibit dezincification corrosion.

The Effects of Hardness

It was previously believed that “temporary hardness” was a controlling factor in dezincification as per the Turner Diagram (Turner 1961). Temporary hardness is an archaic measure that involves hardness, alkalinity, pH, and combinations of these parameters. This work examined the role of hardness directly.

Turner suspended brass specimens in modifications of simulated Sheffield (UK) water (Table 4 - 3, Turner's Sheffield water) for 30 days at 90°C. Water changes and pH control were not mentioned, and Turner stated that the initial pH had no influence on corrosion because all solutions had attained equilibrium with air at 90°C. The net result demonstrated that dezincification attack could be produced in a water containing only calcium, bicarbonate and chloride ions.

A series of follow-up tests were also discussed by Turner without giving specifics. Turner stated that given the same chloride concentration, calcium or magnesium bicarbonate suppressed “meringue” dezincification (Turner 1961). Because alkalinity and hardness are often roughly correlated (Edwards, Schock and Meyer 1996), it was deemed possible that the benefits observed by Turner from temporary hardness might be attributable to alkalinity, as opposed to hardness ions. On the other hand, Turner stated without providing data that sodium bicarbonate did not reduce meringue dezincification.

To examine the role of hardness directly, two sets of conditions were tested at 120 and 270 mg/L Cl⁻ (Figure 4 - 16) with different levels of hardness. Alkalinity was kept the same for all four conditions at 40 mg/L. Regardless of chloride levels, hardness had nearly no effect on Dezincification Index and the amount of zinc leached. The two pairs of Dezincification Indexes were almost identical. Zinc leaching values were slightly different, but not statistically convincing. At 120 mg/L chloride, increasing hardness from 0 mg/L to 160 mg/L increased zinc leaching; while at 270 mg/L chloride, the trend reversed. Increasing hardness from 160 mg/L to 300 mg/L decreased zinc leaching by 13%. Even if hardness had an effect, the effect was weak and inconsistent. The “temporary hardness” used in Turner’s diagram was more likely an agent of alkalinity, rather than hardness.

Conclusions

1. Chloride and alkalinity are very influential factors in dezincification. Higher chloride makes corrosion significantly worse, while higher alkalinity provides protection against corrosion.
2. Sulfate worsens dezincification, but the effect is less significant than chloride.
3. Selective leaching of zinc is maximized around pH 8.
4. Both orthophosphate and silicate inhibit dezincification for a short period of time, but their inhibitive effects disappear after around 100 days.
5. Higher hardness and higher zinc in the water have very limited effects on dezincification corrosion.
6. Benefits from higher alkalinity and detriments from higher Cl⁻ can explain the basis of the Turner diagram, because in some situations “Temporary hardness” correlates with alkalinity.

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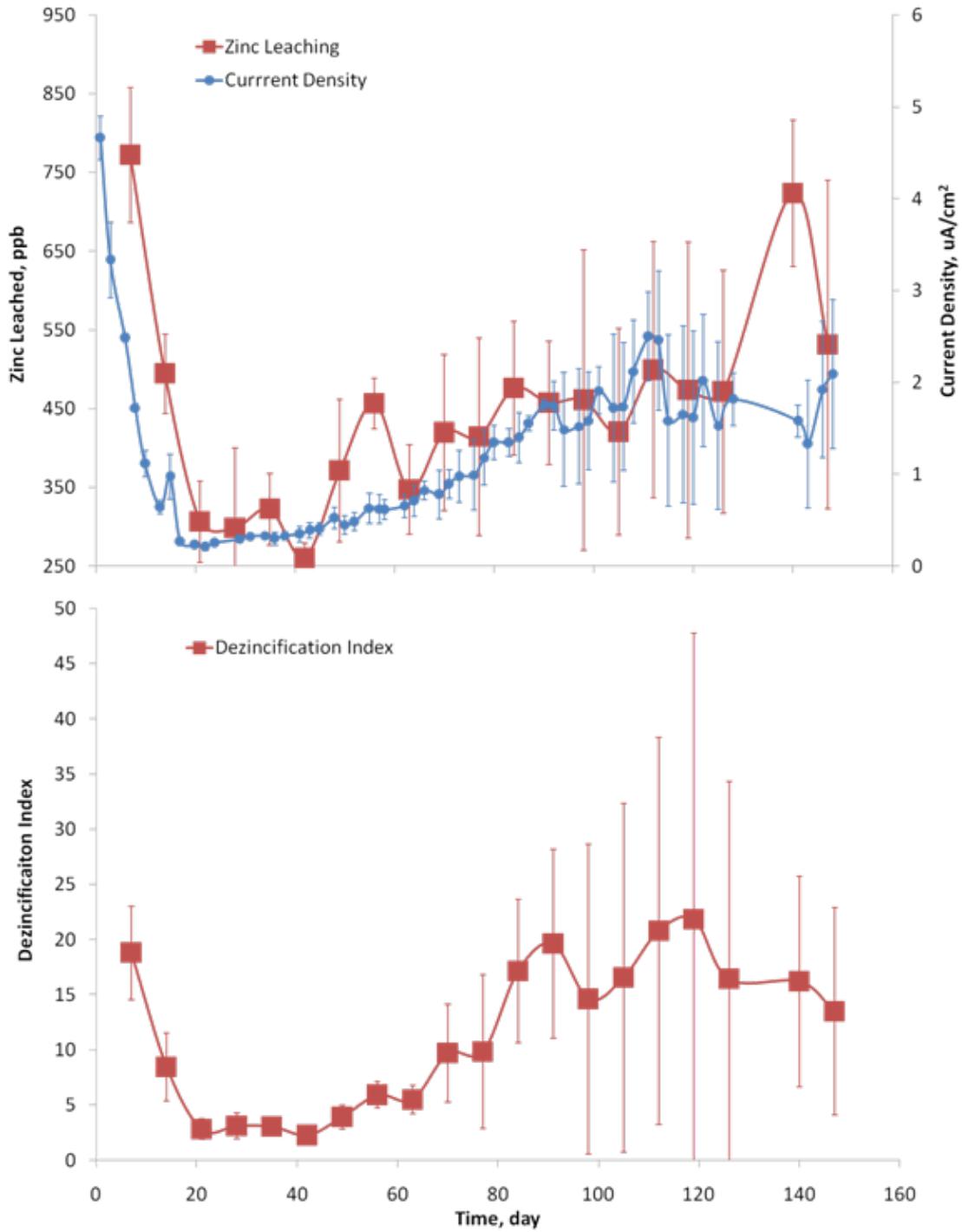


Figure 4 -1 Zinc leaching, current density and Dezincification Index for the control condition
(Error bars represent 95% confidence levels based on triplicates)

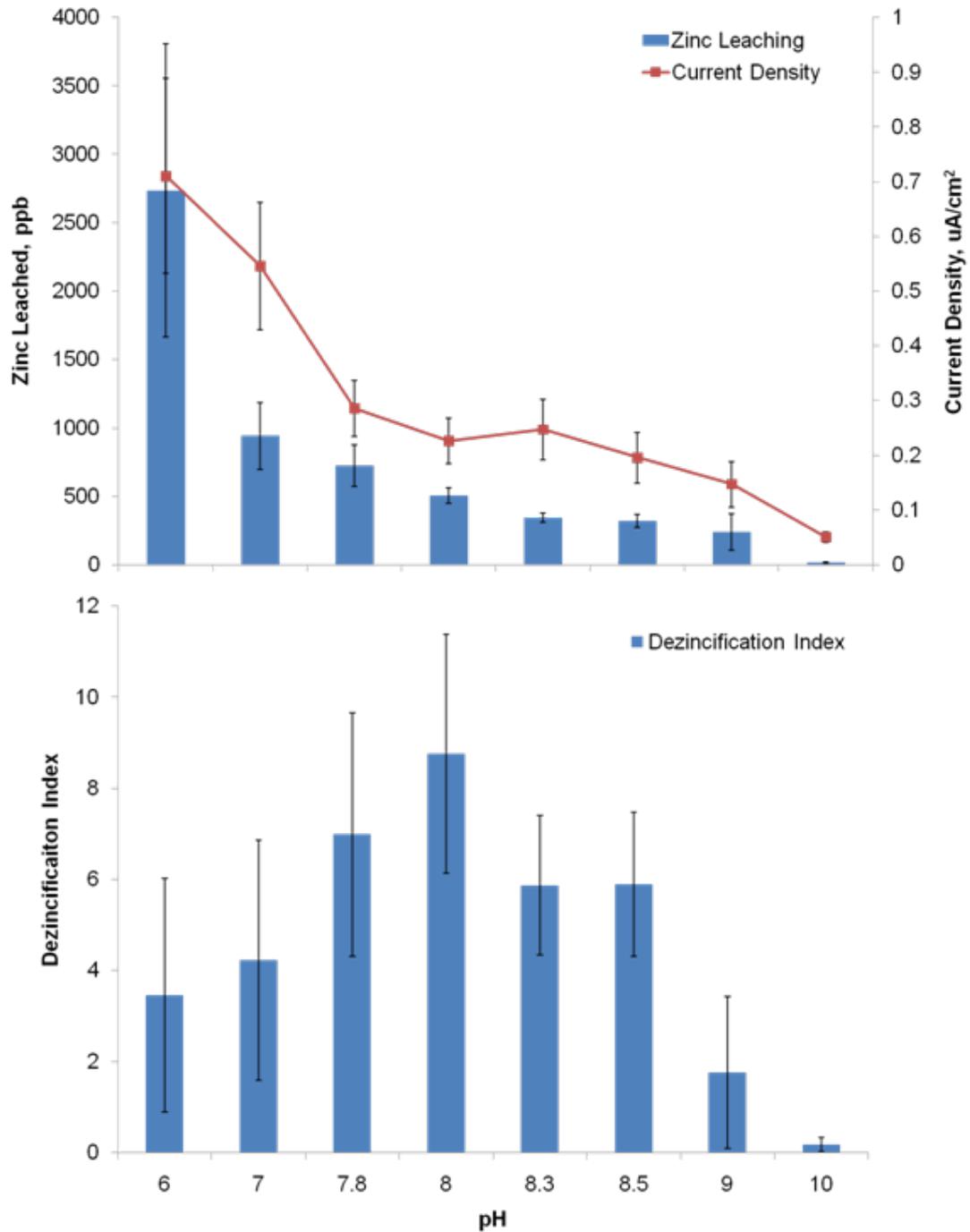


Figure 4 – 2 The average zinc leaching, current density and Dezincification Index from pH 6 to pH 10 (Error bars represent 95% confidence levels based on triplicates and 7 weeks of data)

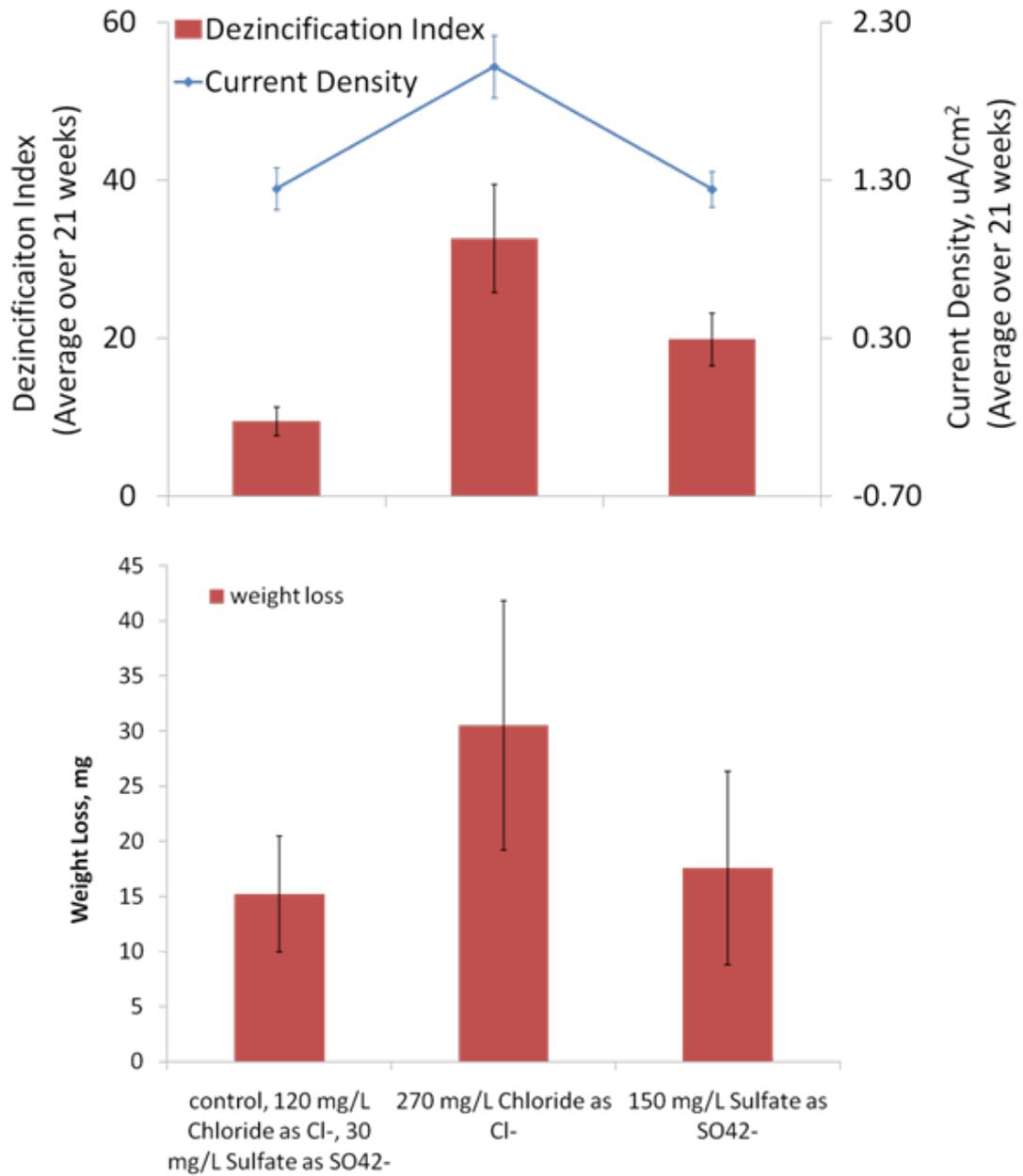


Figure 4 – 3 The average dezincification index, current density and brass weight losses for the control, the higher chloride and the higher sulfate conditions (Error bars represent 95% confidence levels based on triplicates and 21 weeks of data)

