Review of Brass Dezincification Corrosion in Potable Water Systems

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ABSTRACT

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

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1. INTRODUCTION

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

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

When outbreaks of dezincification failures occur in a locality, there is widespread confusion amongst all stakeholders (homeowners, water utilities, contractors, etc.) as to the factors contributing to dezincification failures, terminology, and possible remedial strategies. This paper provides an overview of existing understanding of dezincification in potable water systems and summarizes key research results, which generally pertain to the brass alloy itself and water chemistry. Additionally, hypotheses are developed regarding underappreciated physical factors associated with modern plumbing practice, which have not been specifically researched to any great extent. Finally, means for avoiding dezincification are reviewed and discussed, and arguments are made for more stringent plumbing codes associated with use of brass alloys in potable water systems and development of standard test methods for determining dezincification propensity of potable waters.

1.1 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). Plug dezincification can lead to component failures if the affected regions penetrate deep enough within the metal to compromise mechanical integrity. Dezincification can also attack brass surfaces more uniformly, in which case it is referred to as "layer" dezincification. This tends to result in shallow regions of porous copper, which also exhibit a characteristic uniform red color. Layer dezincification can contribute to brass fitting fragility and increase the likelihood of fracture under mechanical stress.

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

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; Figure 2). Meringue is a characteristic white, voluminous and tenacious deposit that is visually reminiscent of a meringue dessert topping. It tends to form when pH is relatively high (above about pH 8.3) and zinc solubility is low, and is typically a basic zinc carbonate/6/ but may incorporate dissolved constituents of the brass itself or constituents of the system water. Meringue deposition can occur as part of either plug or layer dezincification, and in extreme situations the deposit can completely stop water flow through the brass device and associated plumbing line.

In addition to component failures and associated water damage, release of minor brass alloy constituents is also possible (Figure 1). Lead is a component in many brasses manufactured for use in potable water and even brass advertised as "lead-free" can legally contain up to 8% lead. The potential for lead release via brass corrosion is increasingly of concern/7/, and the literature suggests a relationship between the occurrence of dezincification and persistent lead leaching in many potable water systems/1, 2, 3, 8/ and in "green" buildings./9/ Unfortunately, relatively little research has been conducted conclusively tying the two phenomena together. Some have hypothesized that lead is present in brass alloys as small "islands", rather than being well mixed into the solid solution of copper and zinc, and that the porous structure produced by dezincfication may allow lead to be released more rapidly than would occur otherwise./10, 11/ Work by Triantafyllidou et al. (2007) demonstrated that lead leaching could increase with time when dezincificaiton was occurring in low alkalinity waters/1/, and this trend was confirmed by Maynard et al.)/10/ The latter study speculated that the porous surface structure produced by dezincification may promote lead release either by enhancing diffusion or allowing lead particulates to detach from the surface.

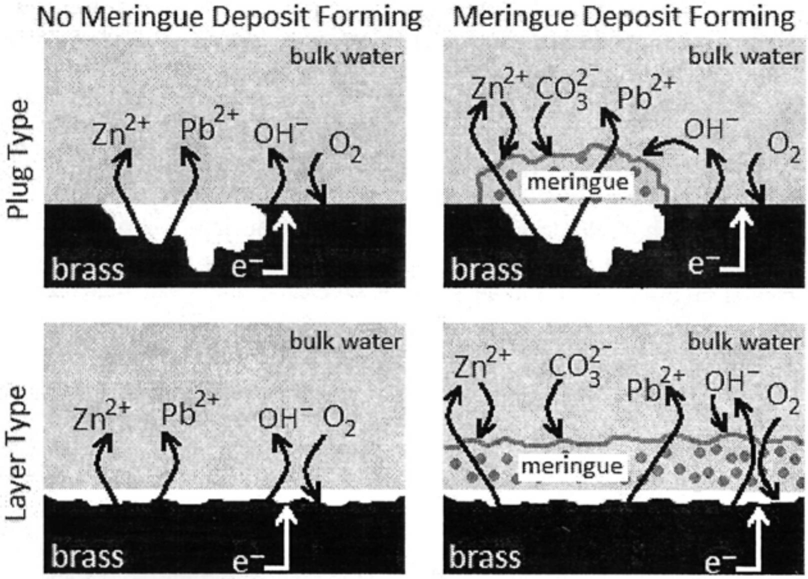


Fig. 1: Dezincification can occur as either the plug (upper left) or layer (lower left) type, either of which may or may not lead to meringue deposition (right). Plug dezincification affects isolated areas of the brass and penetrates into the brass surface, whereas layer dezincification attacks the surface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

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

1.2 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). 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).

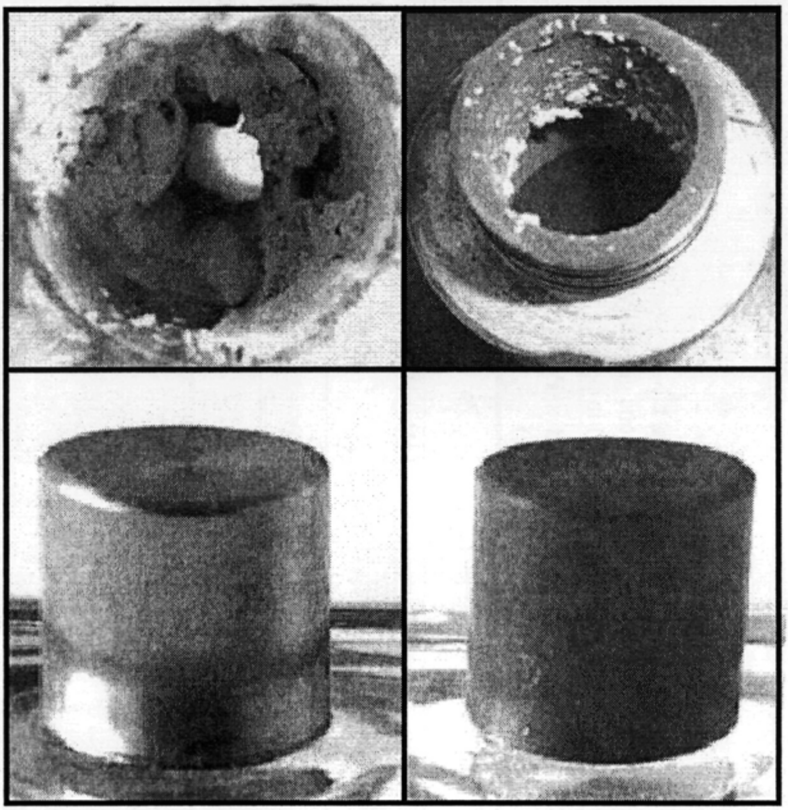


Fig. 2: Meringue build-up inside a brass fitting can effectively block flow (upper left). After several months of plug dezincification, meringue build-up is evident on a brass fitting (upper right). As brass undergoes layer dezincification, its characteristic yellow surface (lower left) turns to a reddish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

