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Stagnation Time, Composition, pH and Orthophosphate Effects on Metal Leaching from Brass

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STAGNATION TIME, COMPOSITION, pH, AND ORTHOPHOSPHATE EFFECTS ON METAL LEACHING FROM BRASS

by

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E. Timothy Oppelt, Director
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ABSTRACT

Plumbing products made of brass and similar alloys are the only lead containing materials still installed in drinking water systems and, by law, may contain up to 8% lead. Brass ranges in metal composition depending on its application. Brass is composed of approximately 60 to 80% copper, 4 to 32% zinc, 2 to 8% lead, ^{5} 6% tin, and trace amounts of iron, tin, and cadmium. The relationship between alloy composition and resulting amounts of metal leached from the alloy in drinking water has not been fully established. Better understanding brass corrosion may provide information and guidance to the use of the safest materials for the production of plumbing fixtures, and optimization of corrosion control treatments.

This study examined the effect of alloy composition, pH, orthophosphate, and stagnation time on the metal leached from 6 different brasses and the pure metals that make-up brass (lead, copper, and zinc) in Cincinnati, Ohio, tap water. Results demonstrated that the amount of various metals leached from the alloys corresponded well with the alloy's composition. Leaching of metal components from brass were generally less affected by pH than the pure metals. A pH of 7.5 and 0.5 to 3.0 mg/L orthophosphate significantly reduced the amount of lead leached from the alloys initially, but had less impact as time continued. Orthophosphate had a minimal impact on copper levels. The impact of stand time was dependent on water quality and alloy composition. This report covers a period from August 1991 to January 1996, and work was completed as of December 1994.

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INTRODUCTION

Water sampling and monitoring requirements described in the Lead and Copper Rule (LCR)[1-3] specify that one liter first-draw water samples must be collected at selected consumer's taps following at least 6 hours of stagnation. Lead service lines, tin:lead solder, and brass fixtures are considered major contributors of lead to that one liter sample. The practice of using lead pipe and lead-based solders in home plumbing systems was eliminated in 1986.[4] In addition, all pipes and fittings were required to be constructed of "lead-free" material which, by legal definition, contain less than 8% lead.

The metal composition of brass ranges from approximately 60 to 80% copper, 4 to 32% zinc, 2 to 8% lead, ≤ 6% tin, and trace amounts of iron and other alloying elements depending on its application. Therefore, by previous definition, plumbing products constructed of brass and similar alloys such as faucets and valves are considered "lead-free" and are the only lead-containing components still permitted for use in drinking water systems. For this reason, understanding the major influences upon and mechanism(s) of metal release from brass and techniques to control that release are important in meeting LCR requirements and limiting metal exposure to consumers.

The effect of water quality (i.e. pH, dissolved inorganic carbon [DIC], sulfate, chloride, free chlorine, dissolved oxygen, etc.) on the solubility of the primary metals that make-up brass (Cu, Zn, and Pb) has been explored to varying degrees by numerous investigators and is generally understood. However, predicting the dissolution of metals from an alloy is likely more complicated than solubility relationships alone, and may be influenced by many factors including alloy composition, structure, and surface area. As an example, initial work conducted by British researchers[5] indicates that the amount of lead leached from brass and lead containing alloys is independent of the percentage of lead in the alloy. Other researchers[6] theorize that dezincification of zinc-containing alloys can result in increased lead surface area which results in increased lead dissolution. Developing a better understanding of the control aspects of brass corrosion will provide additional guidance to water utilities, consultants, and governmental agencies on strategies to reduce lead release into drinking water.

OBJECTIVES

The initial purposes of this multi-year research project was to establish relationship(s) among the composition of six brass alloys and the metal (Cu, Zn, and Pb) concentrations leached from them in Cincinnati (Ohio) tap water and to provide insight into brass corrosion control measures. The same water quality effects on the metals leached from the major pure metal components of brass (Cu, Zn, and Pb) were also explored. The project was expanded to include the evaluation of the impact of pH (7.0 and 8.5) and a non-zinc containing orthophosphate chemical (dosed at 0.5 and 3.0 mg PO_4/L) at pH 7.5 on metal leached from brasses, lead, copper, zinc, and 60:40 Sn:Pb solder. Also, the effect of stagnation period on metal(s) leached from the

brasses, lead, copper, zinc, and 60:40 Sn:Pb solder was examined. Finally, metals leached from a "lead-free" brass were briefly explored.

The experiments were conducted using standard 1"x2"x1/8" metal coupons and a "fill-and-dump" test protocol in chemical variations of Cincinnati tap water. Conclusions were based on graphical and statistical data interpretations.

BACKGROUND

A growing public awareness about the toxicity of lead has brought about the question of the contribution of lead by leaded brass plumbing fixtures and faucets to drinking water. A recent preliminary lead and copper rule survey[7] of 46 large systems and 7 medium and small systems conducted by the Association of Metropolitan Water Agencies stated: "By far the major reason is or is suspected to be lead leaching from new (newer) faucets and fixtures.", referring to reported causes of high lead values in drinking water samples. As the public grows more familiar with the issues concerning safe drinking water, pressure on legislators to reduce or even ban the use of lead (and other contaminants) in plumbing products may grow.

In California, the Natural Resources Defense Council and the Environmental Law Foundation filed a complaint with the California Superior Court on December 15, 1992. The complaint stated that a number of major faucet manufacturers marketed faucets that leach lead into the drinking water at levels exceeding the limit of 0.5 μg/L set under the State's Proposition 65 Standard.[8] The lawsuit targeted 13 major faucet manufacturers. The case was settled in August of 1995 when a number of major manufacturers agreed to meet stipulations which included warning labels and a lead reduction program.[9]

In a similar situation, the Environmental Defense Fund, Natural Resources Defense Council, and the California Attorney General recently filed suit under California Proposition 65 against four manufacturers of submersible water pumps.[10] Some of these pumps, which are used to draw water from private wells, are constructed with brass components and, as a result, can provide a point source of lead contamination.

Brass composition

Brasses are defined as copper alloys that contain zinc (5 to 40% Zn) as the principal alloying element with or without other alloying elements, such as tin, iron, aluminum, nickel, and silicon. Brass can be subdivided into three main families: copper-zinc alloys; copper-zinc-tin alloys (tin brasses); and copper-zinc-lead alloys (leaded brasses).[11]

Zinc is added to copper to increase tensile strength. The tensile strength of the alloy increases significantly with increasing zinc concentration up to 20% zinc, whereas further zinc addition only slightly increases tensile strength. Brasses containing more than 20% zinc are referred to as "yellow brass," while brasses containing less than 15% zinc are referred to as "red

brass." Zinc is soluble in copper, and when added to copper to produce brass, up to 35% of the zinc will dissolve to form an alpha solid-solution (alpha brass). When still more zinc is added, a second or beta, solid-solution is formed. Brasses with 35 to 40% zinc consist of mixtures of these two solutions and are referred to as alpha-beta or "duplex" brasses. Duplex brasses are cheaper and easier to fabricate than alpha brasses. However, they are susceptible to dezincification, a form of corrosion that will be discussed in more detail later in the paper.

Lead is added to brasses to improve machinability of the alloy and make castings pressure tight by filling the voids created as the casting cools. Lead is insoluble in copper-zinc alloys and therefore during solidification, lead precipitates and forms a dispersion of second phase particles or globules both at the grain boundaries and within the matrix. The globules serve to improve the alloy's machinability by acting as chip breakers, reducing tool clogging and allowing increased cutting speed.[12] Lead is found in brass from 0.1 to 12.0%[13], however, brasses most commonly used in household fixtures contain 1.5 to 7.5% Pb[14]. The reference standard for machinability is "free-cutting" or "free-machining" brass, composed of 61.5% Cu, 3% Pb, and 35.5% Zn. This alloy, designated C36000, is given a reference machinability rating of 100% and is the standard to which all other brasses are related. Lead offers little effect on corrosion resistance of the alloy.