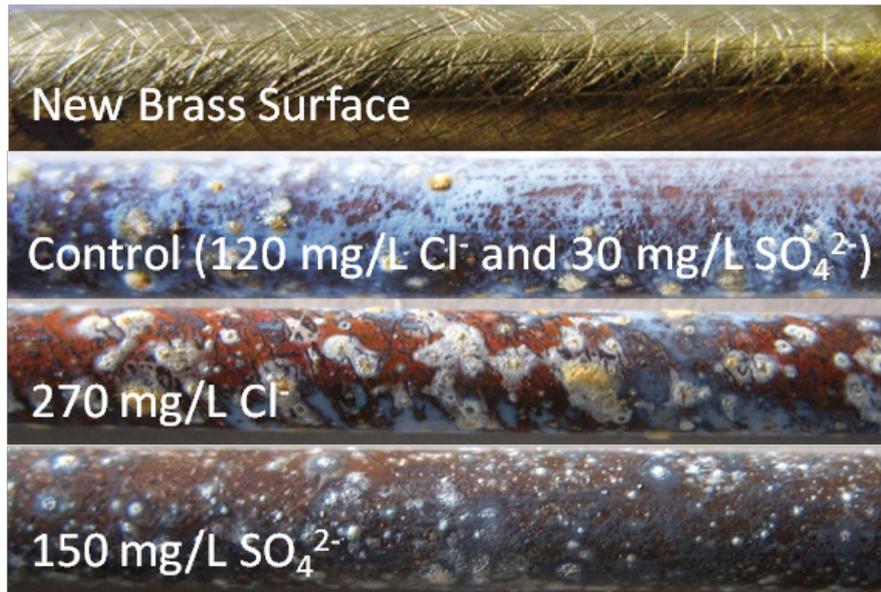


Figure 4 – 4 Surface images for the new brass surface, the control, the higher chloride and the higher sulfate conditions

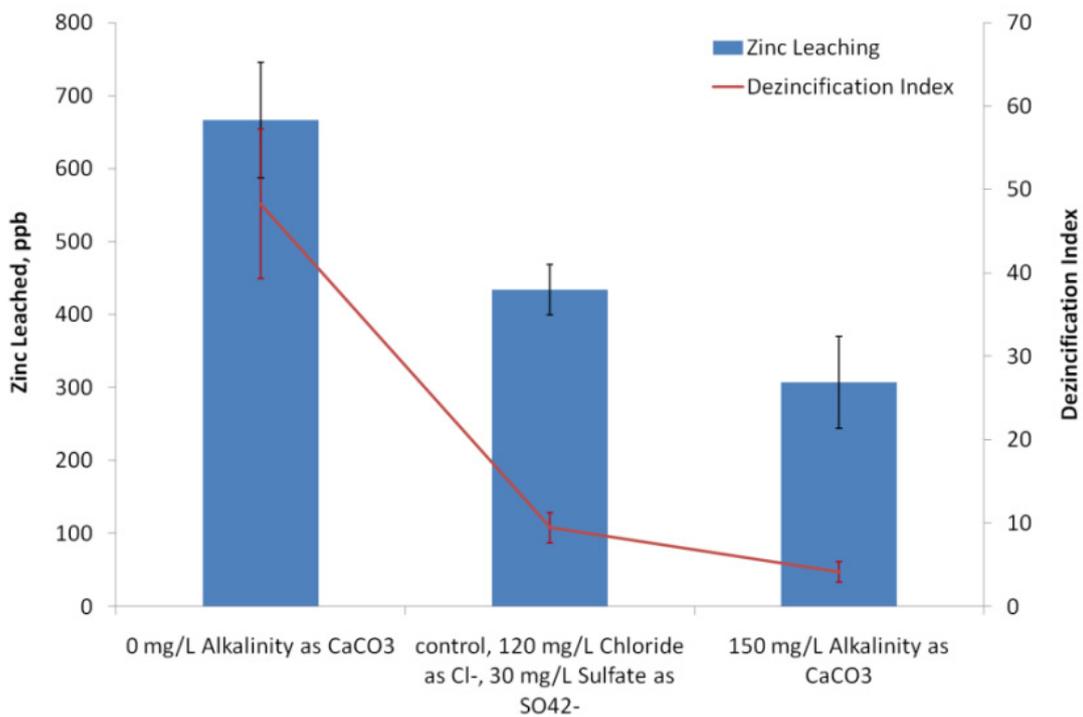


Figure 4 – 5 The average zinc leaching and Dezincification Index for the low alkalinity, the control and the high alkalinity conditions ($[Cl^-]$ and $[SO_4^{2-}]$ were the same for three conditions)

(Error bars represent 95% confidence levels based on triplicates and 21 weeks of data)

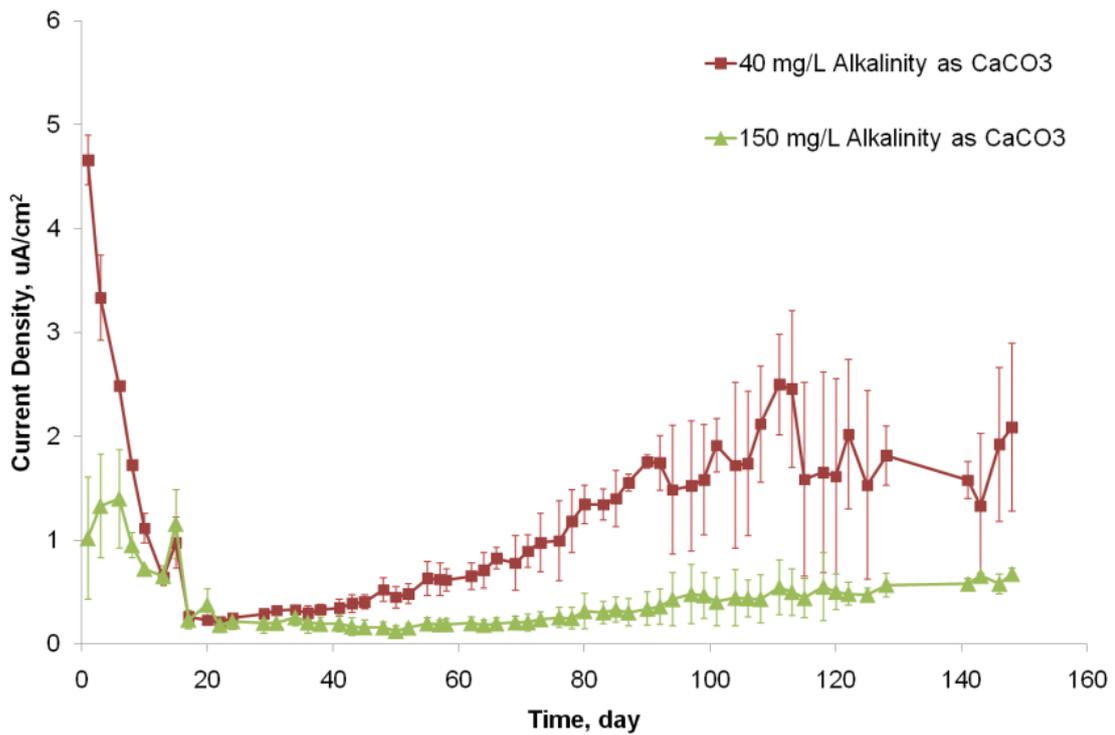


Figure 4 – 6 Current densities for the control and the higher alkalinity conditions (Error bars represent 95% confidence levels based on triplicates)



Figure 4 – 7 Surface images for the new brass surface, the low alkalinity, the control and the high alkalinity conditions

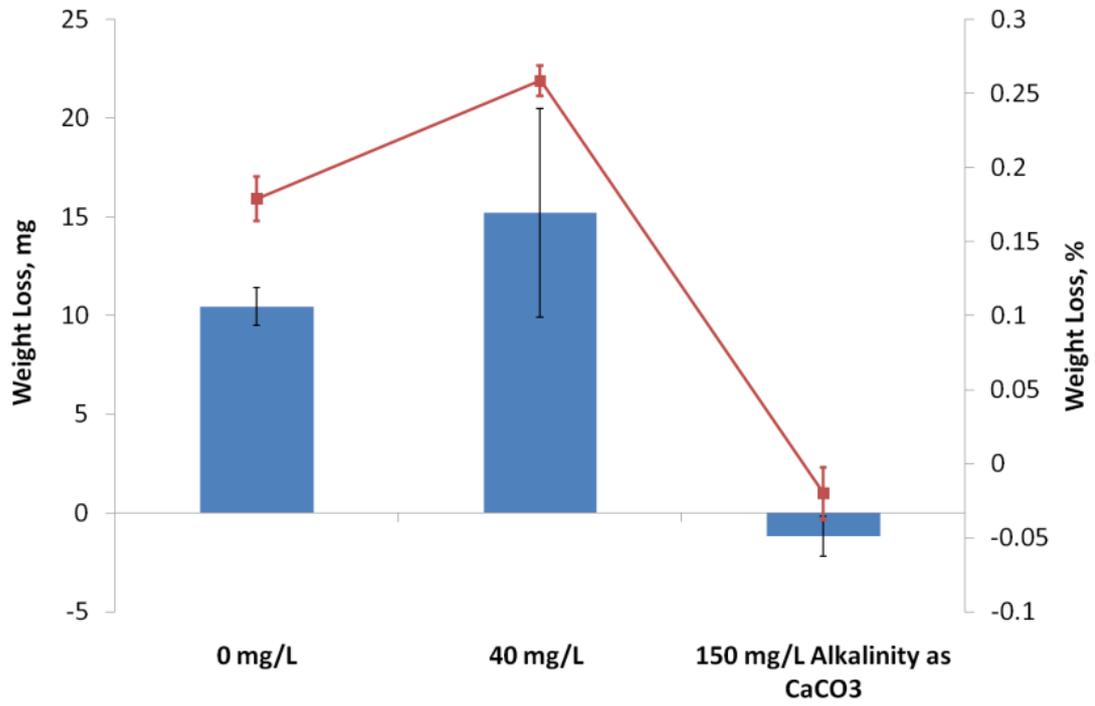


Figure 4 – 8 Brass weight losses for the low alkalinity, the control and the high alkalinity conditions
 (Error bars represent 95% confidence levels based on triplicates)

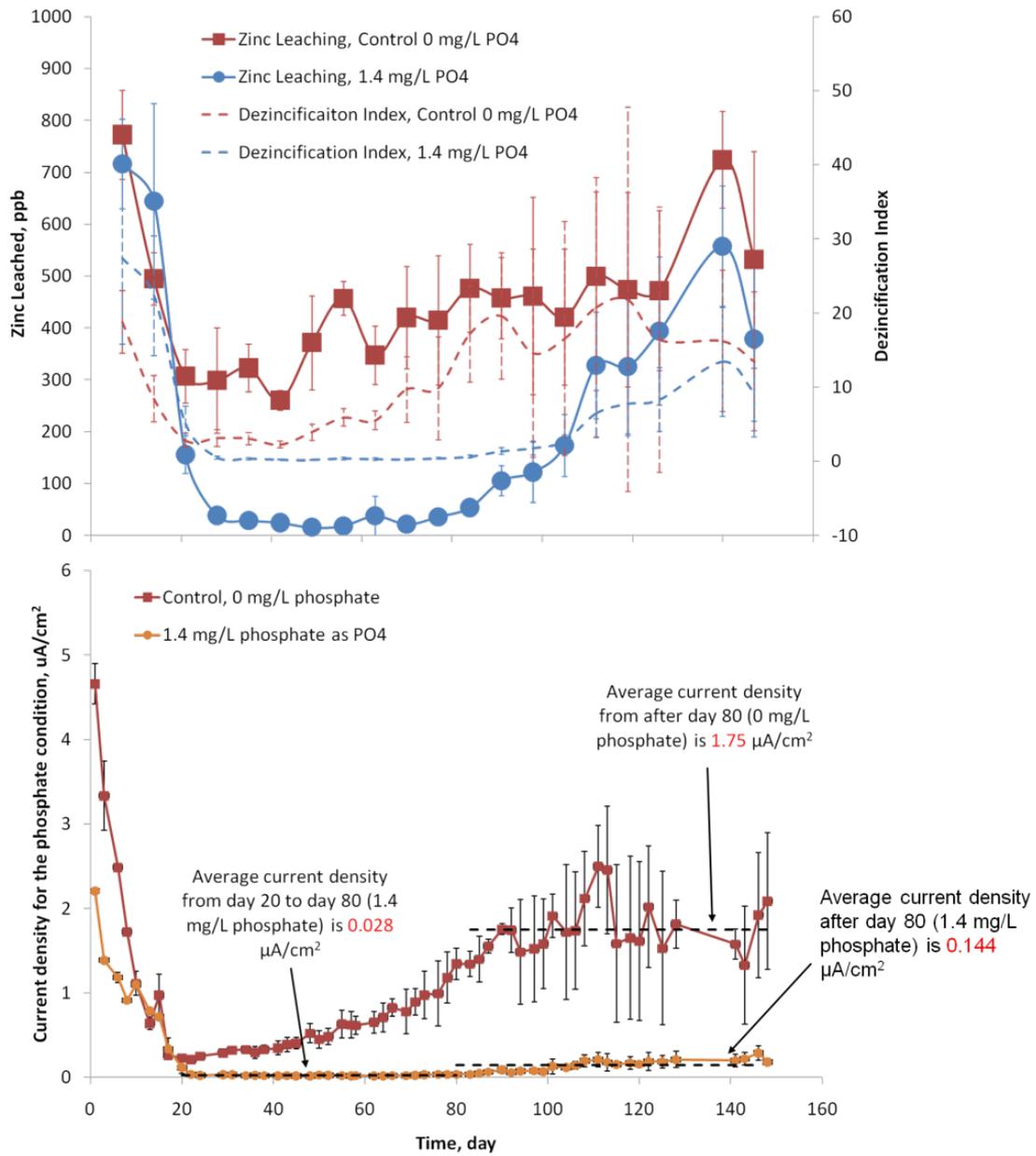


Figure 4 – 9 The zinc leaching, dezincification index and current densities for the control and the added-orthophosphate conditions (Error bars represent 95% confidence levels based on triplicates)