Table 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

Dezincification can also occur by a dual mechanism, in which both copper and zinc are oxidized and dissolved from the brass surface. As the soluble copper accumulates in the water near the dezincifying surface and if oxidation-reduction potential is low enough, an equilibrium between the cupric ion in the water and metallic copper is established. In that event, a substantial fraction of the copper that dissolves will re-deposit or "plate" back onto the dezincifying metal surface, and the net material loss is still via leaching of zinc (Table 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 3).

2. 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.

2.1 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.

2.1.1 Zinc Content

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

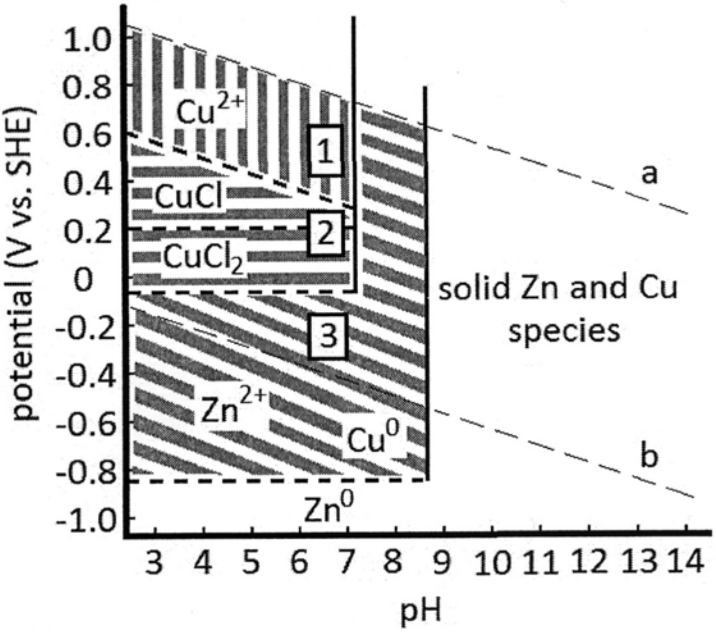


Fig. 3: Illustrative potential-pH diagram for 70-30 brass in 0.1M chloride solution (adapted from Heidersbach & Verink 1972/18/). Region **1** represents uniform brass corrosion via copper and zinc dissolution with no copper re-deposition; **2** represents dezincification via copper and zinc dissolution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

Zinc content is also a key factor in determining the susceptibility of brass to dezincification (Figure 4). Brasses with zinc content below about 15% are generally considered resistant to dezincification/15, 16, 17/; this threshold is based mostly on field experience, but it is rare that brass with less zinc exhibits serious dezincification problems. Brasses with higher zinc contents, including alpha brass with 15-30% zinc and duplex brass (> 30% Zn), can be susceptible to dezincification attack under some circumstances./16/

2.1.2 Effects of Alloy Additives

A substantial amount of effort has been invested in attempting to inhibit dezincification by adding trace constituents directly to the alloy as per a prior review article/16/; a summary of key results is provided in Table 2. While some constituents may render alpha brass (and the alpha phase of duplex brass) relatively immune to dezincification/6, 18, 16/, inhibiting the dezincification propensity of beta brass has proven more difficult./5, 18/ Arsenic and tin are the most common alloy additives, which can profoundly inhibit dezincification of alpha brass even at trace levels, and benefits from these constituents have also been observed for duplex brass./19/

2.1.3 Water chemistry

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

Prior research concluded that that increasing chloride tends to increase dezincification propensity, particularly when hardness or alkalinity of the water is low. Other influential factors have also been identified, including pH, temperature, aeration, disinfectant type and concentration, other anions, and the chemical make-up of surface films or scales. Conclusions as to the role of individual constituents can vary from study to study, most likely because the scope, experimental methods and specifics of exposure have also varied widely. Table 3 summarizes the effects of individual water constituents and/or parameters on brass dezincification reported in the literature.

Table 2
Observed effects of various alloy additives on brass dezincification propensity; partially summarized from Copper Development Association report/16/

Additive	Observed Effect on Dezincification Propensity	Researcher(s)	Source Cited
Arsenic	Inhibits dezincification of 70-30 alpha brass	Bengough and May (1924)	Bengough and May (1924)
	Increases dezincification rate of 60-40 brass at 0.25% As	Sullivan (1971)	CDA (1993)
	Variable results for 70-30 and 60-40 brasses	Lombardi (1954)	CDA (1993)
	Inhibits dezincification	Nothing (1962)	CDA (1993)
	Inhibits dezincification of 70-30 alpha brass up to 0.05% arsenic	Ming and Ruon (1963)	CDA (1993)
	Negligible effects up to 0.014% As; inhibits dezincification of all tested brasses at 0.024% arsenic	Crampton and Burghoff (1941)	CDA (1993)
	Inhibits dezincification of 70-30	Pryer and Giam (1982)	CDA (1993)
	Inhibits dezincification of 60-40 brass with 0.1% As, and navel brass with 0.05% As and 1% Sn	Karpagavalli et al. (2006)	Karpagavalli et al. (2006)
Antimony, Phos-phorous	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)

Table 2 Cont'd:

Tin	Inhibits dezincification for 60-40 brass with 2% Sn, but accelerates dezincification of 60-40 leaded brass	Karpagavalli et al. (2006)	Karpagavalli et al. (2006)
	Inhibit beta brass and deteriorate alpha brass	Desch and Whyte (1913)	CDA (1993)
	Inhibits dezincification of alpha brass	Bengough and May (1924)	Bengough and May (1924)
	Inhibit dezincification of 70-30 alpha brass	Pchelnikov and Marshakov (1986)	CDA (1993)
	Negligible effects for duplex or alpha brass from 1.2 to 3.2% Sn	Weldon (1957)	CDA (1993)
	Inhibits dezincification of 70-30 brass when added with Al	Beccaria (1989)	CDA (1993)
	Optimal dezincification inhibition of 60-40 brass at 1% Sn in sea water	Pai et al. (1987)	CDA (1993)
	Inhibits dezincification of navel brass with 0.5 % Sn and Ni	Sukegawa and Watanabe (1982); Oishi et al. (1982)	CDA (1993)
Silicon	Results in severe susceptibility of 60-30 brass to dezincification at 0.33% Si	Weldon (1957)	CDA (1993)
	Inhibition of dezincification increases with Si content up to 3.7% Si	Staley and Davies (1988)	CDA (1993)
	0.5% Si inhibits dezincification of 60-40 brass, but dezincification proceeds in 70-30 brass	Oishi et al. (1982)	CDA (1993)

Table 2 Cont'd:

Iron, Man-ganese, Nickel, Cobalt	Fe accelerates dezincification of beta brass	Desch and Whyte (1913)	CDA (1993)
	Fe accelerates dezincification of 70-30 brass	Bengough and May (1924)	Bengough and May (1924)
	Fe/Mn and Fe/Ni both result in brass susceptibility to dezincification	Bailey (1960)	CDA (1993)
	0.5% Fe or 0.5% Mn accelerates dezincification of 60-40 and 70-30 brass	Oishi et al. (1982)	CDA (1993)
	0.5-1% Ni inhibits dezincification of 70-30 brass	Bengough and May (1924); Oishi et al. (1982)	Bengough and May (1924); CDA (1993)
Tungsten	Inhibits dezincification of 70-30 brass at 0.5% W	Bengough and May (1924)	Bengough and May (1924)
Lead	Negligible effects	Colegate (1948)	CDA (1993)
	Inhibits dezincification of 70-30 brass	Bengough and May (1924)	
	Inhibits dezincification of 70-30 brass	Desch and Whyte (1913)	CDA (1993)
	Accelerates dezincification of 60-40 brass	Sullivan (1971)	CDA (1993)
	Negligible effects	Heidersbach (1968)	CDA (1993)
Bismuth	Accelerates dezincification of 70-30 and 60-40 brasses	Price and Bailey (1942)	CDA (1993)
	Negligible effects	Staley and Davies (1988)	CDA (1993)
Others	Yttrium accelerates dezincification of 60-40 brass, but inhibits dezincification of arsenical 60-40 brass	Sullivan (1971)	CDA (1993)
	0.1% Mischmetal (rare earth metals) reduced dezincification rate of 60-40 brass	Sullivan (1971)	CDA (1993)
	Gold and silver both inhibit brass dezincification	Kondrashin et al. (1989)	CDA (1993)

Table 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.

Table 3 Cont'd:

Temperature	Lucey, 1973	Meringue	Increased temperature promotes hardness-salt precipitation and increased pH, which both support meringue dezincification.	Experience.
	Simmonds, 1967	Non- meringue; Meringue	Protective scale does not form in cold water, thus dezincification continues unchecked.	Visual observation and experience.
	Nicholas, 1994	Plug; Layer; Meringue	Increased temperature accelerates dezincification.	Corrosion currents equated with general dezincification rates.
	Oliphant & Shock, 1996	Plug; Meringue	Increased temperature accelerates dezincification.	Experience; Literature review.
	Abbas, 1991	Plug; Layer	Increased temperature accelerates dezincification, but not zinc dissolution.	Visual observation; Metal leaching data; Corrosion potential data.
Aeration	Turner, 1965	Meringue	Oxygen is necessary for meringue dezincification.	Visual Observation.
	Kelly, 1980	Non- meringue	Increased oxygen levels (via increased flow velocity) accelerates dezincification.	Corrosion currents were equated with general dezincification rates.

Table 3 Cont'd:

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.

Table 3 Cont'd:

Nitrate	Turner, 1961	Meringue	Nitrate (up to 100 mg/L) has negligible effects on meringue dezincification.	Visual observation.
	Lucey, 1973	Meringue	Nitrate slightly reduces meringue dezincification.	Corrosion currents equated with meringue dezincification rates.
	Oliphant & Shock, 1996	Plug; Meringue	Nitrate reduces meringue dezincification, especially at high sulfate levels.	Experience; Literature review.
Fluoride	Turner, 1965, 1961	Meringue	Fluoride (up to 2 mg/L) does not affect dezincification.	Visual observation.
Silica	Turner, 1961	Meringue	Silica (up to 20 mg/L) has limited effects on meringue dezincification.	Visual observation
	Oliphant, 1978	Un- specified	Silica, when combined with zinc, can effectively inhibit dezincification.	Visual observations; Corrosion currents equated with unspecified dezincification rates.
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.

Table 3 Cont'd:

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 *pseudomonas fluorescens* promote dezincification.	Corrosion currents equated with dezincification rates; Weight loss.

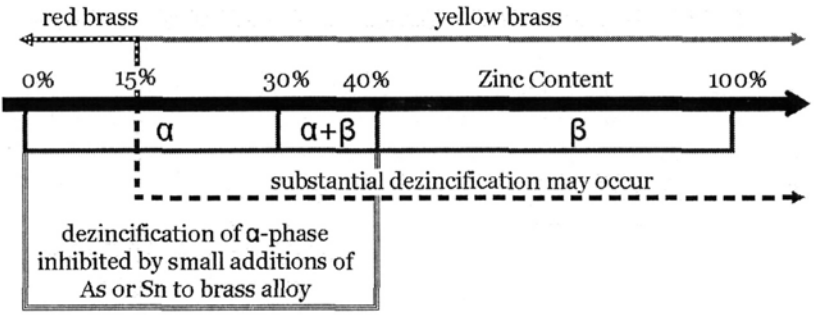


Fig. 4: **General trends for brass alloys as zinc content is varied.**

2.1.4 Chloride and Alkalinity

To provide a rule of thumb, the ratio of chloride to temporary hardness is widely cited as a key determinant in a given water's ability to support dezincification./15/ "Temporary hardness" is an archaic measure of water chemistry, in which the amount of hardness (e.g., Ca^{+2}, Mg^{+2}) lost via precipitation upon heating is quantified. Dependent on circumstance, temporary hardness is sometimes well correlated to modern chemical measures that include alkalinity or total hardness of a water supply. The chloride to temporary hardness ratio was first suggested as a primary criterion for dezincification by Turner, who observed that waters with relatively high chloride and low temporary hardness (Table 3), and having a pH of about 8.3 or greater, were prone to causing meringue build-up./20/ Using both laboratory and practical data, Turner empirically developed a diagram (Figure 5) to indicate water quality regimes in which dezincification problems will likely occur based solely on chloride and temporary hardness concentrations./20/ Turner's diagram has been adopted as a standard in predicting dezincification propensity based on water chemistry.