Tin is added to brass to improve corrosion resistance (particularly impingement or erosion attack), and increase the tensile strength and hardness of the alloy. In addition, tin significantly increases the resistance of the alloy to attack by acidic media and the tendency for dezincification. Admiralty alloy is a tin brass extensively used as condenser tubing. Admiralty brass is made by adding 1% tin to cartridge brass (70% Cu, 30% Zn). Approximately 3 to 5% tin is often added to red or semi-red brasses to increase the strength and hardness of the alloys.

A variety of other elements may be added in small quantities to enhance properties of the alloy. For example, arsenic, antimony, and phosphorous are added to certain brasses to inhibit dezincification. Aluminum is added to provide corrosion resistance and color enhancement and nickel is added as a whitening agent.

Brass production procedures

Brass plumbing fixtures and faucets are most commonly formed by either cast or wrought processes. Cast brass products are made by pouring melted alloy (ingot, virgin metal, or scrap) into a mold and allowing it to cool. Castings offer corrosion resistance, high thermal and electrical conductivities, and good wear qualities. Casting permits the production of irregular and complex internal and external shapes, such as those often seen in faucets. The production of these products may not be practical by forming or machining processes. The major market for cast products in the United States in 1991 was plumbing and heating; 108 million pounds and 26% of the market.[15] The dominant cast alloys were identified as C84400 (75%) and C83800/C84800 (25%).

Wrought (forged) brass products are produced by mechanically forming the alloy to the desired shape while the metal either still hot (700 to 850°C) and ductile, or at room temperature (referred to as cold-working). Wrought alloys have not been remelted. Wrought brass offers many advantages including high electrical and thermal conductivities, facilitating joining by welding and soldering, good corrosion resistance, high strength and ductility, and excellent machinability. Compared to cast products, wrought products have smoother surfaces, a faster production time, greater freedom from porosity, and lower cost. Duplex brasses are easily worked by hot pressing while alpha brasses tend to be stiff to work, even when hot.[16] Additionally, alpha brasses tend to crack during hard working if they contain small amounts of impurities, especially lead (which is often added to improve machinability). Forging brass (60.0% Cu, 38.0% Zn, and 2.0% Pb), alloy number C37700, is the most forgeable and therefore the most common forged alloy. Forging is the method manufacturers prefer using to produce compression fittings.

Brass corrosion

Dezincification

The majority of published research that has examined the effect of drinking water on brass, bronze, and other zinc containing alloys is focused on the corrosion phenomena referred to as "dezincification." Dezincification has received special attention from the drinking water industry primarily because of the physical and visible damage to plumbing systems that results, leading to costly pipe failures and plumbing blockages. Dezincification of small valves and fittings in the United States has not been nearly the problem it has in Great Britain and some other places in northern Europe primarily because standard materials used in the U.S. tend to be low zinc containing red brasses.[17]

Dezincification is a specific form of dealloying or selective leaching corrosion. In the case of dezincification, zinc is preferentially removed from the brass or other copper-zinc alloys. Researchers have developed three main hypotheses to describe the mechanisms of zinc removal. The first hypothesis, and generally more widely accepted, is that simultaneous dissolution of copper and zinc occurs anodically, producing an electrolyte containing both copper and zinc, followed by the redeposition of copper.[18-20] The second and less widely accepted hypothesis is that zinc is preferentially removed from the alloy, thus leaving a porous residue.[21] A third school of thought is that a combination of the two occurs.[22,23] Depending on water composition and service conditions, the dissolved zinc may react with carbonate or oxygen to form a crust of solid corrosion products close to the corroded area. These corrosion products usually form smooth mounds. Upon opening they show a structure made up of many hollow shells resembling the appearance of a "meringue", giving rise to the term "meringue dezincification". This bulky by-product causes home plumbing blockages which often present more of a problem than pipe failure by corrosion. The remaining alloy is a porous, weakened, reddish residue that is susceptible to failure.

The resistance of an alloy to dezincification does not change significantly until the zinc content is greater than 15%; after which the possibility for dezincification increases. Arsenic (typically up to 0.1% As) added to alpha brass effectively inhibits dezincification[24,25], however, does not prevent dezincification of greater zinc-containing duplex brasses. Antimony and phosphorous in amounts of 0.02 to 0.05% have also been used to safeguard against dezincification attack in alpha brasses.[26]

Many researchers have studied the effect of water quality parameters on dezincification. Turner showed that chloride and carbonate hardness contents were major factors influencing "meringue" dezincification.[16,27] He found that in waters where the pH was above 8.3 and the chloride concentration was high relative to temporary bicarbonate hardness, dezincification occurred. He developed the "Turner" Diagram relating chloride concentration and temporary hardness to suitability for resistance to dezincification. Lime softening converts water that does not support dezincification to one that does by increasing the pH and lowering the temporary hardness. Other factors identified in controlling dezincification include: percent zinc in alloy, electrolyte condition of water, galvanic couples or electric currents, and the availability of oxygen and other chemicals in water.

Tabor[28] examined bronze (copper alloy in which zinc or nickel is not the major alloying elements) valve stems from the city of Los Angeles water distribution system that had failed as a result of dezincification. He discovered that in cases where bronzes containing high zinc contents were being used with water that had been softened with lime, dezincification was common. Through experimentation using a galvanic bronze-iron cell, he discovered that generally the higher the zinc content of the bronze, the greater the chance of dezincification. In the case of alloys with low zinc content (less than 15% zinc), zinc and copper acted as a unit, with iron providing the cathodic protection. In alloys with high zinc content (greater than 20% zinc), the zinc and copper acted independently of each other, with zinc being anodic to the iron and copper being cathodic. The zinc rapidly dissipated because of the irons inability to provide protection. There appeared to be a transition zone between a zinc content of 15 to 20% where dezincification may or may not occur. Other findings indicated that the dezincification process may be increased with oxygen content in system, water velocity, temperature, and deposits built-up on the material surface.

Ingleson et al.[29] conducted experiments to examine the effect of chlorination on ball valves made of cast and hot-pressed brass (single alpha-phase brass containing 2 to 3% lead). They concluded that the presence of up to 0.4 mg/L of free chlorine increased the rate of dezincification. They also concluded, however, that the impact of chlorine was low relative to the impact of variations in water composition.

Dissolution

Dissolution refers to the dissolving of the metals composing the alloy into the solution in contact with the metal. As mentioned, the majority of past brass corrosion research has focused

on dezincification and unfortunately in nearly all of those cases metal leaching levels or dissolution was not addressed. Information pertaining to metal dissolution from brass alloys is typically general.

Samuels and Méringer[30] evaluated short-term metal leaching from 8 kitchen faucets in 4 different types of water and aqueous fulvic acid. The study involved measuring metal concentrations in standing water samples taken from inverted water faucets for two 24-hour stand periods. Results showed that lead as well as copper, zinc, chromium, and cadmium leached in varying amounts depending on the type of faucet used and the leach solution.

Nielsen[31,32] found that lead could be picked up in water from household plumbing fixtures composed of brass such as water meters and mixer fittings, and main and stop valves composed of gunmetal (copper alloy containing 5% Pb).

Birden et al.[33] found lead contamination in copper pipe loop systems constructed of no lead containing parts other than brass compression fittings. Lead leaching was attributed to the lead in the brass used to make the fittings.

Schock and Neff[34] obtained data from a 2-year field and laboratory study that implicated brass valves and fittings as potentially significant sources of lead, copper, and zinc in drinking water. The field study indicated that new chrome plated sampling faucets on pipe loops in galvanized and copper systems were associated with 125 mL water samples that exceeded the lead maximum contaminant level which was 0.05 mg Pb/L at the time of the study. As a result, they conducted trace metal leaching experiments on six new sampling taps using an inverted faucet technique. The tests were performed using deionized and Champaign (Illinois) tap water (3 faucets for each tap water). Samples following 24-hour dwell times were taken every 2 days for 2 weeks. The samples were analyzed for lead, cadmium, zinc, iron, and copper. The faucets subjected to deionized water leached about 100 mg Pb/L and dropped off rapidly to less than 10 mg Pb/L at the end of the 2 weeks. Faucets subjected to Champaign tap water initially leached approximately 1 mg Pb/L and dropped to less than 0.3 mg Pb/L at the end of 2 weeks.