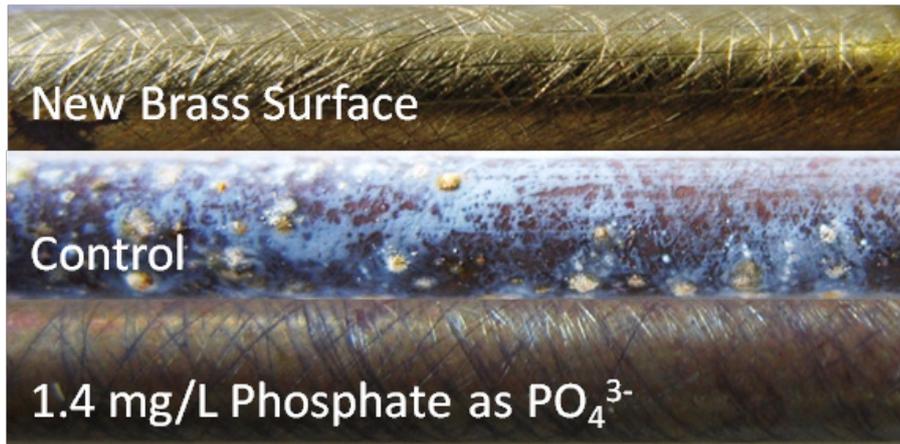


Figure 4 – 10 Surface images for the new brass surface, the control and the orthophosphate conditions

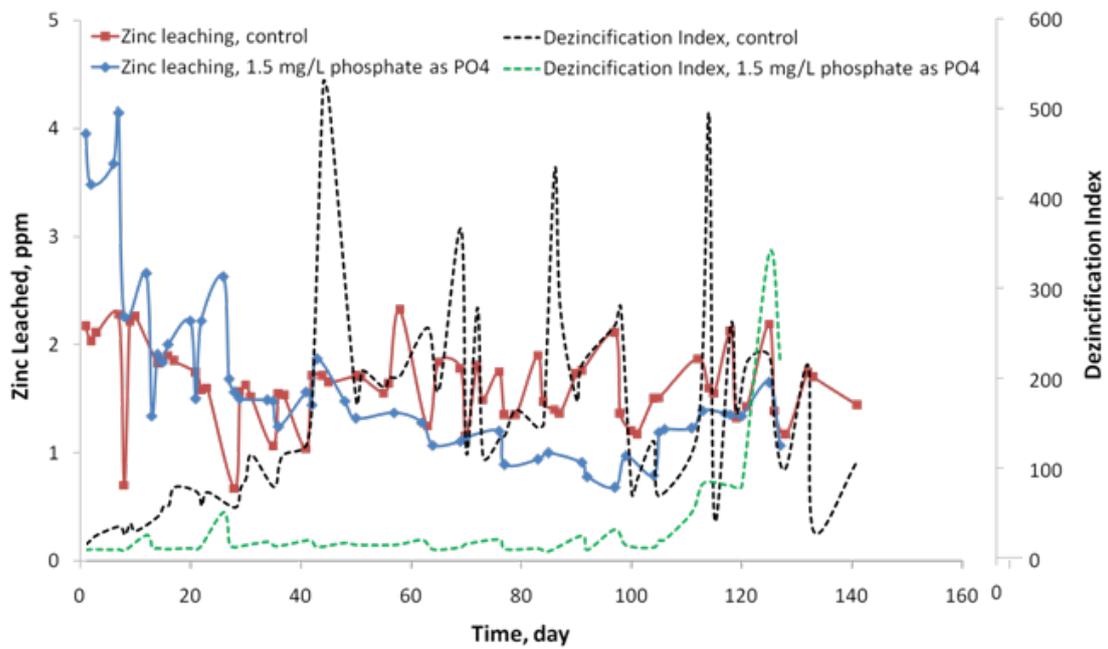


Figure 4 – 11 Zinc leaching and Dezincification Index in the 1996 Lytle and Shock study

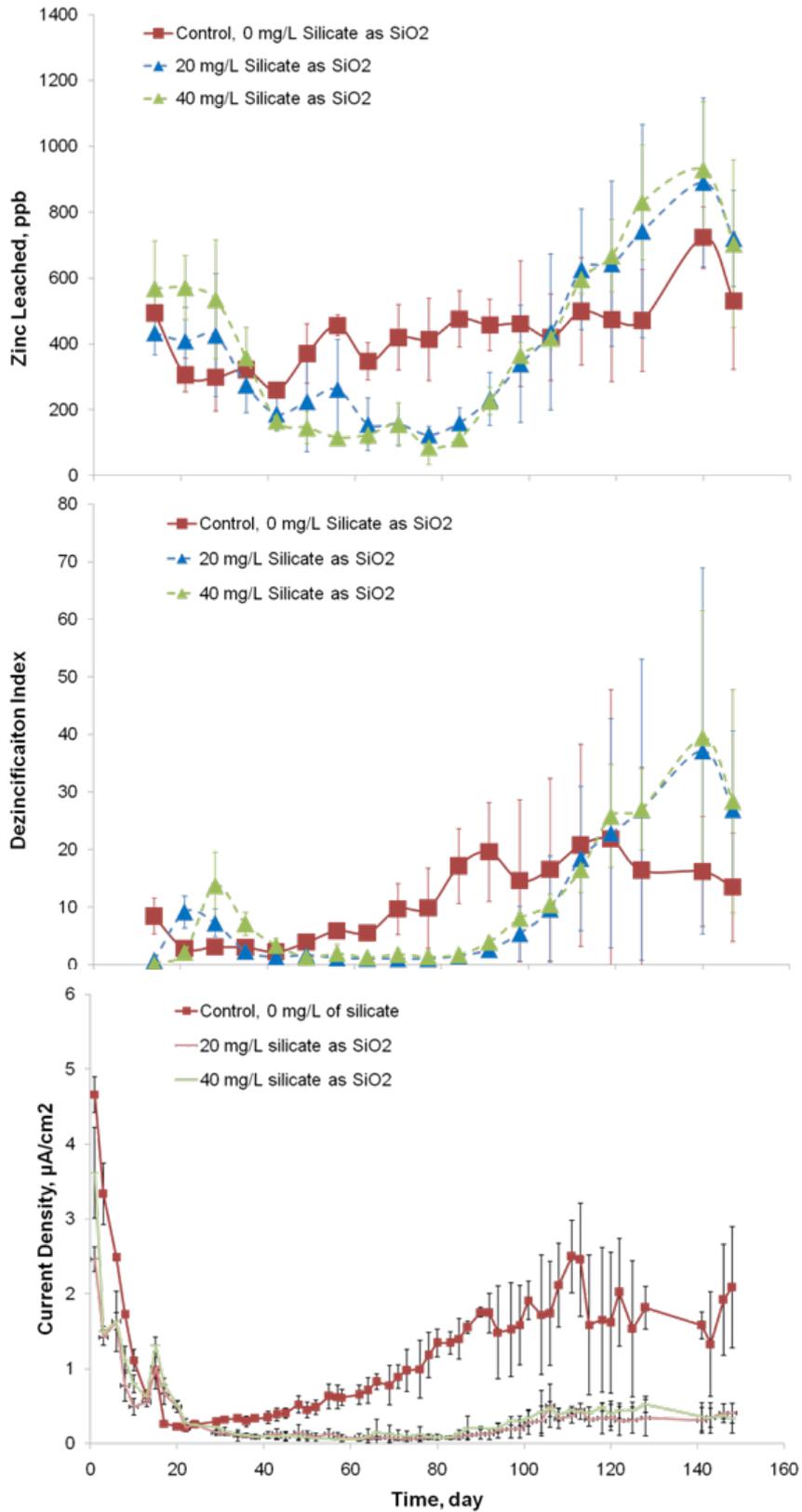


Figure 4 – 12 The zinc leaching and current densities for the control and the added-silicate conditions
(Error bars represent 95% confidence levels based on triplicates)

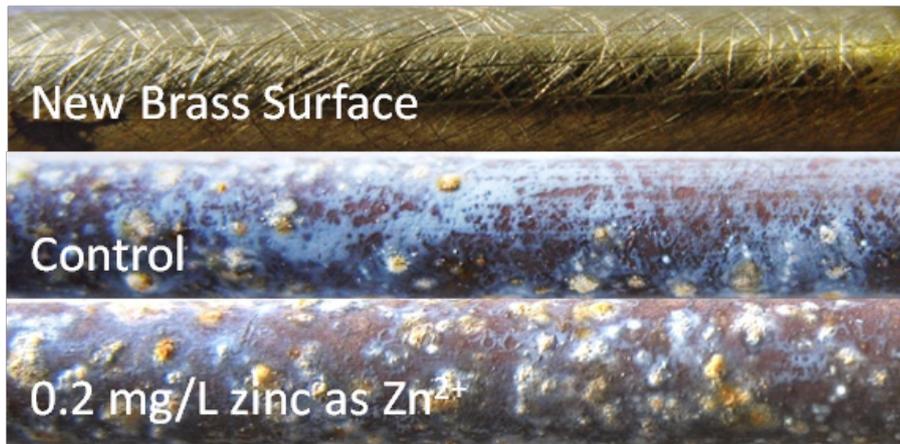


Figure 4 – 13 Surface images for the new brass surface, the control and the added-zinc conditions

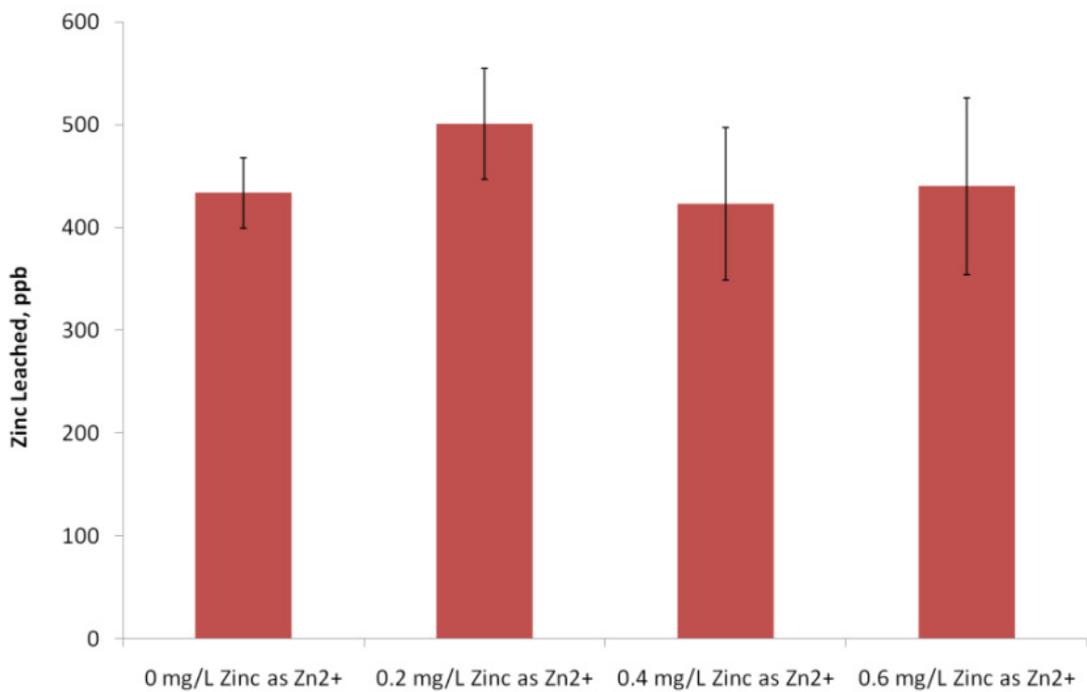


Figure 4 – 14 The average zinc leaching for the control and the added-zinc conditions (Error bars represent 95% confidence levels based on triplicates and 21 or 17 weeks of data)

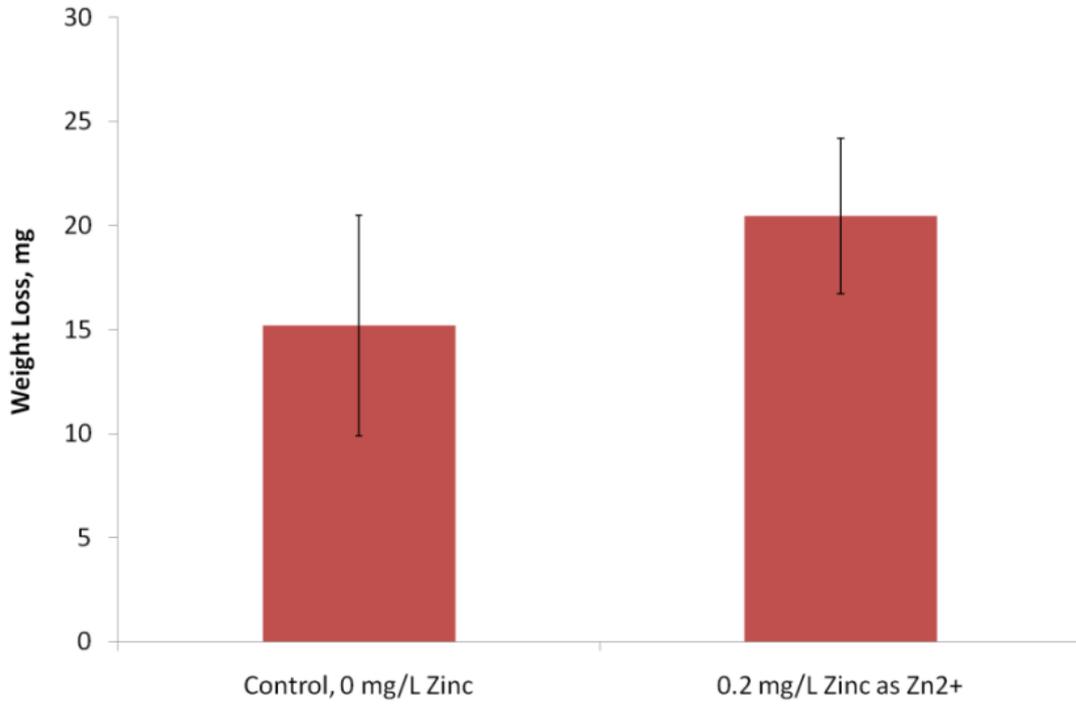


Figure 4 – 15 Brass weight losses (the control and the added-zinc condition)
(Error bars represent 95% confidence levels based on triplicates)