Because the work of Turner is cited so frequently (and often inappropriately) in relation to dezincification failures, it is worth noting the limitations of the work. First, the diagram was developed based on observations from particular regions in Great Britain which were impacted by a specific type of dezincification problem: blockage of hot water pipes by meringue build-up. Consequently, Turner's laboratory tests were primarily limited to synthesized water and natural waters that contributed to pipe blockage. Tests were generally conducted at or near pH 8.3, temperatures around 90°C, and with a galvanic connection between 60-40 duplex brass and copper. A second limitation of Turner's work is that it only assessed meringue dezincification, which is only one manifestation of dezincification-induced failures. Furthermore, the extent of dezincification was determined by visual observation of meringue-type corrosion products under low-power binocular microscope. No data on weight loss or metal leaching that would have provided insights into other modes of dezincification were collected. A third limitation is that Turner's diagram does not account for many water constituents encountered in modern potable water systems including corrosion inhibitors (e.g., orthophosphate or zinc orthophosphate), secondary disinfectants such as free chlorine or chloramine, or natural organic matter – each of which may be expected to influence dezincification.

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

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

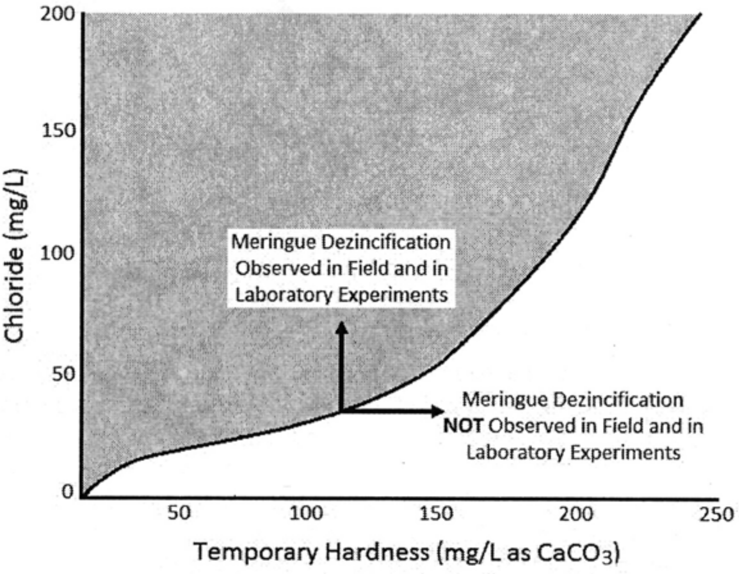
2.1.5 pH, Temperature and Aeration

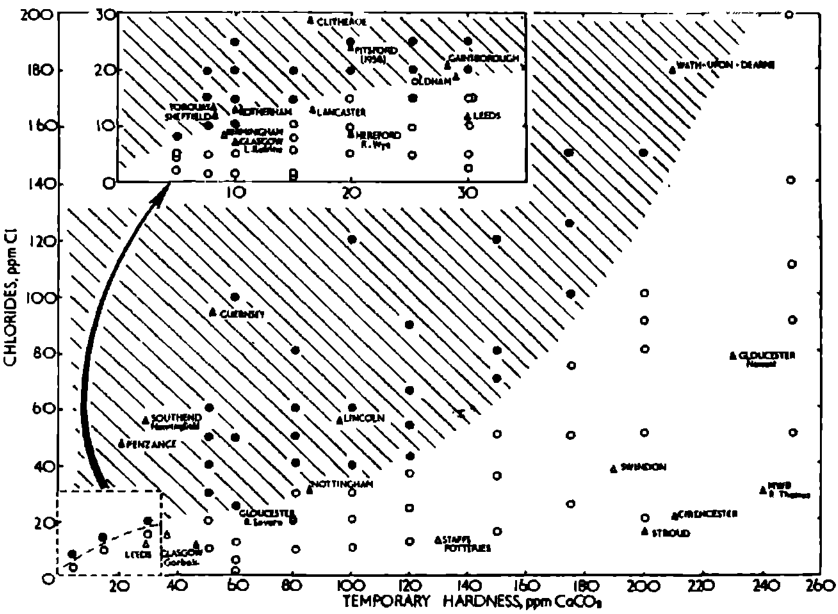
For meringue dezincification, Turner's field experience/20/ and further laboratory tests/22/ indicate that deposit build-up is favored at relatively high pH. Based on the experience of actual water systems in the Mildura Urban Water Trust of Melbourne, Australia, Simmonds recommended that water authorities maintain pH below 8.0 to avoid meringue build-up./6/ While pH 8.3 is commonly cited as the level above which serious meringue deposits will occur, researchers tend to disagree on an an exact value, probably due to significant differences in experimental techniques and waters tested (Table 3). For example, some authors have reported meringue formation in waters with pH only 7.5-7.8, and noted that below this range dezincification without meringue is favored./5, 15/ Jester concurred that meringue could form below pH 8.3, but he added that from pH 7.6-8.3 plug dezincification is favored at the lower end of the range while layer dezincification is favored at the higher end./12/ However, Nicholas determined that corrosion of brass between pH

7.5-9.0 occurred as general dezincification, meaning the pH did not specifically control the mode of attack./5/

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

Aeration can also significantly influence dezincification by mixing and by affecting the dissolved oxygen concentration in water. Turner's tests indicated that oxygen is necessary for occurrence of meringue dezincification, and he found that by replacing dissolved air in water with nitrogen gas the formation of meringue formation was eliminated./22/ Even low levels of dissolved oxygen have been shown to support significant amounts of meringue dezincification, albeit at lower rates than when higher oxygen levels are present./17,22/ Jinturkar et al. studied brass corrosion in sulfuric acid solutions and also found that increased dissolved oxygen enhances corrosion./24/ Ingleson et al. reported that free carbon dioxide promotes dezincification as well./25/





● *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*

Fig. 5: Adapted Turner's Diagram for predicting meringue dezincification based on chloride and temporary hardness concentrations (adapted from Turner, 1961/20/). Waters in the shaded area are considered likely to produce meringue dezincification at pH 8.3 or above.