Gardels and Sorg[35] also evaluated metal leaching from faucets. They used a different metal extraction approach than the fill and dump scenario implemented by the previous investigators. They mounted 12 different faucets upright to a manifold system connected to a pressure activated pump and water storage reservoir. In this position, the faucets were operated under pressure in a similar fashion to how they would be used in a home. Leaching tests were conducted with deionized and Cincinnati (Ohio) tap waters over a 9 month period. Standing water samples were taken at a variety of standing times and sampling schemes. Samples were analyzed for lead, copper, zinc, iron, chromium, and cadmium. Results indicated that lead leached from new cast brass faucets could contribute lead to drinking water in excess of 10 μg/L. They showed that as much as 75% of the lead leached from common kitchen faucets could be collected in the first 125 mL of water from the faucet; more than 95% of the lead was collected in the first 200 to 250 mL.

Dissolution controls

The contribution of brass to lead and other metal concentrations in drinking water has been well established as discussed. However, the factors influencing the degree of preferential metal, particularly lead, dissolution from brass and other alloys have not been well defined. Metal solubility relationships will probably be poor predictors of the amount of lead, copper, and zinc leached from brasses under the normally non-equilibrium conditions found in drinking water. Other mechanisms will likely control the amount of metal leached from an alloy. Physical and structural characteristics of the alloy and alloy's surface (e.g. microstructure, chemical composition, finish, etc..), for example, are important factors to consider. Landolt[36] points out that the surface composition of alloys usually differs from the bulk material due to factors such as spontaneous corrosion reaction with the atmosphere and surface treatment processes.

The role of lead in the alloy's structure may influence metal dissolution rates. Lead is insoluble in brass alloy systems. The melting point of lead with respect to the alloy system is low and therefore is last to freeze. The result is that during the cooling period, lead tends to be squeezed toward the grain boundaries of the alloy in the form of globules. The pattern these globules take at the alloy surface, which contacts water, likely influences the degree and speed of lead leaching by increasing the available lead surface area. Further, cutting tools can smear the lead globules over the surface. These effects may enhance the lead leaching characteristics of alloys of seemingly low lead content.

Alloy surface area is an important driving force for the rate of metal dissolution. For example, surface finishing techniques can increase surface area by creating grooves or etchings in the surface. Polishing may increase lead surface area by spreading the soft lead globules over the alloy's surface. Characteristics of brass production techniques will result in different surface properties. The surface of cast brass, for example, is rough and presents greater surface area than wrought brass, thus driving or increasing metal dissolution rates.

Interactions amongst the metals that comprise alloys may also control metal dissolution rates. Some researchers theorize that dezincification of copper-zinc alloys can result in additional lead surface sites below removed zinc and thus leach as much if not more than a brass containing more lead and less zinc.[6] On the other hand, under certain water quality conditions, zinc may contribute to a protective passivating film over the alloy surface.

Alloy composition would seem to be a logical control on metal leaching levels. Paige and Covino[37] investigated selective metal leaching from 11 different copper based alloys in high purity water of near neutral pH. The study specifically examined the effect of lead concentration in the alloy, contact time, and water temperature on lead leaching from the alloy. Three sets of leaching test runs were conducted. The first run evaluated leaching at three different temperatures: 25°C, 50°C, and 75°C in deionized water for two weeks. The second study used samples which were pre-treated by an acetic acid process prior to being run for two weeks in deionized water at 25°C. The third test run was conducted at 25°C in deionized water for 15 days. Their results indicated

that the dissolution of lead increased with the percentage of lead for all of the alloys tested with the exception of yellow brasses. They found that temperature generally had little effect on increasing the amount of lead leached from the alloys, but may have slightly reduced the lead at higher temperature. They also found that lead leached from the brass alloys decreased by a factor of 2 to 200 times over 14 days of testing.

Jones[38] used electrochemical polarization methods to study the galvanic corrosion of steel coupled to brass. He found that alloy composition (copper and zinc) was important in determining the anode and cathode. When the copper-zinc alloy contained more than 40% copper, the alloy behaved electrochemically like pure copper in that the alloy acted as the cathode. But when the copper content fell below the critical value of 40%, the alloy behaved as pure zinc, acting as a sacrificial anode when coupled with steel.

The internal structure of brass products contribute to metal dissolution concentrations and rates. Faucets, for example, are relatively complex in that bends, angles, and touching metal components are often incorporated in their design. These areas represent locations for erosion corrosion. Faucets and valves are also subject to physical wear associated with opening and closing valves, which may increase metal levels by causing increased fresh surface exposure or by contributing occasional particulate contamination.

Lead release assessment from alloys in drinking water

Several countries have developed metal extraction tests to evaluate the metal release from alloy plumbing materials in contact with drinking water. Mattsson and Eistrat[39] have presented a European summary of metal extraction tests for some materials used in drinking water plumbing systems. The "Nordtest" was the first, and probably most recognized, method used for assessing the potential for lead, cadmium, and other metal release by materials used in drinking water systems.[31] The Nordtest method has been adopted by Scandinavian countries.

The Nordtest procedure is basically carried out as follows: The test specimen (e.g. fitting, valve, or pipe) is degreased with methanol. Flowing tap water is then rinsed through the specimen for one hour. Next, the outlets of the sample are capped with polyethylene plugs and the specimen is filled with synthetic test water (composition shown in Table 1). The test water is replaced 7 times over a 10-day test period (at 1, 2, 3, 4, 7, 8, 9, and 10 days). Water samples are taken on the 9th and 10th days and analyzed for lead, cadmium, and other metal pick-up. Noting the sample volumes and metal concentrations over the 2-day sample period, the metals extracted from the specimen are calculated. The obtained values are believed to be representative of maximum metal pick-up in a first draw sample in home installations and can therefore be related to accepted drinking water standards.

The British Standard Institution (BSI) has also established set procedures and requirements for the suitability of materials used in contact with drinking water.[40] The test procedure is similar to the Nordtest, but differs in the comparison against test limits. The BSI method uses separate

evaluations for pipes and fittings. Lead extracted from pipe specimens should not exceed the limit specified in the European Economic Community (EEC) Directive on water quality for human consumption.[41] For fittings, 5% of the determined amount shall not exceed this limit.

Recently in the United States, a voluntary standard was developed by the National Sanitation Foundation *International* (NSF) located in Section 9 of ANSI/NSF Standard 61 (Drinking Water System Components- Health Effects)[42] pertaining to the leaching of metals from mechanical plumbing devices. The standard establishes an extraction protocol for assessing lead and other metal leachability from plumbing products in contact with drinking water. The procedure describes a protocol for washing and conditioning the components. The devices are then exposed to the extraction water (pH=8, alkalinity=500 mg $CaCO_3$/L, and Cl_2=2 mg/L) for 19 days using a static "fill-and-dump" test protocol. Samples are collected after days 3, 4, 5, 10, 11, 12, 17, 18, and 19 following a 16-hour dwell time and analyzed for lead. The data is normalized, taking into account factors such as water volume and surface area. In the case of lead, the data is statistically manipulated and compared to a maximum allowable level of 11 μg Pb/L. The comparisons serve as a means of accepting or rejecting plumbing products for certification under this standard.

Alternatives to the use of leaded brass

A variety of potential alternatives to the use of leaded brass alloys exist. Products could be redesigned to reduce internal surface area or alternative casting processes could be used. The internal surface of the product could be coated with a lead-free material. Faucets constructed of plastic or faucets with plastic water channels could be used.