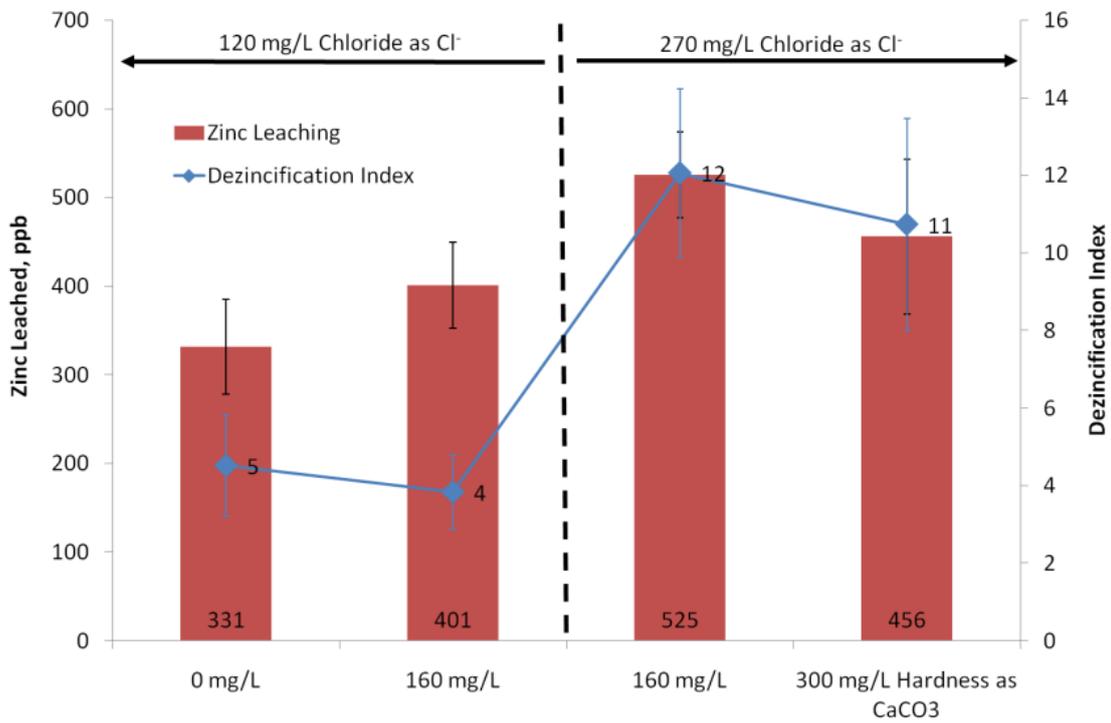


Figure 4 – 16 The average zinc leaching and Dezincification Index for conditions with varying hardness
(Error bars represent 95% confidence levels based on triplicates and 7 weeks of data)

Table 4 – 1 Previous study on the effects of pH over dezincification

Author	Criteria	Key Conclusion
Turner, 1961	Visual observation	Meringue dezincification occurs when pH is above 8.3.
Simmonds, 1967	Visual observation and field experience	The pH of waters should not be increased over 8.0 to avoid dezincification.
Jester, 1985	Visual observation and field experience	Meringue dezincification occurs when pH is above 7.8.
Nicholas, 1994	Electrical-chemical parameters	Meringue dezincification occurs from pH 7.5 to 9. Brass surface is passivated when pH is above 9.5. Critical pH should be dependant of the specific water chemistries.
Oliphant & Schock, 1996	Literature review and experience	Meringue dezincification occurs when pH is above 8.2. Water with pH of 7.6 to 8.2 supports dezincification.

(Turner, 1961) (Simmonds, Dezincification of Water Supply Fittings 1967) (Jester 1985) (D. Nicholas 1994) (Oliphant and Schock, Copper Alloys and Solders 1996)

Table 4 – 2 Composition of free cutting brass C36000

Alloy	Metal Type	Copper (%)	Zinc (%)	Lead (%)	Iron (%)
C36000	FC Brass	60.5	37.6	2.73	0.16

Table 4 – 3 Composition of test water

	pH	[HCO ₃ ⁻] as CaCO ₃ , mg/L	[Ca ²⁺] ppm	[Mg ²⁺] ppm	[Na ⁺] ppm	[K ⁺] ppm	[Al ³⁺] ppb	[Cl ⁻] ppm	[SO ₄ ²⁻] ppm	[SiO ₂] ppm
Test water	8.3	40	31	20	30	2	0	121	34	0
Turner's Sheffield water	8.35	10.9	11.5	2.8	6.1	0	0.3	12	25.9	5.1

Table 4 – 4 Alterations to the test water (all waters are adjusted to pH 8.3)

Type of tests	Modification to Water(Duration of running time)
Test water (control)	pH (21 weeks)
The effects of pH	Adjusted pH to 6, 7, 7.8, 8, 8.5, 9, 10 (7 weeks)
The effects of Chloride	Added 270 mg/L chloride as Cl^- using NaCl (21 weeks)
The effects of Sulfate	Added 150 mg/L sulfate as SO_4^{2-} using Na_2SO_4 (21 weeks)
The effects of Zinc ion	Added 0.2 mg/L as Zinc as Zn^{2+} using ZnSO_4 (21 weeks)
	Added 0.4 mg/L as Zinc as Zn^{2+} using ZnSO_4 (17 weeks)
	Added 0.6 mg/L as Zinc as Zn^{2+} using ZnSO_4 (17 weeks)
The effects of Phosphate	Added 1.4 mg/L Ortho-P as PO_4^{3-} using Na_3PO_4 (21 weeks)
The effects of Silicate	Added 20 mg/L Silicate as SiO_2 using Na_2SiO_3 (21 weeks)
	Added 40 mg/L Silicate as SiO_2 using Na_2SiO_3 (21 weeks)
The effects of Hardness	Added 0 mg/L Hardness as CaCO_3 using CaCl_2 (7 weeks)
	Added 300 mg/L Hardness as CaCO_3 using CaCl_2 (7 weeks)
The effects of Alkalinity	Added 0 mg/L Alkalinity as CaCO_3 using NaHCO_3 (21 weeks)
	Added 150 mg/L Alkalinity as CaCO_3 NaHCO_3 (21 weeks)

Appendix: Relative Effect of Water Composition on Dezincification (Case Studies)

Introduction:

Some types of brass are failing at a high rate in certain parts of the United States. The testing conducted herein, is designed to examine the relative role of water chemistry on brass dezincification. One type of duplex brass was exposed to water from 8 locations to examine the variable role of water chemistry (Table 1). All samples of brass were tested at room temperature (22 ± 2 °C) without stirring. The basic protocol is described elsewhere.

Results and Discussion:

The dezincification propensity of the water were evaluated by comparing zinc, copper and lead leaching over a 2400 hour time period (100 days). In terms of zinc leaching to the water (Figure 1), considering data at the end of the test, the ranking of dezincification propensity from highest to lowest is:

1. Rhode Island
2. San Diego
3. Santa Clarita
4. Las Vegas
5. Chapel Hill
6. Seattle
7. Blacksburg

The selective leaching of zinc versus copper to the water provides another perspective on dezincification as illustrated by the ratio of Zn:Cu (Figure 2). Focusing on the last 1200 hours as indicative of a longer term trend, the ranking is:

1. Santa Clarita
2. Santa Diego
3. Chapel Hill
4. Las Vegas
5. Seattle
6. Blacksburg
7. Rhode Island

The ranking of different waters by zinc to copper molar ratio is very similar to the ranking by merely zinc leached in the water. The only major difference is the water from Rhode Island. As can be seen from Table 1, the Rhode Island water has quite low pH, which allows copper to dissolve together with zinc. It is likely that such low pH environment could cause brass fittings to fail by general corrosion rather than dezincification.

Comparing the zinc to copper molar ratio on the first 1200 hours and the last 1200 hours, San Diego and Santa Clarita have the worst trend. Seattle and Blacksburg illustrated decreasing zinc-to-copper ratio with time.

In prior work, the total metal leached to the water (Figure 3) over the duration of the test, was correlated to the weight loss (Figure 4 and Figure 5). Focusing on the last test period of total metal leached gives the following ranking. Actual weight loss data yield the same ranking.

1. Rhode Island
2. San Diego
3. Las Vegas and Santa Clarita
4. Chapel Hill
5. Seattle
6. Blacksburg

As discussed elsewhere, loose scales on brass samples were removed with a Dremel tool without scraping the intact metal. Visually, Santa Clarita water developed the worst meringue scales, while other waters developed minimal amount. Therefore, for Santa Clarita water, weight losses before and after dremel polishing have the largest difference.

Discussion:

The Turner diagram, which attempts to classify dezincification propensity based on a measured ratio of chloride to alkalinity (Figure 6), does not provide accurate insights to the ranking of a water's dezincification propensity. This is likely because Turner was only predicting the tendency for meringue dezincification, and the diagram also does not account for the effect of corrosion inhibitors such as zinc phosphate which are now often added to a water supply (Table 2).

Conclusion:

On the basis of these measures of dezincification propensity, the Las Vegas water is actually less aggressive than other Colorado River waters tested including San Diego and Santa Clarita, and much more aggressive than waters such as Blacksburg and Seattle.

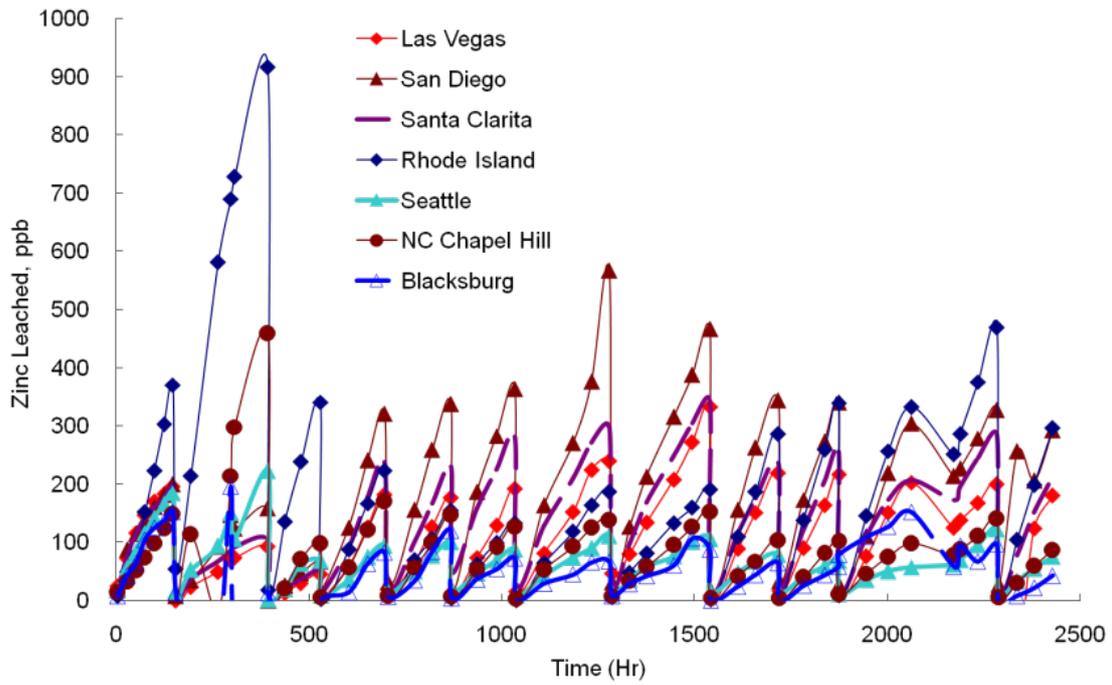


Figure 1. Zinc leached with time

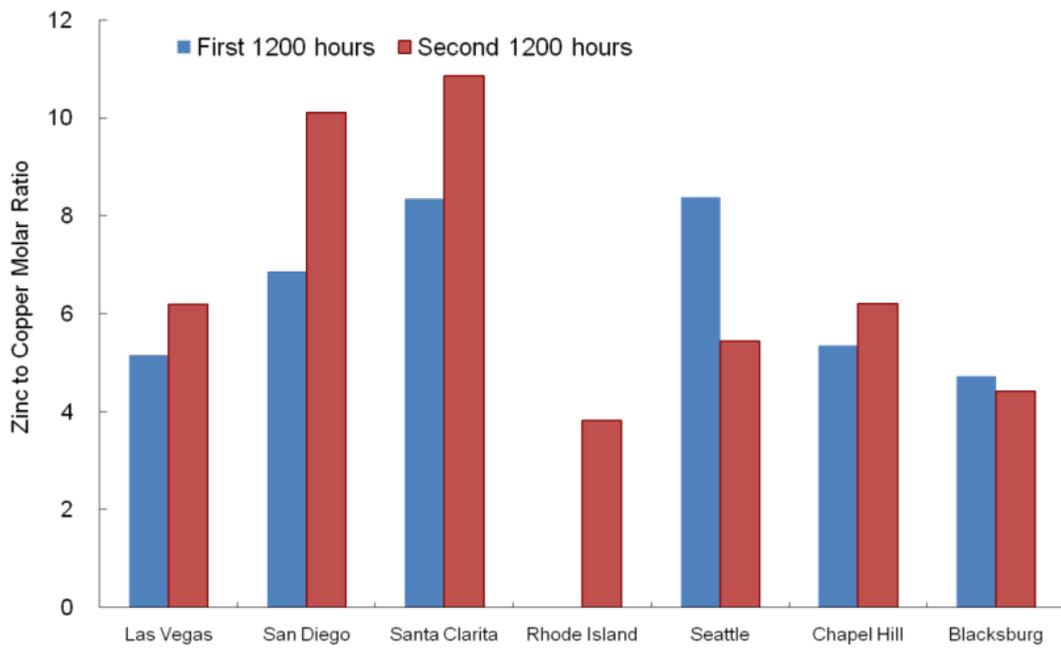


Figure 2. Zinc to copper molar ratio for different waters, averaged over the indicated time periods.