2.1.6 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 3)./25/ The beta phases of the brass were severely attacked leaving behind a spongy deposit of copper. Despite these results, the researchers believed that the effect of chlorination on dezincification rates was small relative to the impact of other factors in the water. Another study in Britain confirmed the deleterious and significant effects of chlorine: the corrosion of both cast and stamped brass was greatly accelerated by the presence of 1 ppm free chlorine./26/ Nicholas also concluded that chlorine worsens dezincification; he determined that addition of 1.0-2.0 mg/L generally doubled or tripled corrosion currents versus those obtained in the presence of oxygen alone./5/

Several studies have also looked at the effects of chloramination on dezincification (Table 3). Stuart, as cited by Nicholas/5/, observed that the penetration depth of dezincification increased linearly with chloramine concentration from 0.1-1.0 mg/L./27/ Shortly thereafter, Moore reported that, per weight loss measurements, an excessive dose of 5.6 mg/L chloramine to a raw water supply was surprisingly determined to be less aggressive than the raw water itself./28/ Moore surmised that a significant pH increase caused by chloramination possibly played a key role in this experiment, and upon later testing Moore observed that chloramination (at 4 mg/L) did indeed increase dezincification of brass as compared to raw water when pH was controlled./29/

In terms of relative aggressiveness of chlorine versus chloramine, the interpretation is quite complicated by the practical behavior of these oxidants and dosing strategies in real systems. For example, although the oxidizing power of chlorine is higher than that of chloramine, the practical circumstances under which each may be present will likely control the overall effects on dezincification. Often, chloraminated water is distributed at higher pH than is chlorinated water, which could directly impact meringue dezincification problems. Moore's observation of apparent decrease in corrosivity of raw water upon chloramination via weight loss measurements/28/ might be explained by the fact that at increased pH, meringue was actually forming from the leached zinc. Thus, net weight loss in that study was low, despite potentially higher rates of dezincification due to the presence of chloramines which might be masked by greater meringue buildup.

Additionally, free chlorine tends to decay in distributions systems faster than chloramine, and is usually dosed at much lower levels to the water. The overall result may be that a switch from chlorine to chloramine might significantly increase the levels of total chlorine oxidant that actually contacts brass in building plumbing. This could potentially result in increased dezincification failures of brass via meringue build-up in situations where use of chlorine disinfectant caused few problems. Indeed, a rash of brass faucet failures in the 1940's and 1950's was attributed to many utilities switching from chlorine to chloramine disinfectant./25, 26, 30/ On the other hand, increased pH of chloraminated waters may decrease occurrence of non-meringue dezincification – depending of course on other water quality parameters. Little research has been done so far on this topic, although it deserves consideration. Many utilities are switching form chlorine to chloramine disinfectant in the United States to control disinfection by-products and some are experiencing increased problems with corrosion of other metals like copper./31/

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

2.1.7 Other Water Quality Parameters

In addition to chloride, the effects of several other common anions have been considered, albeit to a lesser extent (Table 3). The influence of sulfate on dezincification is not straightforward. In Turner's original work, the presence of some sulfate was found to lower the amount of chloride required to cause dezincification, but exact sulfate concentrations were not specified./20/ Lucey's findings appear to show a synergistic effect between sulfate and chloride./21/ He reported that, depending on sulfate concentration, the effects of chloride on dezincification could range from substantial to insignificant based on electrochemical measurements between experimental brass samples and copper pipe cathodes. For example, when sulfate concentration was less than 60 mg/L, chloride could be up to 250 mg/L without rendering the water aggressive. However, when sulfate was above 60 mg/L, chloride concentrations of just 60 mg/L were deemed problematic.

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

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

Based on measured galvanic corrosion currents between copper cathodes and brass samples, Oliphant concluded that silica may temporarily inhibit dezincification./13/ He suggested that in his experiments, lasting up to 48 days, silica may have changed over time from an ionic to colloidal form, as phenomenon previously asserted by Lehrman./33/ Furthermore, Oliphant reported that if the addition of silica is combined with approximately 1 mg/L zinc, stable and strong inhibitive effects were achieved./13/ This was concluded from a separate 25-day experiment, in which corrosion currents were measured to indicate dezincification rates, Based on visual observations of meringue build-up, Turner found, however, that silica has very limited effects up to 20 mg/L./20/ The influence of silica on dezincification and meringue deposit formation deserves further study.

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

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

As a general rule, it is believed that most anions, though not all, tend to increase dezincification propensity of brass. This effect is attributed to increased conductivity, although studies by Jester found no linear relationship between conductivity and the development of dezincification./12/ Indeed, Simmonds' field experience suggested that dezincification failures can also occur at the lower end of the typical conductivity spectrum for potable water./6/ Tabor theorized that some decisive anions (e.g., chloride) are more important than others (e.g., nitrate) for initiating and propagating dezincification, as would be expected based on prior research in other fields./34/

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

2.2 Physical Factors

It is often observed that nearly identical brass components in a given building plumbing system can fail by dezincification at markedly different rates, even though they are obviously exposed to the same water. This suggests an inherent dependence of dezincification on local physical and environmental factors, which can include flow rate, galvanic connections between brass and other materials, surface condition and structure of the brass, and even the placement of brass within a system. Most prior research on dezincification in potable water has emphasized the role of alloy composition and water chemistry, and relatively little work has been done which directly relates physical factors to dezincification. However, the work of the preceding sections can be synthesized and logically developed to provide a conceptual framework to explain how previously underappreciated physical factors may influence dezincification.