Another potential solution is to reduce or eliminate the amount of lead used in brass plumbing fixtures and faucets. Some researchers and manufacturers have marketed alternative alloying materials that enhance the machining properties of an alloy as well as lead does. Others have investigated processes to produce materials of lower lead content for construction of fixtures.

Initial work conducted at the Argonne National Laboratory supported by the U.S. Department of Energy investigated the selective removal of lead from brass and bronze scrap melt.[43] A major source of cast brass is recycled copper base scrap (primarily old automobile radiators) in the form of ingots. The production of cast products from recycled scrap material provides founders with an energy conservative, cost-effective alternative material source to primary ores. However, the scrap typically contains high amounts of lead (more than 7 to 8% Pb) and requires the addition of virgin materials to meet lower lead standards. The researchers have investigated vacuum distillation as a means to selectively "pull-off" or remove lead from the recycled melt. This process is based on vapor pressure differences among materials in the melt. The process has shown promise under laboratory conditions, but cost effectiveness remains an issue.

"Pre-leaching" lead from the alloy has been considered. Prior to distribution, the brass product would be exposed to an aggressive metal extraction solution; perhaps an acidic solution. The solution would extract or dissolve the lead from the brass surface, therefore reducing lead the amount of lead exposed to the water. The process, which could be described as an "aging" technique, may eliminate initial high water lead levels from exposure to new brass products. This solution, however, has considerable drawbacks including cost, and handling and disposal issues associated with the production of a hazardous, lead-containing extraction solution.

Researchers at AT&T Bell Laboratories have been exploring properties of copper alloys substituting bismuth for lead as a solution to lead contamination from leaded brasses.[12] They have found that copper alloyed with bismuth coupled with a ductility-enhancer such as phosphorous, indium, or tin, machines as well as leaded alloys. These studies have been conducted at the laboratory-scale and full-scale implementation issues remain unresolved.

Some manufacturers have been advertising nearly true "lead-free" (advertised to contain trace amounts of lead as a contaminant) brass or bronze alloys as possible substitutes for the lead-containing ones. Leadfree Faucets Inc.[(a)] claims to have developed a method for producing faucets from aluminum bronze (<0.05% Pb).[44] Currently the company produces the faucets solely for components of point-of-use devices. Another company, NIBCO[(b)], has used a brass that contains bismuth as a substitute for lead in their cast brass products.[45] The bismuth-brass alloy was patented and licenced by IMI Yorkshire Fittings Limited[(c)] of the United Kingdom. The alloy contains 2.7% bismuth and < 0.25% lead.[46] While these truly lead-free materials show promise, introducing bismuth to drinking water in the distribution system remains an unexplored issue. Currently, however, no faucets are being made from lead-free alloys on a large scale.

TEST APPARATUS DESIGN AND OPERATION

Test apparatus

The test apparatus consisted of a large water reservoir (100 gallon Nalgene® tank) connected to 12 parallel test loops by 1/2" inside diameter (ID) Schedule 80 polyvinyl chloride (PVC) pipe. Test water contained in the reservoir was recirculated in the tank by a PVC pipe recirculation line and magnetic drive pump system. The water was fed to the loops by a separate magnetic drive pump and line. All pump components in contact with the water were constructed of metal-free materials. Water that had passed through the loops was discharged to a waste drain.

Each test loop was constructed of a variety of PVC Schedule 80 and high density polyethylene (HDPE) valves, fittings, and pipe. The systems each contained a 3-way valve, a

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(a) Leadfree Faucets, Inc., Chagrin Falls, OH.
(b) NIBCO, Inc., Elkhart, IN.
(c) IMI Yorkshire Fittings LTD., P.O. Box 166, Leeds, LS1 1RD, UK.

sample holding cell, and tubing made of Teflon®. The holding cell was sized to tightly hold one 1"x2"x1/8" metal coupon[a] in order to maximize the ratio of coupon surface area to volume of water in contact with the coupon. The coupon surface area was 4.75 in^2 and the volume of water was 26 mL, resulting in a surface area to volume ratio of 0.18 in^2/mL. Figure 1 is a photograph of the test system and Figure 2 is a schematic of an individual test loop.

Coupon material

Six differently composed brass coupons, plus, a pure copper, pure zinc, pure lead, and 60:40 Sn:Pb solder coupon were simultaneously tested. One brass and the lead coupon were tested in duplicate to evaluate material and procedural variability. The brass coupon compositions are given in Table 2. The brasses used were chosen because they represent common materials used to manufacture brass faucets and other fixtures used in drinking water systems. Several coupon finishes were available from the coupon supplier: 120 grit, milled, and glass bead finishes. The 120-grit finished coupons were chosen for this study because it was the finest finish available and was presumed to give the most consistent coupon surface.

The compositions of the brass coupons were reported by the coupon manufacturer as percentage ranges. In many cases, relatively wide composition ranges, such as those given for lead, overlapped among different brasses. The nature of the study, however, required more definitive metal coupon compositions.

For the purposes of this study, the chemical composition of the coupons was assumed to be relatively uniform for the batch, and throughout each coupon. Subsamples consisting of approximately 0.1 grams of material cut from the corners of unused coupons from the same batch were used for the chemical analysis. Microwave digestion procedures were used to digest pieces of the lead coupons[47], Sn:Pb solder coupons[48,49], and copper, zinc, brass coupons[50]. The digestates were analyzed for lead, copper, zinc, iron and tin by flame atomic absorption spectroscopy and results have been included in Table 2.

Coupon and test system cleaning procedures

Problems with coupon contamination, lead to the development of a thorough coupon pre-cleaning procedure.[51] The cleaning procedure was, in part, a combination of two American Society for Testing and Materials (ASTM) coupon wash procedures: designations G31-72[52] and D2688-83[53]. The procedure used and recommended for cleaning new metal coupons to be exposed to static leach testing was as follows:

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[a] Metal Samples, Inc., Munford, AL.

1. Clean milled specimens (Cu, Zn, solders, and brasses) by ultrasound in 0.5% Triton X-100®[a] surfactant for 5 minutes. Clean each coupon individually in a small glass beaker (containing Triton X-100®) surrounded by water. Following 5 minutes of ultrasonic treatment, discard the cleaning solution and rinse the metal coupon with distilled water. Repeat the ultrasonic cleaning procedure for an additional 5 minutes after replacing Triton X-100® with distilled water.

2. Soak copper and brass coupons individually in 1:4 HCl for 30 minutes at room temperature. Rinse the coupons thoroughly with distilled water and dry with a Kimwipe™.

3. If the lead coupons are covered with a dark coating, sand the surfaces clean with fine emery cloth or sand paper (e.g. special emery grinding paper, grit 0[b], designated for metallography). Polish with a paper towel. Ultrasonic cleaning in distilled water may be used to remove any solid particles adhering to the coupon, but it is probably unnecessary. If ultrasound is used, 30 seconds to 1 minute is sufficient. Longer times result in attack of the Pb metal surface.

4. Finally, rinse the coupons in acetone and air dry. They may be used immediately or stored in a desiccator for later use.

Prior to starting the study, the entire experimental system was cleaned with a 5% solution of Contrad 70©[c] detergent. The solution was recirculated through the feed tank and rinsed through the loops for 10 to 20 minutes. The solution was then held in the cells (empty cells), as if coupons were being tested, for 24 hours. Next, the entire system was drained and the procedure was repeated. The system was thoroughly rinsed with Cincinnati tap water until the Contrad© solution was satisfactorily removed. The preceding steps were repeated using 0.15% HNO_3 solution in place of the detergent except that after 24 hours standing, the acid solution held in the test cells was analyzed for metals (Pb, Cu, Zn, Fe, and Sn). The acid cleaning steps were repeated until standing metal levels were consistent with background Cincinnati tap water metal levels. The cleaning procedure was also used to clean the system before the start-up of new water quality tests. Analysis of the acid cleaning solution showed that metals were adsorbed onto the surface of the test loop components during a test run, and several acid rinses were required to remove the contamination before re-starting.