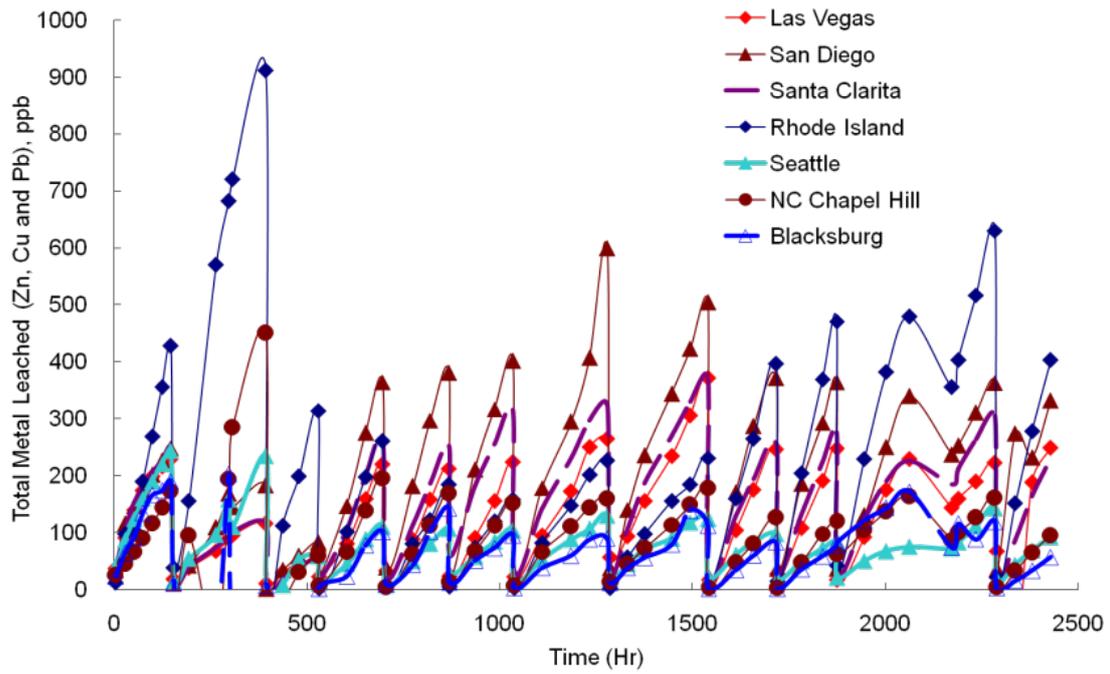


Figure 3. Total Metal leached with time

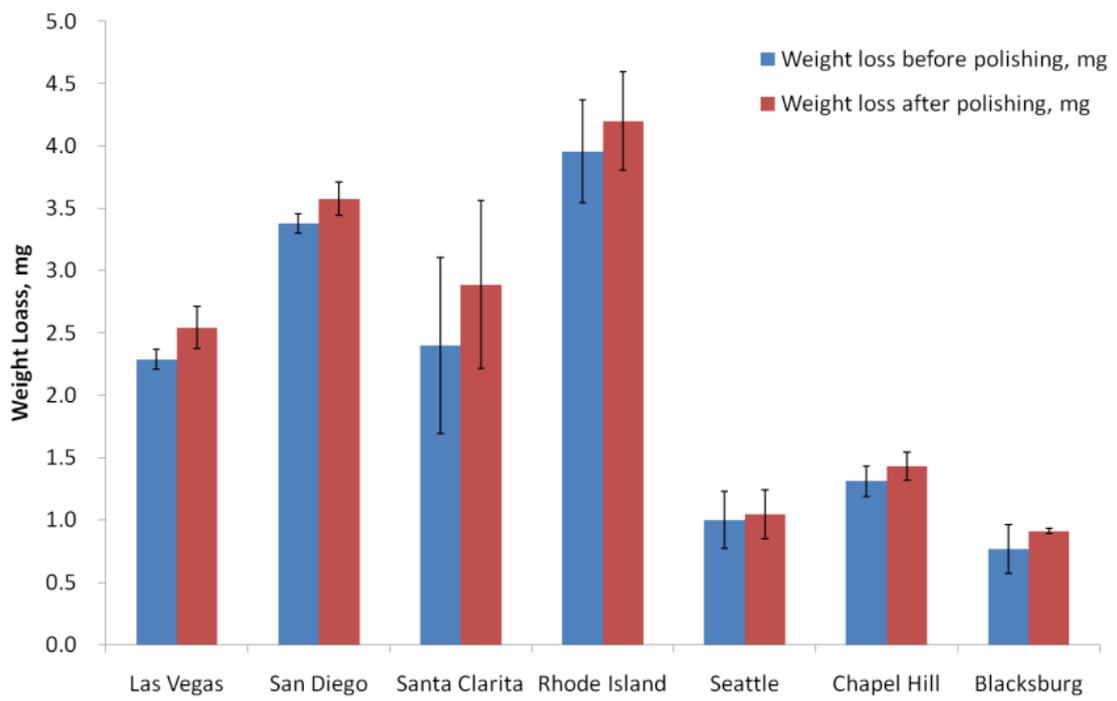


Figure 4. Weight loss of brass in different waters

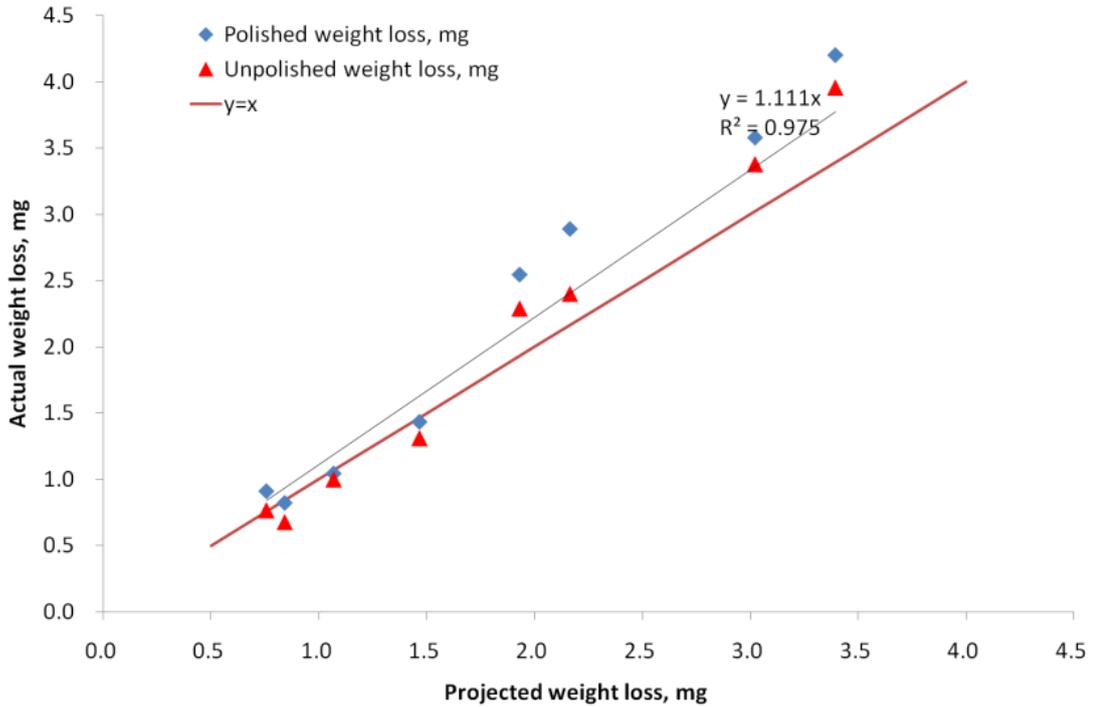


Figure 5. Correlation between actual weight loss and total metal leached for different waters

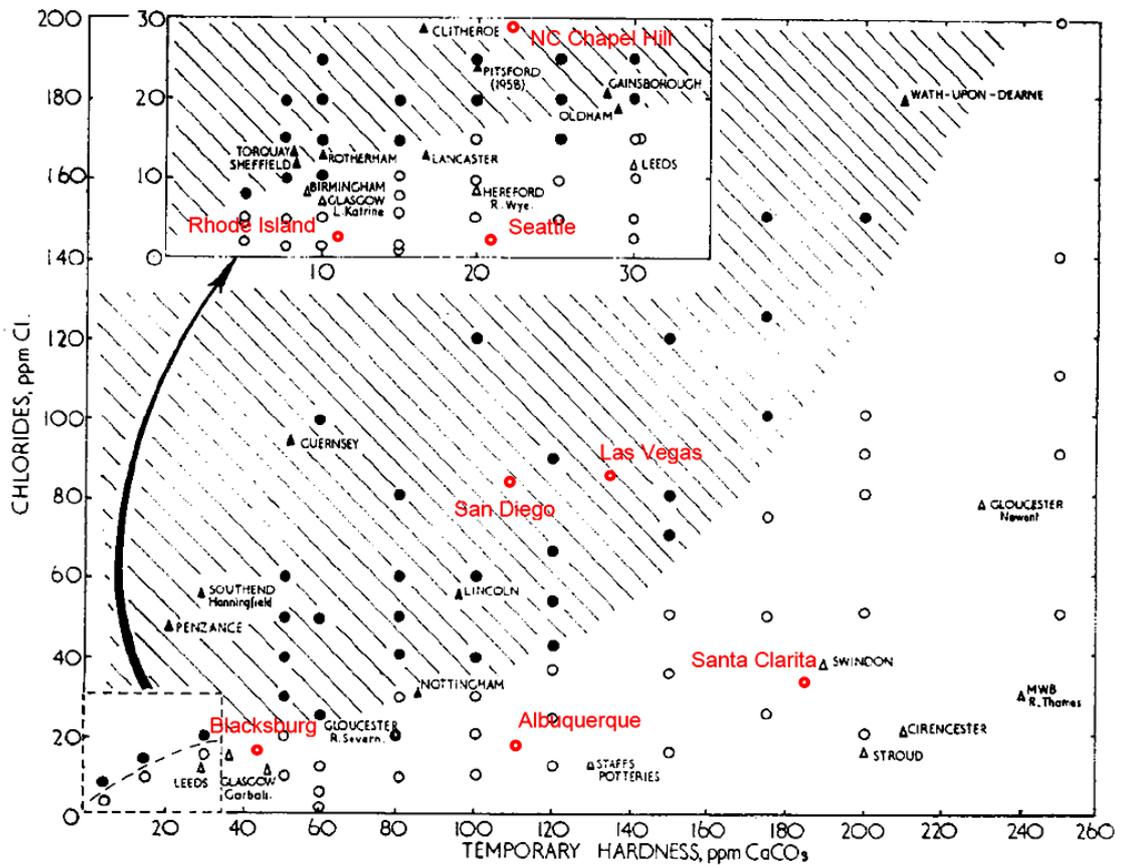


Figure 6. Studied water on the Turner Diagram

Table 1. Summary of waters tested.

Locations	pH	Disinfectants	Alkalinity	Hardness	Zn	Chloride	Known
Unit		mg/L	mg/L as CaCO ₃	mg/L as CaCO ₃	ppb	ppm	Dezincification*
Las Vegas	7.74	0.62 chlorine	130	260	202	87.7	Yes
San Diego	8.1	2.23 chloramine	107	207	3.2	89.9	No
Santa Clarita	8	3.5 chloramine	185	246	3.7	36.6	No
Rhode Island	6.82	0	13.2	14	31	2.8	Yes
Seattle	8.3	1.0 chlorine	20.8	23	3.6	3.4	Yes
NC Chapel Hill	7.59	2.9 chloramine	25.2	32	20	28.8	Yes
Blacksburg	7.39	1.65 chloramine	42	51	182	16.9	No
Albuquerque	7.8	0.9 chlorine	112	105	4.8	20.0	No

*Based on reports of failure

Table 2. Detailed Water Chemistry Data for Test Water

	pH	[Na]	[Mg]	[SiO ₂]	[PO ₄ ³⁻]	[SO ₄ ²⁻]	[Cl ⁻]	[K]	[Ca]	[Cu]	[Zn]
		ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm
Las Vegas	7.74	80	23	7	182	252	85	4	64	47	185
San Diego	8.1	76	21	7	1	180	89	4	48	1	2
Santa Clarita	8	54	17	24	55	160	35	2	70	1	5
Rhode Island	6.82	3	1	9	0	3	3	1	4	135	29
Seattle	8.3	1	0	4	13	1	3	0	8	3	3
Chapel Hill	7.59	29	3	2	957	33	29	4	8	72	18
Blacksburg	7.39	8	5	6	650	7	19	2	11	7	172
Albuquerque	7.8	34	2	23	0	37	55	2	39	26	7

Chapter 5 Effect of Alloy and Water Chemistry on Lead Leaching from Brass

Abstract

Higher chloride and lower alkalinity increase dezincification and lead leaching from brass, whereas addition of 1.4 mg/L of orthophosphate as PO_4 effectively inhibited lead leaching. Silicate inhibitor at 40 mg/L greatly reduced lead leaching over a short time; while after 100 days, there were little benefits. Considering a wide range of alloy composition, lead leaching from brass tends to decrease with zinc leaching (zinc content). When a wide range of water chemistries for the same alloy composition is considered, lead leaching from brass instead increases with zinc leaching (zinc content). The mechanisms behind these observations are not clear yet and need future studies.

Keywords: brass dezincification; lead leaching; zinc leaching; correlation

Introduction

Brass components are widely used in drinking water distribution systems as valves, faucets and other fixtures because of their excellent machinability, good resistance to bio-film growth, and good corrosion resistance (Kumar, et al. 2007) (Abbas 1991). Lead is often added to brass to increase machinability and reduce the corrosion of other metals in the alloy (Showman 1994) (OECD 1994). Leaded brasses and bronzes are still routinely installed in potable water systems in buildings although lead free brass (<0.25%) is sometimes available (Sandvig, et al. 2009). Leaded brass is an important source of lead in potable water (D. Kimbrough 2001) (D. E. Kimbrough 2007) (Schock and Neff 1988) (Gardels and Sorg 1989) (Lee, Becker and Collins 1989) (Samuels and Meranger 1984) even in new construction (Nguyen, et al. 2009). Lead can be preferentially leached from brass (Paige and Covino 1992) (Korshin, Ferguson and Lancaster 2000).