2.2.1 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 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 completed 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 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 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.

2.2.2 Variable or Differential Flow in Case of Single Piece of Brass

Water flow has typically been treated as an "on/off" parameter in prior dezincification research, and most experimental work has been done under low-flow or stagnant conditions. Indeed, corrosion textbooks state that dezincification is encouraged by such conditions./38, 39, 40/ Seemingly in direct contrast with many textbooks are practical observations that brass corrosion (including dezincification corrosion) is often accelerated by water movement and flow./17, 41/ This discrepancy is noted by Kelly et al. and is not inconsistent given considerations of separate of anodic and cathodic areas used in the different experimental set-ups./17/

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

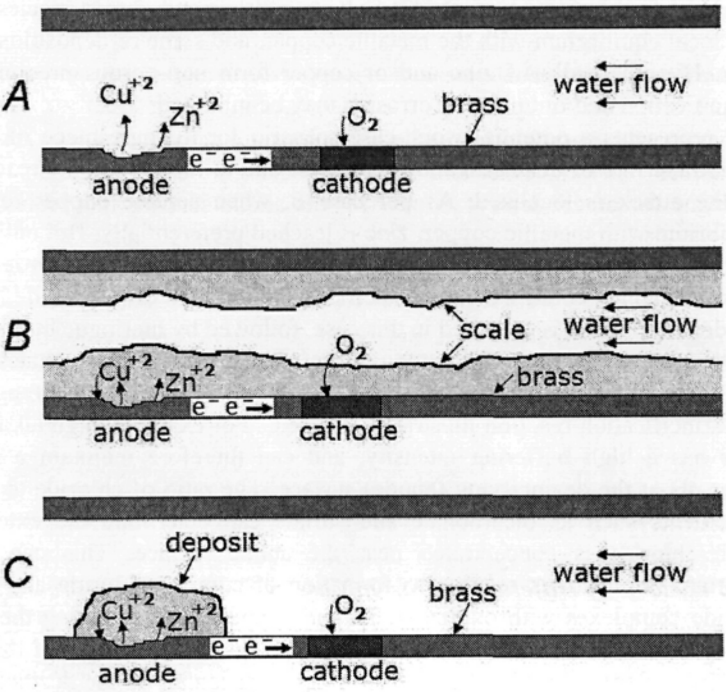


Fig. 6: Potential manifestations of dezincification for a single piece of brass in potable water. On clean brass with or without flow, the anode and cathodes are located very near each other and corrosion proceeds uniformly (*A*). With time, deposits may grow and completely coat the brass surfaces (*B*),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

For a single piece of brass in isolation, three representative extremes may be defined for exposure in potable water (Figure 6). First, if the anode and cathode are both exposed to significant flow as in case *A*, rapid dezincification is not expected because corrosion is relatively uniform. If the oxidation-reduction potential of the system is relatively low, some layer-type dezincification may occur, but the rate will be low because a differential aeration cell does not develop.

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

C represents a potential worst-case scenario for a single piece of brass because the rate of dezincification is highest due to rapid cathodic reactions and the attack is localized. As per case *B*, when soluble copper reaches equilibrium with metallic copper, zinc is leached preferentially. But unlike *B*, there is a locally low pH, higher level of chloride and lower oxidant level at the anode, which could worsen dezincification by orders of magnitude. Plug-type dezincification is expected in this case, followed by meringue build-up if the water chemistry favors formation of basic zinc carbonate precipitates.

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

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

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

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

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

To measure the possible impacts of the above idea on brass corrosion, a series of experiments was conducted in a re-circulating flow apparatus with 60-40 brass electrodes./17/ Some brass specimens were exposed to flow (cathodes) but were electrically connected to others which were recessed from flow (anodes), As expected, the in-flow brass became highly cathodic relative to the out-of-flow brass. Moreover, as a cathode was subjected to increased flow rate, the galvanic current between the cathode and anode increased. This observation was attributed to the increased availability of dissolved oxygen at the cathode. The authors also observed that when transitioning from laminar to turbulent flow conditions at the cathode, the corrosion current density at the anode increased by over an order of magnitude. It was asserted that the increased electron flow from the anode to the cathode indicated accelerated dezincification on the anodes, which seems highly likely given the above conceptualization. The authors noted that the anodes exhibited a characteristic red color of dezincification, although no soluble ion concentration or other data was used to verify the belief that zinc was leaching selectively.

2.2.4 Other Effects of Flow

In addition to the primary role of flow in removal and/or delivery of electrochemical constituents in potable water systems, other effects may be seen. In an early report on the topic of brass corrosion, Bengough and May recognized in 1924 the importance of flow with respect to air bubbles./41/ They noted that impingement of bubbles could often remove the protective scale that sometimes develops on condenser tube brass, especially the tube end first contacted by water where more turbulent conditions were observed. Additionally, they reported that the corrosion rate 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./47/ As discussed above, when only parts of a scale are removed from a single piece of brass, localized environments may more easily develop underneath the remaining scale as illustrated by case *C* in Figure 6./48/

Additionally, erosion corrosion should be considered. In this case, the shear stress and turbulence of the flow still acts to mechanically remove protective surface scale from part of the brass surface, revealing bare metal which is subsequently corroded when exposed to the water. In some situations the bare metal can become highly anodic (instead of cathodic as in case *C*), while the metal beneath remaining scale continues to be protected. Sakamoto et al. conducted laboratory tests wherein both 60-40 and dezincification resistant brasses were subjected to high-velocity water jets, which impacted the brass surfaces perpendicularly./49/ They reported that flow-induced localized corrosion (or erosion corrosion), identified by the presence ring-shaped grooves, was occurring in the vicinity of the jet impact for both types of brass. Furthermore, dezincification, identified by a distinct change in surface color, occurred along with the erosion corrosion on the 60-40 brass specimens. Weight loss data suggested that the corrosion rate increased with exposure time.