Operating procedures

The daily operating procedure of the test system was as follows:

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[a] Curtis Matheson Scientific, Inc., Houston, TX.
[b] Buehler LTD., Evanston, IL.
[c] Godax Laboratories, Inc., New York, NY.

During the first three test runs, the Nalgene® tank was filled with approximately 30 gallons of Cincinnati tap water. Water pH was chemically adjusted, if necessary, by adding 6 N HCl or 8 N NaOH. The tank recirculation pump was in continuous operation during the make-up of the feed water to assure complete mixing and dispersement of chemical additives. In the last two test runs, the water was determined to be stable enough (i.e., did not significantly change chemically) that the storage tank was filled to 80 gallons and that water was used over the following several days. The free chlorine residual and pH was checked daily and chemically adjusted as necessary to meet standards. Free chlorine residual was maintained by adding sodium hypochlorite solution (4 to 6% available chlorine).

After the water was prepared, all valves in the loops were opened to the waste drain. The feed pump was activated. Test water was flushed through the loops simultaneously at a flow rate of approximately 0.15 L/min for a brief rinse period of 5 to 10 minutes for total flow of approximately 10 gallons. The valves in the loops were then closed, holding the water in the cells in contact with the metal coupons. The water was held in the cells for approximately 22 to 24 hours during weekdays (Monday thru Friday) and 72 hours over weekends (Friday thru Monday). Next, the cells were sampled by opening the labcock above the cell to the air and then opening the 3-way Teflon® stopcock below the cell while simultaneously holding a 60 mL Nalgene® HDPE sample bottle below the stopcock sample port. Air admitted through the top stopcock, allowed the leach water to drain by gravity into the sample bottle. The total sample volume was only about 26 mL, most of which was contained in the Teflon® sample cell. The valves were then closed and newly prepared source water was again flushed through the cells, as mentioned, repeating the procedure. Initially, sampling from the cells was conducted daily. After several weeks of operation, sampling was reduced to 3 times per week (two 24-hour samples and one 72-hour sample). Water was flushed through the cells daily (Monday to Friday), even when sampling was not done. Air was in contact with the metal coupons for a short period of time; however, the coupon surface was not exposed long enough to completely dry.

Test runs were generally terminated after approximately 150 days. Termination was based on apparent stabilization of metal leaching levels. At the end of each test run, the coupons were removed from the cells, the system was cleaned as previously described, new coupons were installed, and the study was repeated with a different extraction water.

Sampling

Water samples taken in 60 mL bottles from the sample cells, as mentioned, were preserved in 0.15% ultrapure HNO_3[54] and analyzed for lead, copper, zinc, iron, and tin. Free chlorine, total chlorine, and pH were measured daily and dissolved oxygen was measured weekly in the tank feed water. These parameters were measured immediately, prior to fresh water being fed to the loops. Additionally, three feed water samples were taken: a 250 mL 0.15% HNO_3 preserved sample for background metal analysis (Ca, Cu, Fe, K, Mg, Mn, Na, Pb, and Zn); a 250 mL sample for background wet chemistry analysis (alkalinity, Cl, NH_3, NO_3, PO_4, SiO_2, and SO_4); and a 30 mL sample for total inorganic carbon (TIC) analysis. All sample bottles, with the exception of the

TIC bottle, were Nalgene® HDPE bottles. TIC samples were taken in 30 mL glass vials having caps with conical polyethylene liners. Special care was taken to insure that no air or air bubbles were trapped in the sample.

Analytical procedures

Unless otherwise specified, all chemicals used in this study were Analytical Reagent (AR) grade. Deionized (DI) water was prepared by passing building distilled water through a Milli-Q Plus© cartridge deionized water system[a], having a resistivity ≥ 18.2 MΩ.

Glassware (excluding pipets) used for the preparation of standards and solutions was cleaned using a 5% solution of Contrad 70©. The glassware was thoroughly rinsed with deionized water. Reused glassware was immediately cleaned by soaking in 10% (v/v) concentrated HNO_3 and rinsed with DI H_2O. Glass pipets were cleaned by at least an overnight soaking in 5% Contrad© solution, followed by rinsing with dilute AR-grade HCl in a plastic pipet washer. The final rinse was a minimum of 8 total volumes of deionized water cycled through the pipet washer. Air displacement micropipets with disposable tips were used for handling and transferring solutions.

Ultrapure nitric acid, HNO_3[b] was used to preserve samples. 0.15% of the sample volume was the volume of nitric acid added to the sample (1.5mL/L). 6 N HCl[c] and 8 N NaOH[d] were used to chemically adjust feed water pH. Sodium phosphate ($Na_3PO_4*H_2O$)[b] was used to adjust the phosphate concentration in the feed water.

Instrumentation

Lead was analyzed with a Perkin Elmer Model 4000 Spectrophotometer[e] equipped with a Model HGA 400 furnace programmer and AS 40 autosampler. Initially, all other metals were analyzed with a Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer and an AS 50 autosampler. After August 1, 1993, these metals were analyzed with a new Thermo Jarrel Ash[f] 61E® purged inductively coupled argon plasma spectrometer (ICAPS). The ICAPS was implemented between test runs and improved detection limits of most metals analyzed (see Table 3). The change did not affect conclusions of the report since metals leached from the coupons were well above the detection limits of both methodologies. Lead results, which did fall below the detection limit, were not impacted because the method remained the same. The pH was

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[a] Millipore Corp., Bedford, MA.
[b] Ultrex, J. T. Baker Chemical Company., Phillipsburg, NJ.
[c] Mallinckrodt, Inc., Paris, KY.
[d] Fisher Scientific, Failawn, NJ.
[e] Perkin Elmer Corp., Norwalk, CT.
[f] Thermo Jarrel Ash Corp., Franklin, MA.

measured with a Orion Model EA 940 pH meter[a] and an Orion Ross Sure-Flo™ electrode. Free and total chlorine were analyzed with a Hach DR/2000 spectrophotometer[b]. TIC was analyzed by a coulometric procedure on a UIC Model 5011 CO_2 coulometer[c] with Model 50 acidification module, operated under computer control. A complete list of analytes and analytical methods is shown in Table 3.

Quality assurance and quality control

Laboratory quality assurance (QA) procedures for analytical precision and accuracy for all samples followed procedures established by the Treatment Technology Evaluation Branch (TTEB) for all research studies. QA practices include requirements for analysis of duplicates and spikes of samples comprising more than 10% of the sample load, and verification of instrument calibration and some interference checking through external certified reference standards at multiple times during each analytical run. The exact location and frequency of different types of quality control spikes, standards, blanks, and duplicates, along with accuracy requirements, are specified in those documented procedures for each type of analysis. They cannot be generalized because the precision and accuracy expectations vary with the type of instrument used and the levels of the analyte encountered in the different experiments.

Quality control charts for the major analytes are given in Appendix Tables 39 to 41for QA samples analyzed during the study period. Duplicate difference, spike recovery, and standard recovery information is presented for analyte concentration ranges.

Statistical data analysis and interpretation

Differences in metal leaching trends where determined using several statistical approaches. Data normality was determined by the Kolmorogov-Smirnov Test. In most cases of this study, data distributions were not normal (at 95% confidence), suggesting the use of the following non-parametric statistical data interpretation techniques. The Kruskal-Wallis One Way Analysis of Variance (ANOVA) on Ranks was used to demonstrate differences in metal leaching trends from coupons. The Kruskal-Wallis Test is necessary when (a) determining if three or more groups are affected by a single factor (e.g. brass composition), and (b) samples are not normally distributed or do not have equal variances.[55] Since ANOVA statistics only indicate whether two or more groups are different, the Student-Newman-Keuls method and the Dunn's method were used to make multiple comparisons between all possible group pairs. The Student-Newman-Keuls test is used when group sizes are equal and Dunn's test is used when group sizes are unequal. All statistical comparison tests were made at 95% confidence (P=0.05), that is to say with 95% confidence that the groups differ significantly. In the few cases were the data were normally

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[a] Orion Research, Inc., Boston, MA.
[b] Hach Company, Loveland, CO.
[c] UIC Inc., Joliet, IL.

distributed, The Kruskal-Wallace one way ANOVA test on ranks was used to demonstrate differences in leaching trends.[56] All statistical calculations were made using Sigmastat™[(a)] (version 1.0) statistical software. Detailed and understandable statistical procedure descriptions can be found in S.A. Glantz's *Primer of Biostatistics*[56] and W.W. Daniel's *Biostatistics: A Foundation for Analysis in the Health Sciences*[57] or any other acceptable statistical reference.