There is some evidence that for a given alloy, persistent lead leaching is sometimes linked to waters prone to dezincification corrosion (Maynard, Mast and Kwan 2008) (R. J. Oliphant 2007) (Triantafyllidou and Edwards 2007) (D. E. Kimbrough 2007). Dezincification can create brass devices with a reddish copper

hue, a porous/fragile structure that is prone to failure, or with an internal coating of voluminous corrosion products that can block water flow through the device.

Lead is not uniformly distributed throughout the copper and zinc alloy, but it is instead present in concentrated “islands” (CDA 2005). Maynard et al. (Maynard, Mast and Kwan 2008) speculated that the loss of zinc allows lead in the alloy to detach and diffuse more rapidly from the brass surface into solution. There has been little research on the relative leaching of lead as a function of the zinc content of the alloy, and this work is aimed at better understanding the relationship between dezincification corrosion, elevated lead leaching from brass, and water chemistry.

Materials and Methods

Effects of Alloy Composition

Seven different types of brass alloy (Table 5 - 1 Alloy A to G, also see Chapter 3) fittings were machined into rings or half rings of ~~weight~~ ^{weight}gram. The composition of brass was measured by Innov-X ALPHA X-ray fluorescence (XRF). The brass samples were exposed in triplicate to water using PVC holders in two-liter Nalgene HDPE jars (See Chapter 3). Waters were shipped from communities known to have dezincification failures for testing (Table 5 - 2, real water).

All jars were kept at room temperature ($22^{\circ} \pm 2^{\circ} \text{C}$) without stirring. Chlorine was added to a level of 1.1 mg/L with sodium hypochlorite (NaOCl). The value of pH was adjusted to and maintained at $\text{pH } 7.80 \pm 0.2$ units with small amounts of nitric acid (HNO_3) to lower pH or sodium hydroxide (NaOH) to raise pH. Chlorine levels and pH were readjusted to target values every other day. The experiments continued for over 2700 hours. The first 750 hours were run without any water change for conditioning. Thereafter, water was changed completely every week. Between water changes, the released metals built up in the water and were highest immediately before a water change. For simplicity in presenting trends, only the metal concentrations before water changes are plotted after the first 750 hours for each type of brass. Metal concentrations leached to the water from the brass rings were analyzed by Thermo Electron

X-Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) per Standard Method 3125-B (APHA 1998).

Before the experiments, each cut brass ring was lightly sanded and washed 3 times with pure water. After drying in the desiccator for two hours, each brass ring was precisely weighed with ± 0.1 mg accuracy. After the experiment, the rings were dried and weighed again, both before and after a light polishing step using a Dremel tool equipped with a soft cloth polishing pad. Our experiments and experience have demonstrated that this polishing pad removes loose scale and rust on the brass ring, but does not remove intact metal. “Weight loss” is determined by difference between the initial and final weight of the sample.

Data from Prior Research

The relationship between lead and zinc leaching was examined using data collected during prior research published elsewhere (Lytle and Schock 1996) (Triantafyllidou and Edwards 2007) (Maynard, Mast and Kwan 2008). In most of those efforts, data on lead release were the focus of the work, but data collected by the authors on zinc release were collected and not examined in detail.

Effects of Water Chemistry Study

In this phase of work cylindrical brass samples (Table 5 - 1, free cutting brass C36000) were connected to copper pipes (See Chapter 3). The copper pipes were filled with tap waters synthesized to examine specific aspects of water chemistry on brass corrosion (Table 5 - 2, 3, synthetic water and its alterations). The water in the pipes was changed with a dump and fill protocol three times a week. The pH of the water was adjusted using 0.01 M nitric acid and 0.01 M sodium hydroxide and the final nitrate concentration was less than 0.6 mg/L. Galvanic currents flowing between copper and brass were measured 30 minutes before and after every water change using a Fluke 189 True RMS Multimeter.

Results and Discussion

Different Brasses Exposed to the Same Water

A 2700 hour experiment was conducted using a water shipped from Las Vegas which is known to cause dezincification corrosion failures. Lead leaching decreased rapidly with initial exposure, and then eventually stabilized after about the fourth water change (Figure 5 - 1). Alpha brass C and DZR G were shown to be most resistant to dezincification (See Chapter 3), but they also leached the most lead.

Thus, for a range of alloys, lead leaching was not exacerbated by dezincification or higher zinc content, but was inversely related to zinc leaching and zinc content (Figure 5 - 2). To examine whether the inverse relationship is simply due to higher lead content in the alloy, and normalize for different lead content in the brasses, a “Lead Leaching Index” is defined:

$$\text{Lead Leaching Index} = \frac{[Pb/(Zn + Cu + Pb)]_{\text{leached into the water}}}{Pb \text{ percentage in the alloy}}$$

Zinc, copper and lead leached to the water are measured in ppb and the denominator is lead content in percent weight in the alloy. If the Lead Leaching Index is larger than 1, lead is selectively released versus other metals in the alloy, and the greater the magnitude of the index the more preferential lead leaching is (See Chapter 3 for Dezincification Index). The inverse relationship between lead leaching and zinc leaching was still valid after normalizing for lead content (Figure 5 - 3). It appears that dezincification resistant (DZR) brass and red brass have higher propensity to leach lead than did yellow (high zinc) brass in this particular water. Lead leaching is also inversely related to brass weight loss (Figure 5 - 4). Surprisingly, use of brasses that minimize dezincification problems might increase lead leaching.

Revisiting Prior Research Data

The inverse relationship between lead leaching and zinc leaching was also confirmed by re-analysis of data from prior research. Lytle and Shock (1996) exposed six different brasses to variations of Cincinnati, OH tap water for about 150 days. Metal leaching is calculated by averaging over time and over different water chemistries. This analysis indicates that lead leaching is inversely related

to zinc leaching (Figure 5 - 5). However, under the conditions in the Schock study, the amount of metal leached can also be correlated with the corresponding lead content in the alloy (Figure 5 - 6). In particular, lead leaching increases with increasing lead percentage ($R^2 = 0.987$).

Triantafyllidou (2007) examined four brasses with lead content ranging from 0.25 to 5% using the NSF 61 Section 9 protocol. Lead leaching was again inversely correlated (roughly) with zinc leaching (Figure 5 - 7).

Maynard incorporated six new faucets and six meters of a variety of ages in automatic rigs to simulate daily household use over a one-year time frame (Maynard, Mast and Kwan 2008). Lead leaching was negatively correlated with Zn:Cu ratio in the alloy, generally being consistent with results presented herein (Figure 5 - 8). Maynard further discussed a correlation between Pb leaching and lead content in the brass. The relationship, however, is largely based on the high lead content in one sample. Comparatively, the correlation with Zn:Cu is stronger, incorporating all the brass samples.

To summarize, in several studies, lead leaching from a variety of brasses were almost always negatively correlated with zinc leaching or zinc content. The mechanism behind these observations is believed to be related with galvanic interactions between zinc, lead, and copper in brass, but the exact explanation requires future studies.

The Same Brass Exposed to Different Waters

To explore the relationship between lead leaching and zinc leaching in a range of waters, C36000 free cutting brass samples were exposed to fifteen different waters (Table 5 - 2, 3, synthetic water and its alterations) for 150 days. Lead leaching generally stabilized after about 60 days (Figure 5 - 9). Confirming findings of previous studies (Edwards and Triantafyllidou 2007) (Y. Zhang, et al. 2009) (Zhang, Griffin and Edwards 2008) (Zhang, Griffin and Edwards 2008) (Lytle, Schock and Sorg 1996), higher chloride and lower alkalinity increased lead leaching from brass components. On the contrary, adding orthophosphate and silicate as corrosion inhibitors reduce lead released. However, the lead leaching values picked up after about 100 days into this experiment for the silicate conditions. When error bars are accounted, the long term effects of silicate are slightly ambiguous in that dosing silicate no longer makes a

noticeable difference compared to the control.

Zinc orthophosphate significantly reduced lead concentrations in the tap water of a new building (Lytle, Schock and Sorg 1996). Zinc, however, does not play an important role in corrosion control based on data in this work (Figure 5 - 9) and (Schneider, et al. 2007). Although the lack of benefits for zinc may be limited to certain brass types and water compositions, there does not appear to be any basis for adding zinc to reduce brass corrosion.

Dosing orthophosphate alone at 1.4 mg/L effectively inhibited lead leaching over the duration of this study (Figure 5 - 9). The inhibitive effect, however, is very sensitive to the orthophosphate concentrations. Dosing 0.5 and 1 mg/L of orthophosphate significantly reduced lead leaching in the first 60 days. But their comparative benefits gradually disappeared as the lead leaching from the control condition dropped (Figure 5 - 10). Overall, orthophosphate proved to be an effective lead leaching inhibitor, if a proper concentration is dosed.

Surprisingly, when different waters were considered, the relationship between lead leaching and zinc leaching somewhat reversed (Figure 5 - 11). Lead leaching data in Figure 5 - 11 were averaged over 150 days, and plotted versus copper and zinc values that were collected at the same time. Lead leaching appeared to increase with zinc leaching. For the same alloy, a corrosive water was corrosive to both zinc and lead indiscriminately; while a non-corrosive water protected both zinc and lead.

The same results were shown by synthesizing Lytle and Shock's results (1996). Lytle and Schock investigated the effects of pH and orthophosphate by comparing metal leaching in five waters across 6 brasses (Figure 5 - 12). The five conditions were Cincinnati tap water at pH 7, pH 7.5, pH 8.5, pH 7.5 with 0.5 mg/L of orthophosphate as P, and pH 7.5 with 3 mg/L of orthophosphate as P. Lead leaching and zinc leaching were averaged over time first, and then averaged across brasses or waters accordingly. Considering every brass along the lines, lead leaching increased with increasing zinc leaching.

The exact mechanism is still unclear at this point. Isolate lead "island" may be bundled together with zinc in the alloy and detached as the zinc phase is dissolved. Or as Maynard speculated, the porous surface left by zinc leaching may allow lead in the alloy to dissolve and diffuse more rapidly from the brass

surface into solution (Maynard, Mast and Kwan 2008). However, the observation that lead leaching is sometimes linked to waters prone to dezincification corrosion in practice may be explained by this correlation. Although a high zinc brass by nature tends to leach less lead (Figure 5 - 3, 5, 7, 8), the effect of an extremely corrosive water may overshadow the benefits and eventually dissolve more lead. The amount of lead leached must be determined by both mechanisms – water chemistries and metallurgical compositions – at the same time. However, a detailed clarification will need future studies.

Conclusion and Summary

Lead and zinc leaching from a range of brasses were negatively correlated. The mechanism behind this observation is not clear yet and needs future studies. But as a result DZR and red brasses release more lead to water, and a greater percentage of lead in the alloy to water.

Lead leaching is also found to be greatly influenced by water compositions. Higher chloride and lower alkalinity increase lead leaching. Orthophosphate at 1.4 mg/L decreases lead leaching, but the inhibitive effects are very sensitive to phosphate dosages. Initially, dosing 40 mg/L of silicate also inhibited lead leaching, but the inhibitive effect of silicate diminished after 100 days of experiment. Adding 200 ppb of zinc slightly increased the lead concentrations in the water. Zinc does not seem to play a significant role in mitigating either dezincification or lead leaching from brass alloys.

When different water and the same alloy are considered, lead leaching was found to increase with higher zinc leaching. This result may help explain why some lead leaching cases were related with dezincification in practice. Overall, there is a complex interplay between water chemistry and metallurgical composition that determines lead leaching to water.

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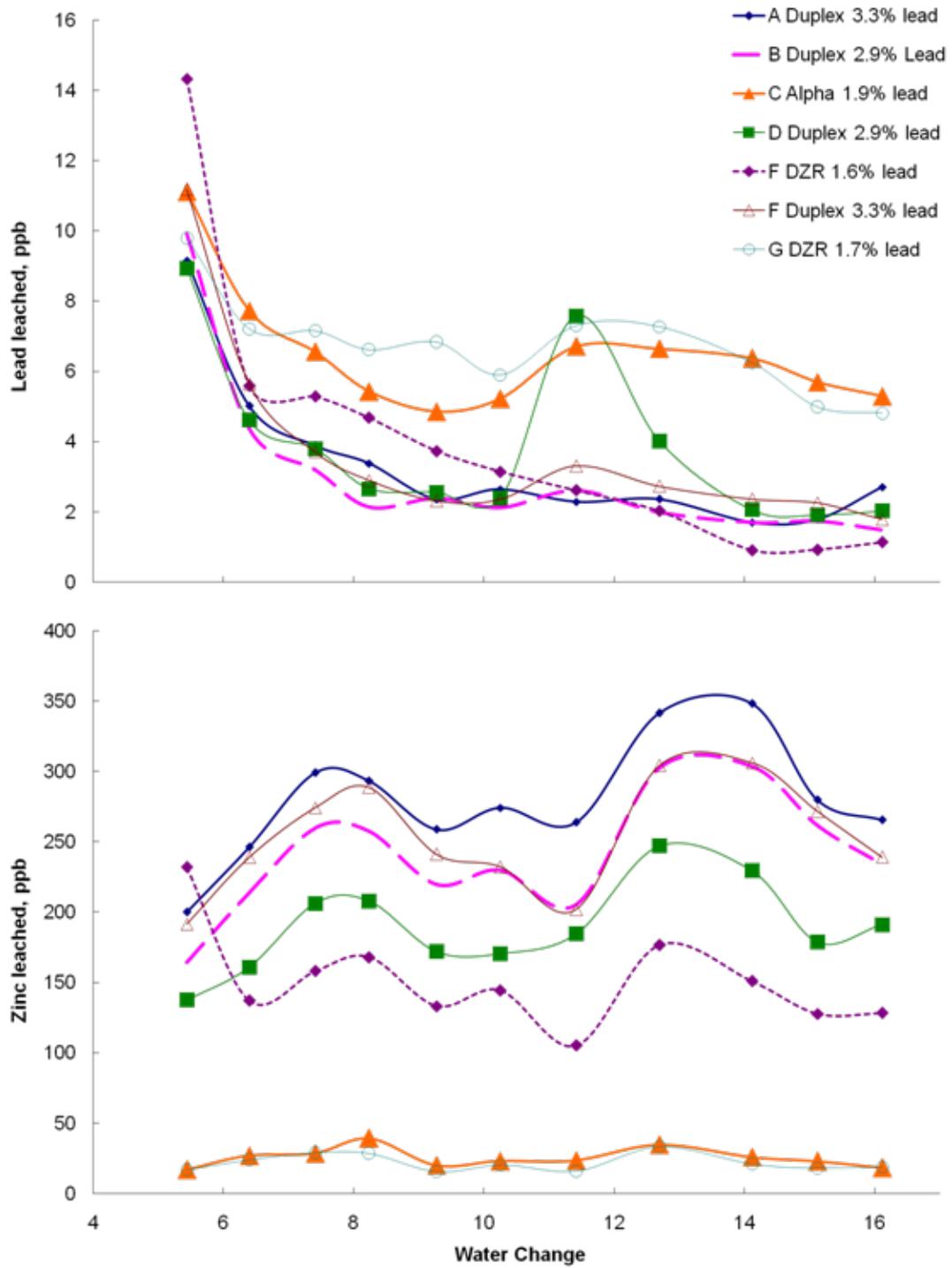