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

2.2.5 Concentration Cell Development Via Galvanic Connections

Dezincification on a single piece of brass, or between two pieces of brass exposed to differential flow, results via a concentration cell based on water chemistry differences at the surface of a single type of metal. A voltage drop or electrical current is present that can sometimes be measured experimentally as electrons flow between the anode and cathode sites. In most potable water systems, brass is often connected to copper, in which case dissimilar metal galvanic corrosion can occur. Copper is the more noble metal and may function as the cathode, while the brass is the anode and is sacrificed. Due to these differences in electrochemical activity, galvanic connections between brass and other metals can dramatically increase the rate of dezincification./53/ Additionally, the large surface area of the copper pipe network can also increase the rate of dezincification, since the copper pipe is the site of the cathodic reactions which are often rate limiting. Indeed, as mentioned previously, some researchers have purposefully connected copper to brass in their experiments in order to promote more rapid dezincification./13, 21/

Galvanic connections between copper and brass may also help to initiate rapid dezincification. For example, Nielsen and Rislund observed that when brass samples were attached to copper hooks, dezincification initiated more rapidly than in the instance of brass alone./45/ As for the instance of a single piece of brass, three general scenarios may exist for the instance of a galvanic connection between brass and another metal. Figure 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 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 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 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./13, 21/ Oliphant noted that dezincification of duplex brass became anodically controlled (i.e., controlled by the rate of zinc dissolution) when the copper cathode surface was more than eight times larger than the brass anode./13/ This observation is likely to depend on the specific system and is deserving of additional research, because in most practical situations the copper to brass surface area ratio far exceeds the 8:1 ratio.

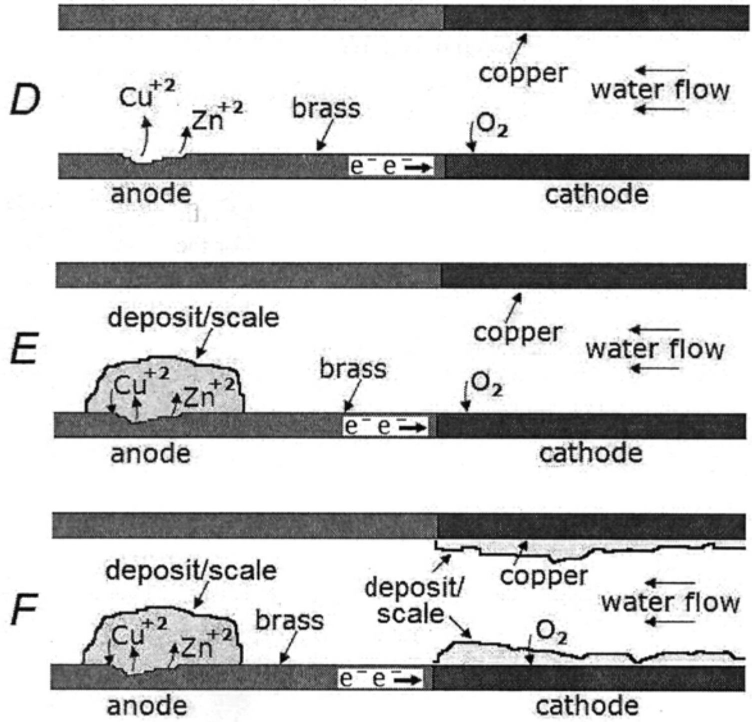


Fig. 7: Potential manifestations of dezincification for a galvanic couple between brass and copper in potable water. *D* represents slow dezincification; *E* represents severe dezincification whereby a localized environment develops at the anode while the copper cathode is supplied with oxidant; and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

2.2.6 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 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 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.

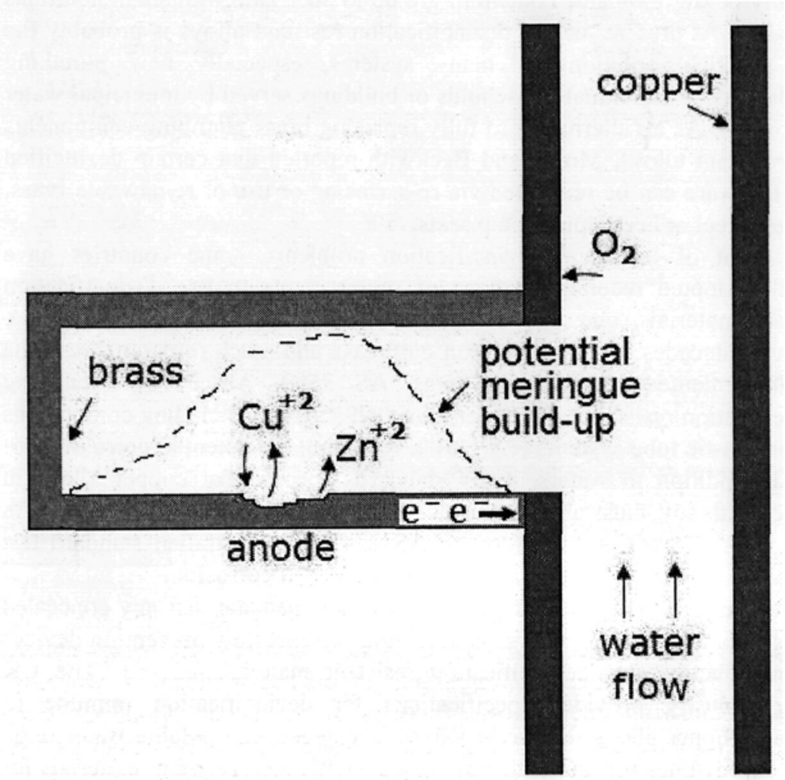


Fig. 8: Hypothesized worst-case scenario for dezincification in the case of a galvanic couple between brass and copper in potable water. Due to its position in the system, the brass is removed from flow and a localized environment may quickly develop to promote dezincification and eventual meringue build-up.