Data outliers (data points that fell well beyond the majority of set measurements and reasonable expectations) were occasionally encountered. The first approach used to treat data outliers was to look for an assignable cause (e.g., a misidentified sample bottle or a leaking coupon holder cell). Quality assurance data from analytical test runs, laboratory log books, and bottle labels were examined for errors and documented problems. Where an explanation for a suspected outlier could not be found, the data was tested statistically according to the United States Department of Commerce National Bureau of Standards[58] for the case where the population mean and standard deviation are known at a confidence level of 90% (P=0.10). Identified outliers were recorded, however, were not included in statistical analysis and graphical representations.

RESULTS

Table 4 is a summary of the general water quality conditions and time periods of each "test run" of the study for future reference. Test runs were continued until metal leaching "trends" visually "leveled-off" or their slopes approached zero. The terminology "metal leaching trends" is used in this report to describe the curve of metal concentration leached from a coupon over a time frame (study period). Unless otherwise noted, the following results refer to samples collected following approximately 22- to 24-hour stagnation times. Raw metal analysis and extraction water quality data is compiled for all test runs in Appendix Tables 1 to 35. Values less than analytical detection limits including negative numbers are presented in the tables. Since those values represent real instrumental outputs, it has been recommended that they are retained for statistical calculations.[59] Tables 5a to 5e summarize the extraction water qualities used in each test run.

Test run #1

Extraction water quality

Non-chemically adjusted Cincinnati tap water was used in test run 1. As a result, larger than desired pH fluctuations (0.18 pH units standard deviation) were observed throughout the test run. The solubility of copper, in particular, is strongly impacted by pH[60] and even small pH fluctuations (0.1 pH units) have been shown to considerably influence copper solubility.[51] The mean sulfate concentration (116.3 mg SO_4/L) was higher during this test run than in others. Researchers[60,61] have suggested that sulfate negatively impacts copper corrosion at pH values above approximately 7.5 and may be beneficial at lower pHs in new systems. The mechanism(s),

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[(a)] Jandel Scientific, San Rafael, CA.

however, have not been established and clearly greater research efforts are required to understand the role of sulfate. Free chlorine, a strong oxidizing agent and an influential parameter on metal dissolution rates, averaged 2.0 mg/L which was more than 0.5 mg/L greater than values observed in any other test run. Free chlorine has not been conclusively demonstrated to alter metal equilibrium conditions. Perceived increases in metal levels associated with free chlorine increases are often misinterpretations of increased oxidation rates. The increased sulfate and free chlorine levels observed during this test run were likely related to seasonal water quality variations in the Ohio River (main source of Cincinnati tap water). Dissolved oxygen and TIC were not directly measured during this test run. TIC was calculated using WATEQX[62], a computer FORTRAN 77 program, and source water quality values. The calculated value was 14.3 mg C/L with a standard deviation of 1.2 mg C/L.

Lead leached from brass coupons

Figure 3 shows lead leaching trends from the brass coupons (C36000 was tested in duplicate) and duplicate pure lead coupons during test run 1. The greatest amount of lead leached from the brass coupons occurred during the first 7 days of the test run. During this time lead levels dropped off sharply with time and trends were difficult to differentiate. Initial high values were thought to be related to new, clean coupon surfaces and thinly dispersed lead globules present on the coupon surfaces at the start-up. The concentration of lead leached during this period varied amongst brasses by no more than approximately 80 μg/L and was generally a function of the lead content of the brass; brasses with higher lead contents tended to leach higher amounts of lead.

From approximately 7 to 15 days into the test run, lead concentrations gradually leveled off and the variance between the magnitude in lead levels leached from the brasses narrowed. During this time period, the relationship between the lead content of a brass and the amount of lead leached from the brass became less apparent. Statistical comparisons between the lead leaching trends during this time period showed that there was no significant difference between most trends at 95% confidence.

After 15 days, the lead leaching trends appeared to split into two distinct groups. For future reference, the groups will be labeled as the "low" group and the "high" group, in reference to the relative magnitude of lead leached from the coupons. During the period between 15 to 60 days, the general trend of both groups continued to be a gradual downward one. The trends visually appeared to level-off or stabilize after 60 to 70 days.

The "low" group consisted of the duplicate free-cutting brass (C36000) coupons and one yellow brass (C85400) coupon. The amount of lead leached from these brasses was nearly indistinguishable for the remainder of the run (after 60 days) as confirmed statistically in Appendix Table 36. The similarity in lead leaching patterns was reflective of the similarity in compositions of the two brasses (see Table 2). The quantity of lead in the two brasses overlapped while free-cutting brass contained slightly more zinc and slightly less copper than the C85400

coupon. As a group, the amount of lead leached at the completion of the study was approximately 8.5 μg/L. The brasses in this group were two of the three lowest lead containing brasses evaluated. Lead levels dropped by approximately 90% over the remainder of the test run.

The "high" group consisted of the three red brasses: C83600, C84400, and C84500, and yellow brass C85200. From 60 to 125 days, these brasses followed parallel lead leaching trends but differed in magnitude by as much as 50 μg/L. C85200 brass leached the least amount of lead in the group over this time period. The average lead concentration leached from the brasses in the group during the last 21 days of the study was approximately 28 μg/L. Lead levels dropped by approximately 80% over the study period. There was no statistical difference among brasses in this group (Appendix Table 36)

With the exception of the C85200 brass, the magnitude of lead leached from the brasses corresponded well to the lead composition of the brass alloy after 60 days of leaching. In other words, brasses containing greater amounts of lead tended to leach greater amounts of lead than brasses containing lower amounts of lead. C85200 brass is a yellow brass and has a similar composition as brasses in the low group. Based upon the similarity, it was expected that the amount of lead leached from C85200 brass would have been similar to the amount of lead leached from brasses in the low group. The difference between the two brasses is C85200 brass contained slightly more copper and slightly less zinc than C85400 brass.

A white precipitate formed on several of the brasses. Upon close visual examination, it was noted that the density of the coating increased as the zinc composition of the brass increased. A nearly identical appearing but denser solid formed on the pure zinc coupon. Based upon the visual examination, water chemistry, zinc solubility chemistry, and findings by others[63-66], the film was believed to be basic zinc carbonate (hydrozincite). The film may have provided corrosion protection by acting as a diffusion barrier and reducing the amount of lead leached from the brasses. This observation could explain why more lead was leached from the lower zinc-containing C85200 brass than expected.

Localized upward and downward patterns in the leaching trends were occasionally observed in varying degrees throughout the test run. In most cases, the trends appeared to closely parallel changes in water quality (pH and chlorine residual).

The pure lead coupons leached more lead than any of the brasses during all stages of this test run. This observation demonstrated that the rate of lead dissolution from the brasses was significantly hindered. Physical characteristics of the brass coupon surface such as exposed lead surface area and the formation of corrosion deposits comprised of alloy materials other than lead at the coupon surface were believed to be limiting factors.

Statistical comparisons of the lead leaching trends made over the entire test run and after the lead trends appeared to stabilize (after 60 days) showed that the majority of trends were significantly different ($p < 0.05$) (Appendix Table 36). Good reproducibility between of lead

leaching of duplicate free-cutting brass coupons was observed (i.e., no statistical difference was observed).