Figure 5 – 1 Lead and zinc leached to the water before each weekly water change

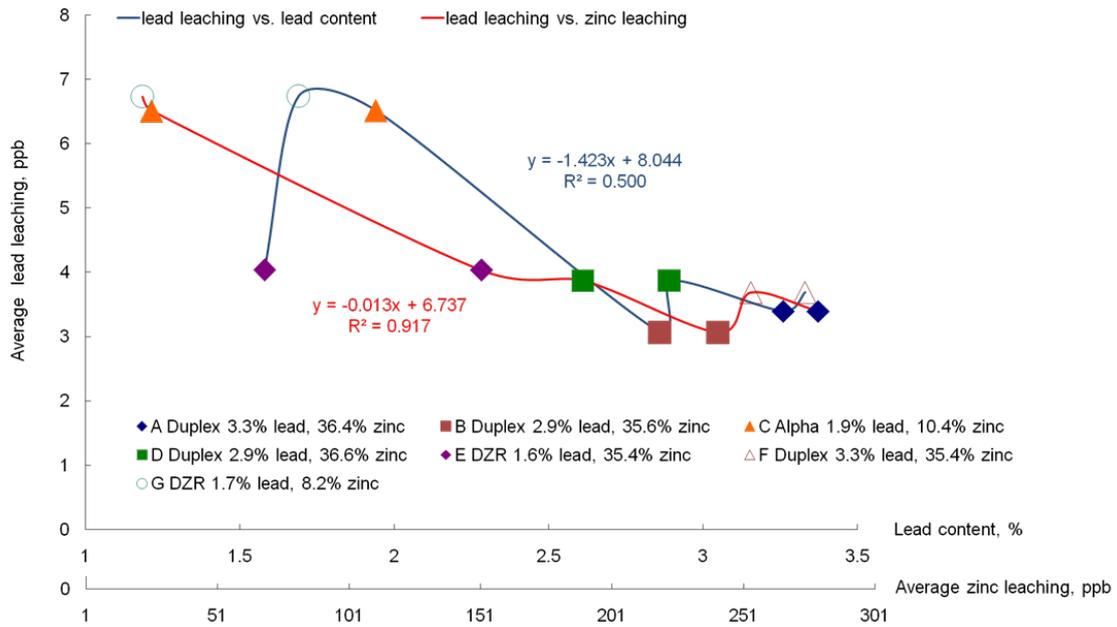


Figure 5 - 2 Lead leaching versus zinc leaching, and lead content

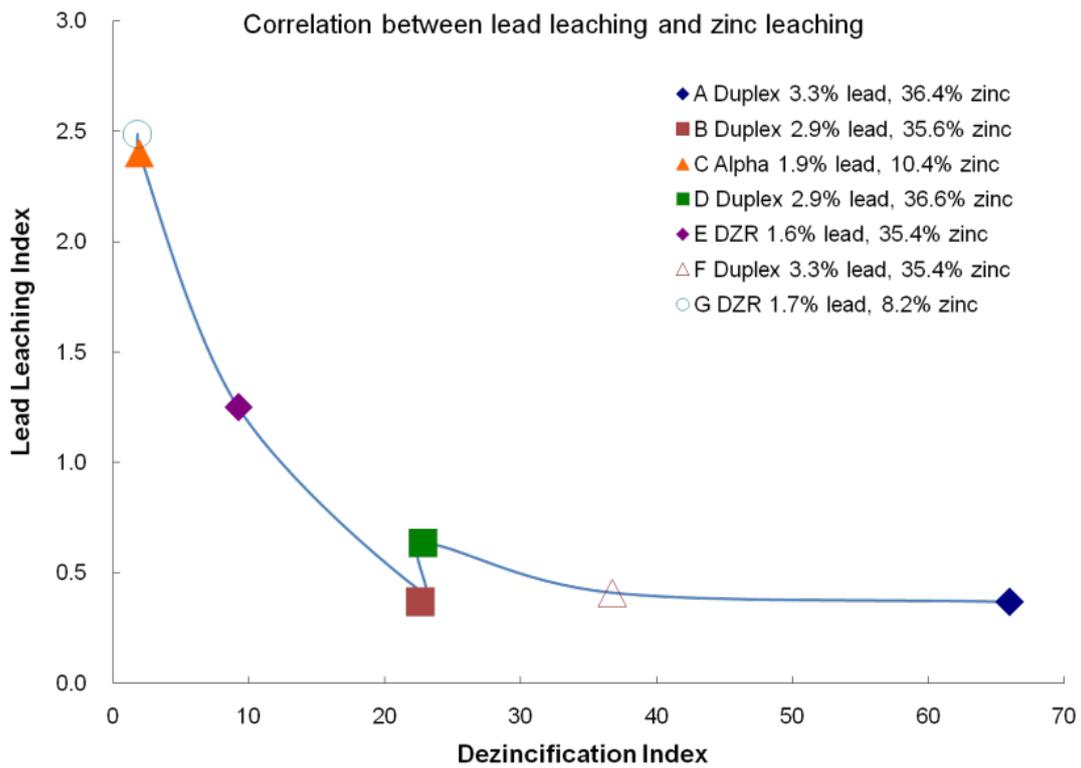


Figure 5 - 3 Correlation between Dezincification Index and Lead Leaching Index

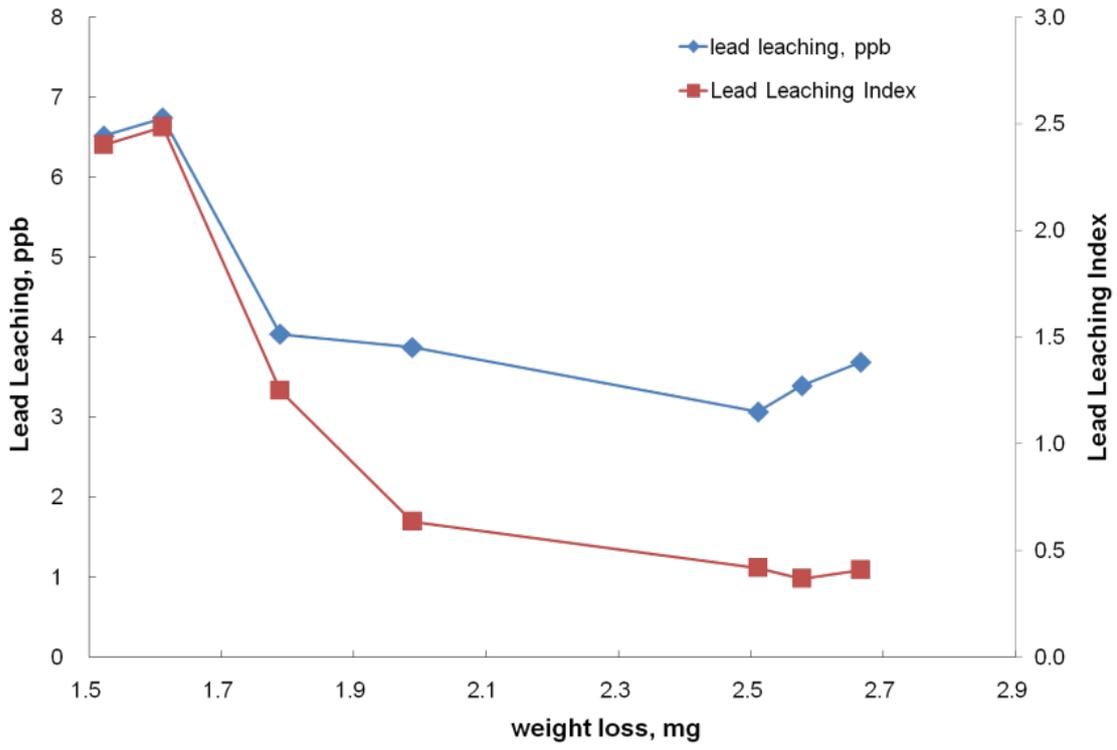


Figure 5 – 4 Correlation between lead leaching and weight loss

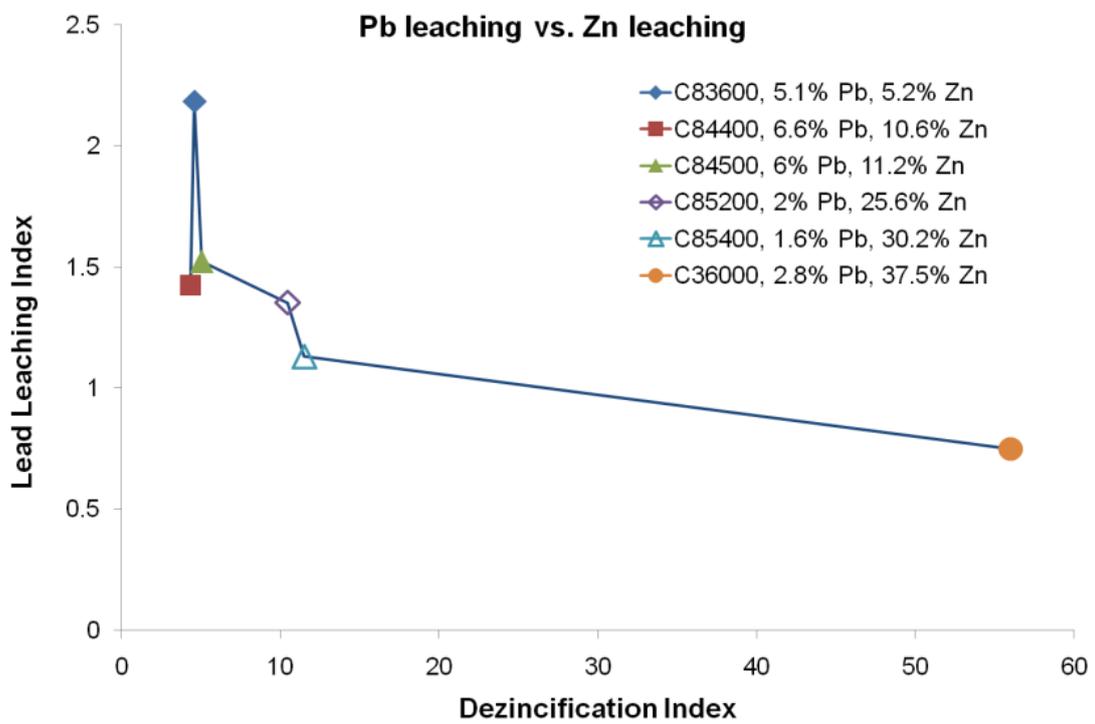


Figure 5 – 5 Correlation between lead leaching and zinc leaching (Lytle and Shock's study)

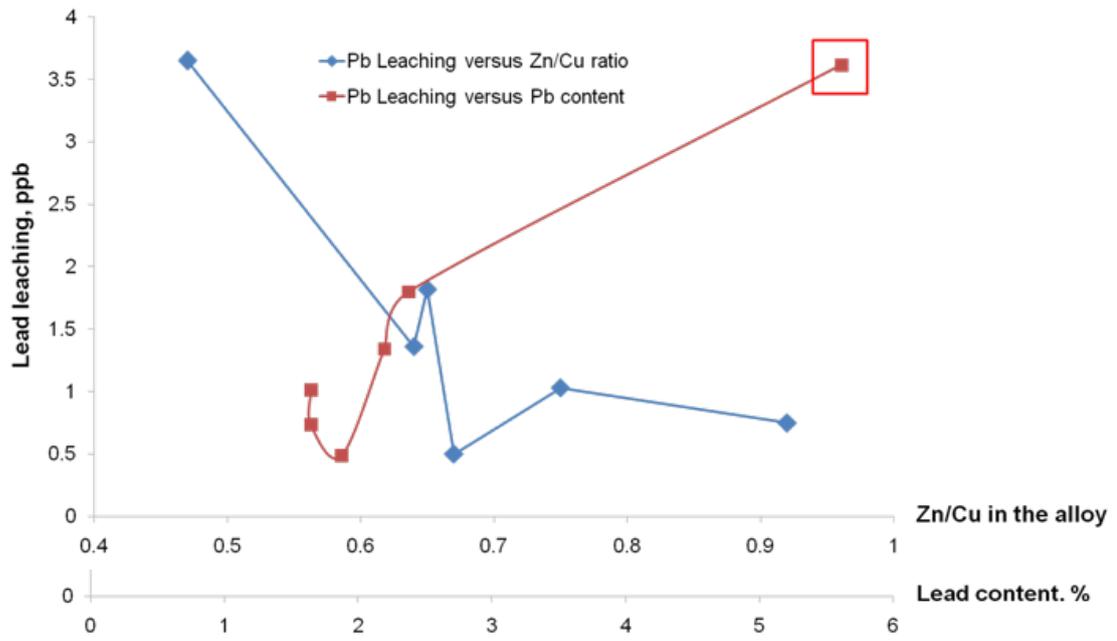


Figure 5 – 8 Correlation between lead leaching and lead content (Maynard's study)