3. COMBATING DEZINCIFICATION IN POTABLE WATER SYSTEMS

Considering the influence of alloy composition, water chemistry and physical factors highlighted above, it is possible that brass dezincification can be avoided or overcome by controlling factors in any or all of these three categories. A range of approaches have been proposed for mitigating dezincification in potable water systems (Table 4)./6, 7, 14, 13, 29, 46, 50, 54, 55, 56, 57, 58/ The most common recommendation by far is to simply use unsusceptible brass alloys (see Alloy Composition section), which are typically below 15% zinc content or are up to 30% zinc with small additions of arsenic. At present, use of dezincification resistant alloys is probably the most practical solution for many systems, especially new plumbing installations or individual households or buildings served by municipal water distribution. As an alternative to fully replacing brass plumbing components with resistant alloys, Moore and Beckwith reported that certain dezincified brass tap-ware can be reinstated via re-surfacing or use of re-newable brass, stainless steel or acetyl plastic tap seats. /50/

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

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

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

Table 4
Summary of Recommendations for Avoiding Brass Dezincification in Potable Water Systems

Researcher(s)/ Author(s)	Recommendations
During (1997)	Use of inhibited brass or copper; prevention of deposit formation on brass surface
Kuppan (2000)	Use of unsusceptible alloys
Marshakov (2005)	Use of unsusceptible alloys, such as those containing additions of As, Sn, Al, remove oxygen from water
Moore (1998)	Continued mandatory use of dezincification resistant alloys in water supplies in Australia
Moore & Beckwith (1982)	Use of dezincification resistant alloys such as gunmetal, alpha or arsenical brasses for tapware; use of re-newable components made of either brass or alternate materials like acetyl plastics or stainless steel
Nicholas (1983)	Bicarbonate dosing to corrosive water supplies.
Oliphant (1978)	Maintain sufficient carbonate hardness to ensure non-dezincifying water according to Turner's Diagram (Figure 5); maintain pH 8.3 or less to prevent meringue dezincification, but must ensure that accelerated corrosion rates of brass and other system materials are acceptable; blend naturally-inhibited waters with dezincification-prone waters; use polyphosphate and zinc inhibitor treatment
Oliphant (2003)	Use of dezincification immune (e g , arsenical alpha brass) or resistant brasses in waters known to initiate or propagate dezincification
Selvaraj et al (2003)	Use of unsusceptible alloys such as those containing additions of As, Sn, B, Mn and Bi
Simmonds (1967)	Maintain pH 8 or less to prevent meringue dezincification
Uhlig (1985)	Use of unsusceptible alloys such as red brass or admiralty (Sn) brass
Waterton (1973)	Adjust alkalinity to maintain satisfactory temporary hardness to chloride ratio to ensure non-dezincifying water; avoid increasing chloride concentration during water treatment

the United States./66/ In many ways, this equates to a costly way of re-learning past lessons. Incorporation of formal standards in to the United States plumbing codes, such as those used in Australia, should be strongly considered.

Now that high-zinc brasses have been installed throughout newer housing developments in the United States, water chemistry modifications to mitigate dezincification problems might be desirable or necessary (Table 4). Practically speaking, these modifications may be considered where point-of-use water treatment is employed or a significant number of municipal water customers are affected by dezincification problems. For example, in cases where high chloride is suspected to contribute to brass dezincification, simply switching from chloride- to sulfate-based coagulants might be expected to reduce the dezincification propensity of the water supply. Waterton suggested such modifications where applicable for problematic waters in the United Kingdom, but noted the relatively high associated costs./58/ On top of evaluating the advantages, expenses and/or complexities of changing treatment processes to modify water chemistry, potential effects on water quality and other materials in a distribution system should also be considered. For instance, the cost attractiveness of chemical dezincification control strategies which use additive inhibitors may be increased if the inhibitors could benefit system materials other than brass (e.g., copper or concrete). Information on such inhibitors is lacking in the literature and is thus a topic for future research.

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

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

Finally, modifications to physical factors in potable water systems which are suspected to influence propensity for brass dezincification (see *Physical Factors* section) should be considered. Oliphant noted the importance of plumbing system configuration in dezincification testing, and attempted to build a representative test apparatus./13/ And Nicholas reported that investigations of actual dezincification occurrences suggest that a number of variables (not just chemical) are influential./56/ Additionally, Zhang found that when identical brass alloys were subjected to a matrix of waters from locations both with and without known dezincification problems, results were not well correlated with field failure reports; waters from locations reporting most severe dezincification problems were not necessarily the most aggressive to the tested brass with respect to dezincification, and vice versa./67/ Zhang concluded that other factors, perhaps physical factors of actual plumbing systems, must be significant. However, the current lack of research results in this area makes it difficult to confidently recommend specific system configurations (e.g., avoiding differential flow patterns or decreasing design flow velocity) or materials (e.g., dielectric components between dissimilar metals). Following development of a standardized test to determine the dezincification propensity of a given water, tests might also be developed to pinpoint critical physical factors and suggest optimal plumbing design modifications.

4. SUMMARY AND CONCLUSIONS

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

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

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

- Dezincification may occur by either a singular or dual mechanism, depending on the water chemistry to which the brass is exposed and the oxidation-reduction potential
- Dezincification attack may manifest itself as either plug- or layer-type, and meringue deposits may form under circumstances of low zinc solubility
- Brasses with zinc content lower than 15% are generally free from serious dezincification problems, and the alpha phase in brass can be inhibited effectively by adding arsenic and tin in the alloy.
- While high chloride and low temporary hardness do appear to enhance meringue dezincification, the Turner diagram is based on data that are limited in scope, and will not prove to be an acceptable predictor of dezincification problems in modern water systems.
- Meringue dezincification is favored by higher pH, temperature and aeration.
- Increased free chlorine and chloramine may promote dezincification.
- Most anions are believed to worsen dezincification. However, some prior work has indicated that nitrate and phosphate may slightly inhibit dezincification in some cases.
- The effects of zinc and silica (as either natural constituents or added inhibitors) are largely unclear at this time. Based on limited data, both zinc and silica have been found to reduce the rate of dezincification in some circumstances,
- The influence of water flow on dezincification is expected to be highly dependent on the condition of the metal, galvanic connections and types of deposits present on the surface.
- Separation of anodic and cathodic areas promotes dezincification via development of differential concentration cells. Thus, scales, deposits and crevices tend to initiate and/or accelerate dezincification
- Galvanic connections between brass and other materials can promote dezincification via the difference in metal activities and increased cathode to anode surface area ratios. While the cathodic reaction is often rate limiting for brass in isolation, when coupled to long sections of copper pipe the anodic reaction may become rate limiting.
- The worst-case scenario for meringue buildup with respect to physical factors in a traditional plumbing system is hypothesized to be a case in which brass is out of flow but connected a larger, more noble pipe (e.g., copper) exposed to flow.

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

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