Copper leached from brass coupons

Copper leaching trends were similar to those observed for lead in that two groups, a "high" and a "low", were established (Figure 4). The major difference was that the division into trend groups took place at the beginning of the test run.

The high group consisted of the three red brasses: C83600, C84400, and C84500. Unlike lead leaching trends, a relatively constant amount of copper (approximately 0.22 mg/L) was leached from the brasses in the high group throughout the entire test run (Appendix Table 37). The leaching patterns and copper levels of the high group brasses were nearly identical throughout the entire test run. These results showed that smaller differences in copper composition in similar alloys did not translate into significant differences in copper leaching levels.

The low group of brasses consisted of C36000, C85200, and C85400 which were also the brasses that contained the lowest percentage of copper. The copper leaching trends among these brasses were also nearly identical. Copper levels gradually decreased over the first 20 to 40 days followed by a leveling off trend at a concentration of approximately 0.03 mg/L. No statistical differences between trends in this group were discovered (Appendix Table 37).

After approximately 120 days, the pure copper coupon leached nearly the same amount of copper as the red brasses. This showed that there was a critical alloy composition in which the brass alloy took on the leaching properties of pure copper.

A number of gradual concentration peaks and valleys were observed in the copper leaching trends. The gradual change in copper levels was characteristic of a response to fluctuations in extraction water quality rather than the collection of dislodged particulate material which would result in single random copper spikes. A review of the extraction water chemistry during periods of peaks and valleys frequently showed a relationship between pH and copper concentration. For example, in one instance over a 35-day period (from 95 to 130 days into the test run), the pH of the extraction water gradually dropped from approximately 8.7 to 8.2 (Appendix Figure F1). A corresponding increase or inverse pattern was seen in copper levels. This was especially evident with the high group brasses, where copper levels more than doubled during this time period. Similar relationships were not always obvious or apparent as this particular case. A number of factors such as coupon age and water quality probably impact the occurrence and degree of such relationships.

In most cases, trends within groups were not statistically different from each other. Also, duplicate copper (C36000) was not statistically different over the entire test run or after 60 days, which demonstrated good experimental reproducibility (Appendix Table 37).

Zinc leached from brass coupons

Zinc leaching trends (shown in Figure 5) behaved differently from those observed for both copper and lead in that there were not groups of distinct leaching trends. Zinc levels leached from the brasses were a function of the percentage of zinc in the brass throughout the entire study. Zinc concentrations appeared to slightly decrease over the first two weeks. They stabilized after about 60 days in the concentration range of about 0.05 to 0.30 mg/L. Zinc leachate concentrations fluctuated slightly throughout the study. As was the case for copper, fluctuations often appeared to correlate with changes in background water chemistry (i.e., pH and chlorine residual).

The pure zinc coupon leached as much as 11.3 mg/L at the start of the study, but dropped rapidly to about 0.32 mg/L after 40 to 50 days. By the end of the study, the amount of zinc leached from the pure zinc coupon was lower than the amount leached from the yellow brasses and nearly the same as the red brasses. As was the case for copper, there appeared to be a zinc content threshold where the alloy took the leaching qualities of pure zinc. The zinc composition of the alloy was low relative to copper content and the pure zinc coupon. Despite this condition, zinc dissolution rates were not hindered and in some cases appeared to even be slightly enhanced. A simple explanation would be that the amount of zinc in the alloy and at the alloy surface in contact with the water were sufficient to avoid kinetic limitations. A more complex theory would be that the selective removal of zinc from the alloy, possibly enhanced by galvanic interactions among other elements within the alloy, contributed to the observations. Of course these explanations are speculative thoughts made by the authors. Without a detailed scientific investigation on the electrochemical interactions between the elements that make up brass and a high degree of knowledge of the structure of brass alloys (which were well beyond the scope of this project), a valid scientific explanation cannot be given.

Statistical analysis of zinc leaching data showed that nearly all case comparisons were statistically different (Appendix Table 38). Zinc leaching trends observed after 60 days showed that duplicate coupon (C36000) were not statistically different.

Test run #2

Extraction water quality

Table 5b summarizes the extraction water quality used during test run 2. The pH of the tap water was strictly controlled at an average of 7.01 with a standard deviation of 0.05 by the addition of HCl and/or NaOH. Sulfate levels were lower during this test run than the first by approximately 50 mg/L, averaging 68 mg SO_4/L. Free chlorine was also lower during this test run than the first, averaging 1.4 mg/L with a standard deviation of 0.28 mg/L. Measured TIC and DO averaged 12.6 mg C/L and 8.9 mg O_2/L, respectively.

Lead leached from brass coupons

Figure 6 shows lead leaching trends from the six brass coupons (and one duplicate C36000 coupon) and duplicate pure lead coupons during this test run. The greatest amounts of lead leached from the coupons during the first 14 days of the run, with levels dropping off rapidly during this period. The relative amount of lead leached from the brass during this period was generally dependent on the amount of lead in the brass. The magnitude of lead leached from the brasses during the first 14 days differed by as much as 300 μg/L among the brasses.

From 14 to approximately 40 days, the lead leaching trends began to level off. During this period, lead trends aligned themselves in the direction and order they would follow for the remainder of the study. Alignment appeared haphazard initially, with trends overlapping and following no distinct pattern. By 40 days, the patterns established a clear position and direction.

From 40 days to the end of the test run, the tendency of the majority of the lead leaching trends was to slightly decrease. Yellow brass C85200 was the exception in that the decrease was more apparent. Also, C85400 brass, oddly, exhibited a gradual increasing lead leaching trend before finally leveling off. C85400 is a yellow brass containing the most zinc but the least lead of the brasses tested. The most plausible explanation was the theory that zinc dissolution subsequently lead to the exposure of additional lead surface sites resulting in increased corrosion rates [6]. However, for this theory to hold, similar observations should be observed with similarly composed brasses which was not the case for C85200 brass.

A distinct set of trend groups like those observed in test run 1 did not develop during this test run. In some cases, lead concentrations observed at the end of this test run were one order of magnitude greater than levels observed for the same coupon during the test run 1. By the end study, trends tended to be evenly separated by roughly 10 to 50 μg/L. The percentage of lead leached from brass was directly related to the amount of lead in the alloy (i.e., the more lead in the alloy the more lead leached from the brass). As was the case in test run 1, the pure lead coupons leached more lead than any of the brasses.

Statistical comparisons of the leaching trends made over the entire test run and following the period after 60 days show that approximately half of the trends are significantly different at the 95% confidence interval (Appendix Table 36). Trends that are not significantly different are mostly of the same group or brass type, yellow or red brasses. The duplicate C36000 trends were significantly different over the entire study and after 60 days were significantly different which was, in part, probably due to the high lead levels leached from the coupons.

Copper leached from brass coupons

Copper leaching trends differed from lead leaching trends in that copper levels did not start out extremely high, followed by a rapid drop and gradual leveling off (shown in Figure 7). With the exception of C36000 brass, the trends gradually increased over the first 60 days of the test run

to a plateau which they stayed at for the remainder of the study. This pattern was believed to be due to the slow dissolution of an oxide film thought to have formed on the coupon surface during coupon atmospheric storage prior to study initiation. The film provided some corrosion protection to the coupons initially, however, with time dissolved and new films and equilibrium conditions were established. The C36000 brass leaching trend decreased gradually during the first 60 days, after which the trend leveled off.

There was difficulty in accurately distinguishing or ranking leaching trends, with the exception of the two C36000 brass coupons. The C36000 brass coupons stood out from the other brasses in that significantly lower amounts of copper were leached from them. They contained the least amount of copper of the brasses tested. The difficultly in detecting differences or ranking copper leaching trends among the remaining brasses was due to the inconsistency or sporadicness of the leaching trends despite strict control on pH leaching trends. This demonstrates that even under well controlled laboratory conditions, a high degree of random variability occurred. The cause (s) are difficult to determine since a number factors such as small water quality differences, disturbance of the test apparatus, small stagnation time differences, and the dislodging of particulate material could contribute to such behavior.