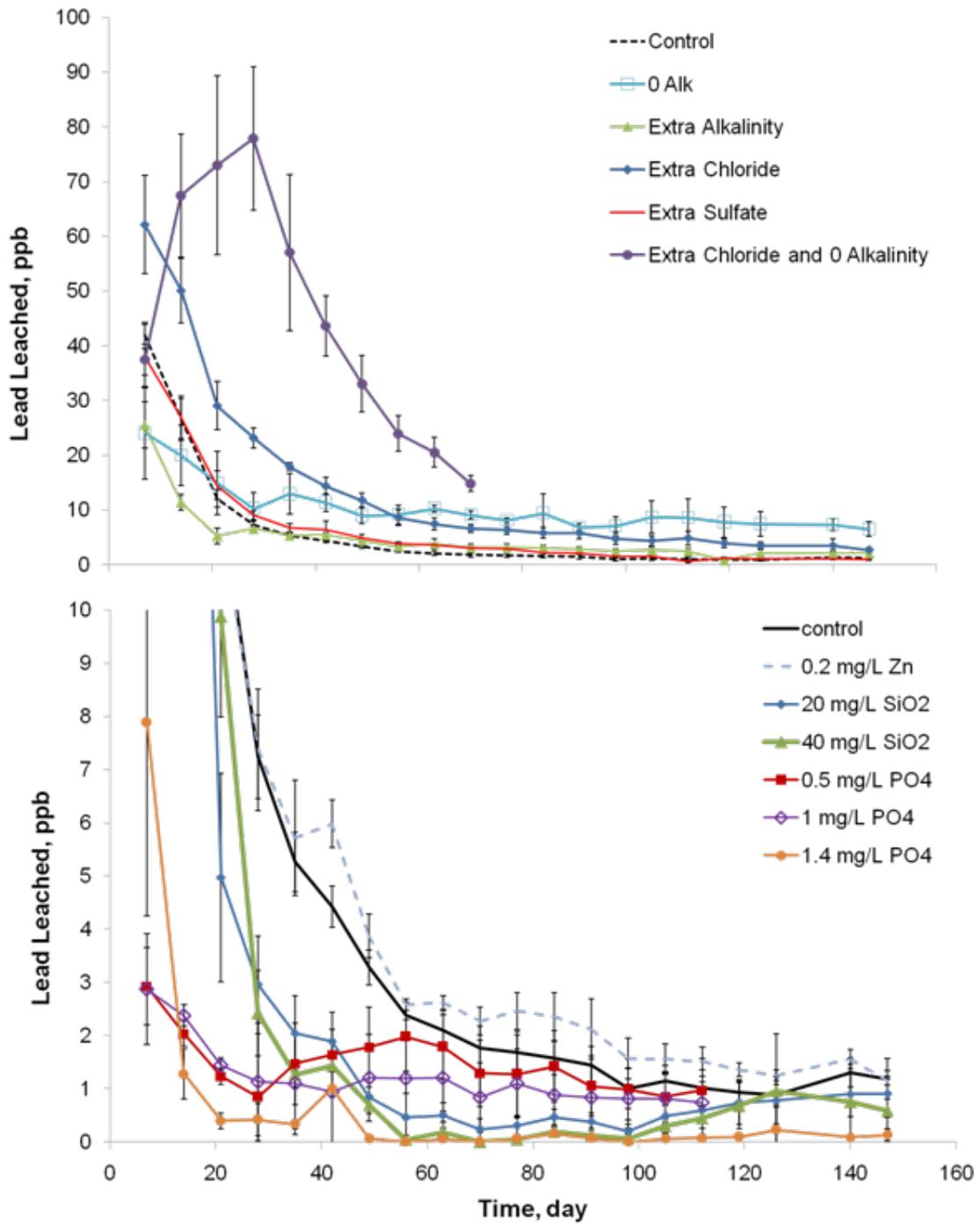


Figure 5 – 9 The effects of water chemistries parameters over lead leaching (Top: chloride, sulfate and alkalinity; bottom: orthophosphate, zinc and silicate) (Error bars represent 95% confidence intervals)

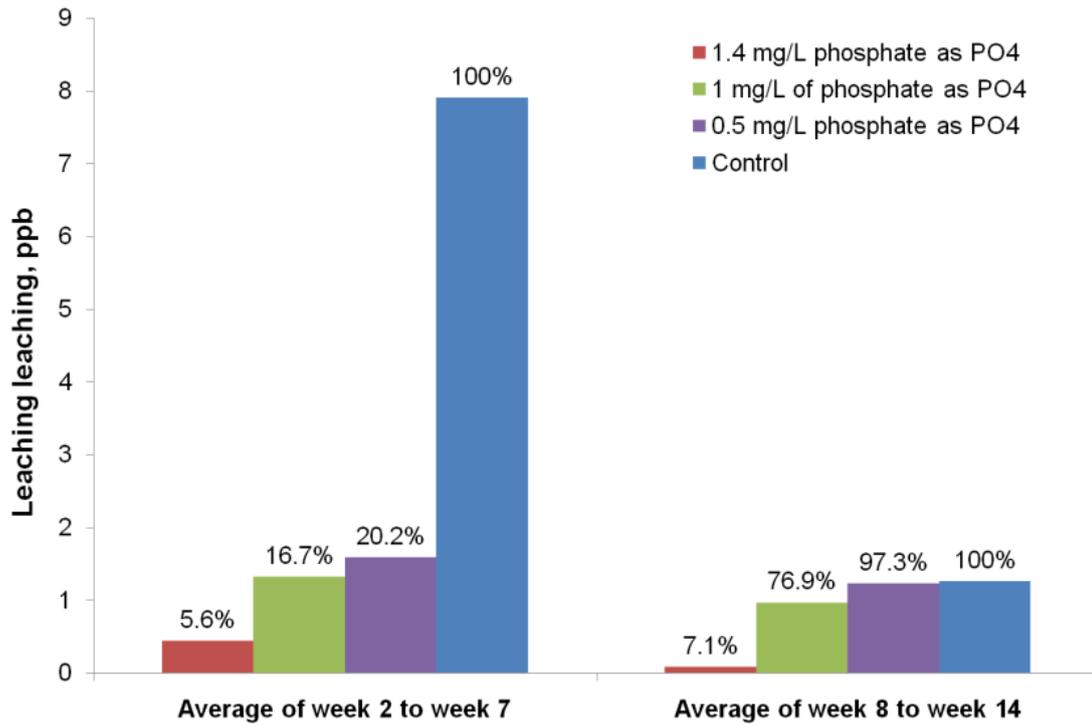


Figure 5 – 10 The inhibitive effects of orthophosphate

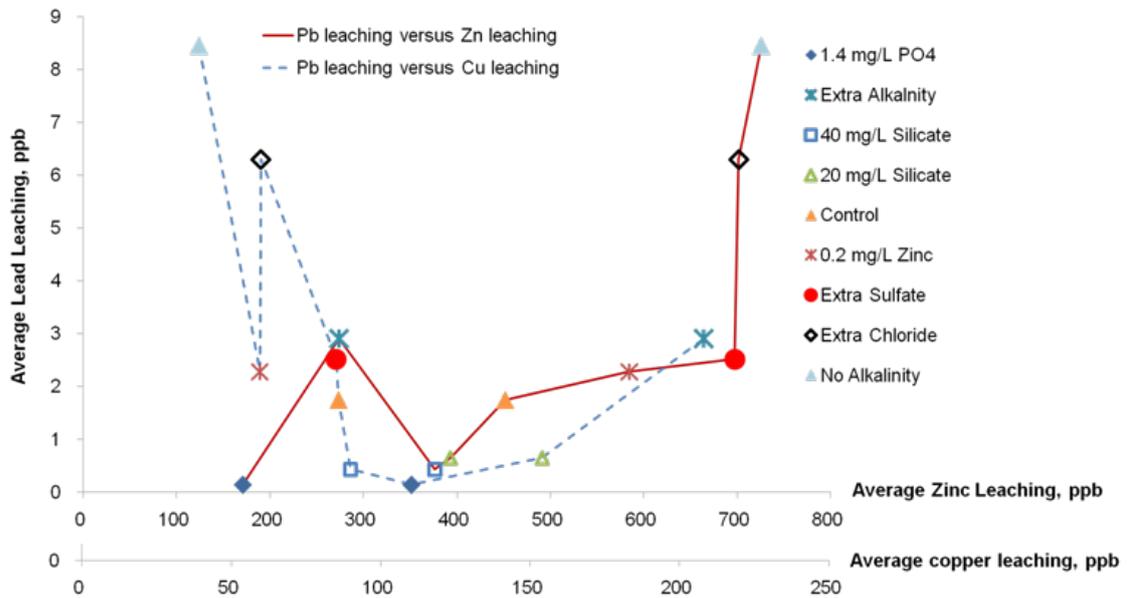


Figure 5 – 11 Lead leaching versus zinc leaching and copper leaching (All waters are adjusted to pH 8.3)

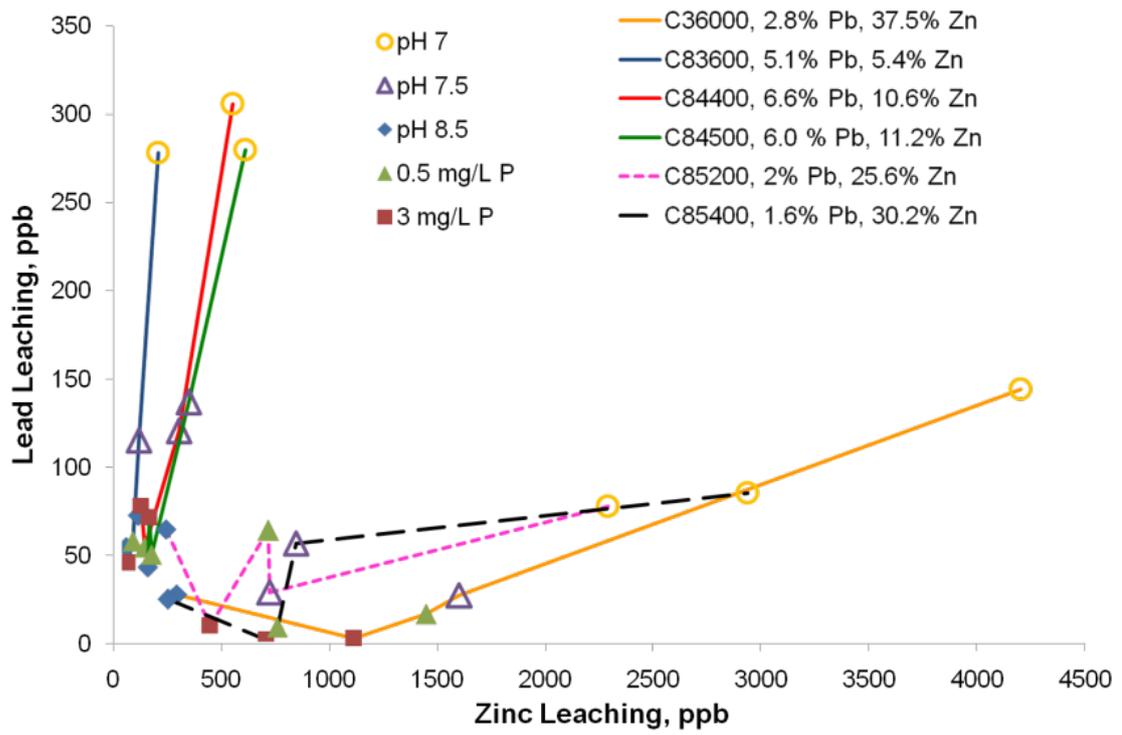


Figure 5 - 12 The Correlation between lead leaching and zinc leaching (Lytle and Shock's study)

Table 5 – 1 Composition of brass samples

	A	B	C	D	E	F	G	C36000
Brass Type	Duplex	Duplex	Alpha	Duplex	DZR	Duplex	DZR	Free Cutting
Zn Content, %	36.4	35.6	10.37	36.55	35.37	35.38	8.2	37.6
Cu Content, %	59.2	61.2	87.62	60.15	62.5	60.92	89.3	60.5
Pb Content, %	3.26	2.86	1.94	2.89	1.58	3.33	1.69	2.73
Sn Content, %	1.2	0.1	ND*	0.1	0.1	0.1	0.3	0.16
Ni Content, %	0.4	0.1	ND	0.1	0.1	0.1	0.5	ND
Fe Content, %	0.6	0.1	ND	0.1	0.1	0.1	0.1	ND

Table 5 – 2 Composition of test water

	pH	Alkalinity as CaCO ₃ , mg/L	[Ca ²⁺] ppm	[Mg ²⁺] ppm	[Na ⁺] ppm	[K ⁺] ppm	[Zn ²⁺] ppb	[Cl ⁻] ppm	[SO ₄ ²⁻] ppm	[PO ₄ ³⁻] ppb	[SiO ₂] ppm
Real Water*	8	119	75	25.6	93	4.8	191	96	252	147	7.6
Synthetic water	8.3	40	31	20	30	2	0	121	34	0	0

* This water was known to cause serious dezincification failures with brass A

Table 5 – 3 Alterations to synthetic water (all waters are adjusted to pH 8.3)

Type of tests	Modification to Water(Duration of running time)
Synthetic water control	pH(21 weeks)
The effects of Chloride	Added 270 mg/L chloride as Cl ⁻ using NaCl (21 weeks)
The effects of Sulfate	Added 150 mg/L sulfate as SO ₄ ²⁻ using Na ₂ SO ₄ (21 weeks)
The effects of Zinc ion	Added 0.2 mg/L as Zinc as Zn ²⁺ using ZnSO ₄ (21 weeks)
	Added 0.4 mg/L as Zinc as Zn ²⁺ using ZnSO ₄ (17 weeks)
	Added 0.6 mg/L as Zinc as Zn ²⁺ using ZnSO ₄ (17 weeks)
The effects of Phosphate	Added 0.5 mg/L Ortho-P as PO ₄ ³⁻ using Na ₃ PO ₄ (17 weeks)
	Added 1 mg/L Ortho-P as PO ₄ ³⁻ using Na ₃ PO ₄ (17 weeks)
	Added 1.4 mg/L Ortho-P as PO ₄ ³⁻ using Na ₃ PO ₄ (21 weeks)
The effects of Silicate	Added 20 mg/L Silicate as SiO ₂ using Na ₂ SiO ₃ (21 weeks)
	Added 40 mg/L Silicate as SiO ₂ using Na ₂ SiO ₃ (21 weeks)
The effects of Hardness	Added 0 mg/L Hardness as CaCO ₃ using CaCl ₂ (7 weeks)
	Added 300 mg/L Hardness as CaCO ₃ using CaCl ₂ (7 weeks)
The effects of Alkalinity	Added 0 mg/L Alkalinity as CaCO ₃ using NaHCO ₃ (21 weeks)
	Added 150 mg/L Alkalinity as CaCO ₃ NaHCO ₃ (21 weeks)