Copper levels generally remained between 1 to 2 mg/L of copper throughout the duration of the study for the group of coupons. Similarly to test run 1, the amount of copper leached from the pure copper coupon was initially higher than levels leached from brasses, however, rapidly fell below those levels leached from the red brasses.

Trends were determined to be statistically different in most cases, leaching trends were significantly different ($P<0.05$) (Appendix Table 37). However, leaching trends crossed over each other frequently making it difficult to distinguish or rank trends. Good reproducibility of copper leached from the duplicate free-cutting brass coupons was found.

Zinc leached from brass coupons

Zinc leaching patterns followed a slightly different trend than lead and copper (Figure 8). In almost all cases, zinc levels gradually fell with time, in most cases leveling off by approximately 60 days. The amount of zinc leached from the coupons was directly dependent upon the amount of zinc in the alloy. C36000 leached the most zinc, leaching as much as 2 mg/L more than the next closest alloy, and averaged about 4 to 5 mg/L by the end of the study. The levels leached from C36000 were nearly the same as the levels observed with the pure zinc coupon. C85400 and C85200 brasses were next in order of leaching. The two yellow brasses contained the next greatest amount of zinc. Zinc leached from them appeared to be still decreasing at the end of the study. Red brasses C84500 and C84400 were next, and very close, averaging around 0.5 mg/L and C83600 leached at <0.25 mg/L. In nearly all cases (after 60 days and over the entire study), zinc leaching trends were statistically different. Reproducibility of zinc leached from the duplicate free-cutting brass coupons was good.

Impact of pH on metal leached from coupons

Brass coupons

The influence of pH on metal dissolution from the alloys and pure metals was evaluated by comparing metal levels leached from the coupons exposed during test runs 1 and 2 (Appendix Figures F3 to F24). The results showed that the three red brasses all behaved similarly with respect to the influence of pH on lead levels leached. As expected, the water considered to be most corrosive towards lead, the lower pH water, leached the most lead from the red brass coupons. This was particularly evident with C83600 and C84400 coupons, where a difference between the two pH leach trends of approximately 100 μg Pb/L was maintained throughout the duration of their respective studies. The influence of pH on lead leached from C84500 was not as significant and at one stage, between 20 and 60 days, appeared to be insignificant. The most notable difference was that C84500 brass contained the most zinc of the three red brasses tested. As a group, the red brasses contain the most lead, nearly doubling the lead content of the yellow brasses.

The two yellow brasses (C85200 and C85400) exhibited different lead leaching responses to pH than the red brasses. Interestingly, lead leached from C85200 (Appendix Figure F8) showed pH had no visual impact on lead concentration while the impact of pH on lead leached from C85400 (Appendix Figure F9) brass was small (10 μg Pb/L) relative to the red brasses. The major compositional differences between the red and yellow brasses are red brasses contain more lead but far less zinc. These observations suggest that the dissolution of lead from brass was not solubility controlled, otherwise lead levels would be higher at pH 7.0 due to higher lead solubility.

The differences between the amount of lead leached from C36000 (Appendix Figure F4) at pH 7.0 and 8.5 fell between differences observed with yellow and red brasses. Lowering the pH to 7.0 increased lead levels significantly (by approximately 30 μg Pb/L) but not to the degree observed with the red brasses. Free-cutting brass contains the most zinc of all the brasses tested and contains less lead than the red brasses and more lead than the yellow brasses.

Copper leaching levels were significantly higher at the lower pH for all brasses except C36000 brass. The difference was greater amongst the red brasses, and (Appendix Figures F11 to F15) with copper levels being more than 1.5 mg/L higher at pH 7.0. The difference between copper leached from the coupons at pH 8.5 and 7.0 appeared to widen as the percentage of copper in the alloy increased. Free-cutting brass leached the least copper and the differences between copper leached at pH 7.0 and 8.5 was insignificant.

Zinc leaching levels were significantly higher at the lower pH for all brasses. As with copper, the difference between zinc leached at pH 8.5 and 7.0 appeared to increase (Appendix Figures F16 to F20) as the percentage of zinc in the alloy increased. The largest difference was seen with the free-cutting brass (which contained the most zinc) and the smallest difference was red brass C83600 which contained the least zinc.

Lead coupons

The pH 7.0 test water was more corrosive towards lead than at pH 8.5 (Appendix Figure F21). At pH 7.0, lead levels were highest at the start of the study and gradually dropped with time. The lead levels never appeared to stabilize, even by the completion of the test run at 160 days. At pH 8.5, lead levels appeared to stabilize after only approximately 25 days. At the end of the test runs, lead levels were more than 200 μg/L higher than observed at pH 8.5. The results show that pH clearly impacts lead solubility of pure lead.

Copper coupon

The pH 7.0 test water was also more corrosive toward copper (Appendix Figure F22). The leaching pattern over time was unlike lead in that copper levels started low (approximately 1 mg Cu/L) but increased rapidly to a peak at approximately 4 mg/L by 40 days. This pattern was similar to that observed with copper leached from the brass for the same reasons. The copper leaching trend proceeded to drop gradually for the remainder of the study, falling back to the original level of about 1 mg/L in 160 days. It appeared that at the termination of the test run, the copper levels were still decreasing and further time would be required for copper levels to stabilize. This showed that it took a greater amount of time for copper concentrations leached from new copper surfaces to stabilize under exposure to corrosive conditions.

Increasing the pH from 7.0 to 8.5 had a much different effect on the copper leached from pure copper. The copper levels were significantly lower under these conditions and the trends followed a different pattern. Copper levels started out at about 0.5 mg/L and gradually dropped to approximately 0.25 mg/L by 120 days. It appeared that by 80 days into the test run leaching trend had leveled off. The leaching trend was also smooth in comparison to the lower pH trend.

Zinc coupons

The lowest pH (7.0) test water was also the most corrosive towards pure zinc (Appendix Figure F23). At pH 7.0, zinc levels started high (approximately 9 mg/L) then dropped rapidly to about 4 mg/L by 20 days. The levels increased slightly to about 4.5 mg/L after about 60 days, then leveled off for the remainder of the test run at about 4.5 mg/L. Zinc values, however, were not smooth, fluctuating randomly about 4.5 mg/L.

Lower zinc levels were observed at pH 8.5. The zinc levels started out quite high, but decreased rapidly over the first 30 days, falling to a more gradual decreasing slope. The trend appeared to level off at about 60 days, to a concentration of about 0.25 mg/L. The curve was relatively smooth.

60:40 tin:lead solder coupons

Solder coupons exhibited unexpected leaching trend results (Appendix Figure F24). Initially, over the first week of the study, the coupon exposed to the pH 7.0 test water leached the most lead. The lead levels dropped off rapidly, then leveled off and stabilized after about 70 days. High levels were also observed initially with the pH 8.5 test water, however, not to the degree observed with the pH 7.0 water.

Impact of orthophosphate on the metal leached from coupons

Extraction water quality

Tables 5c to 5e summarize the quality of extraction water used in test runs 3, 4, and 5. With the exception of sulfate in run 5 and phosphate, water qualities were generally similar in composition. The pH was tightly maintained at 7.5 because orthophosphate is most effective at reducing lead solubility in a pH range of approximately 7.3 to 7.7. Orthophosphate averaged 2.8, 0.46, and <0.02 mg PO_4/L in test runs 3, 4, and 5, respectively. A non-zinc containing orthophosphate chemical was used to avoid potential questions, confusion, and interpretation difficulty associated with separating the well-documented influence of orthophosphate and potential impact of zinc, as suggested by some, on metal leached from the brasses.

Brass coupons

Figures 9 to 14 show the effect of orthophosphate on lead leached from the brass coupons. The most notable impact of orthophosphate on lead levels was on the rate at which lead was reduced. Orthophosphate reduced the time (days) for lead levels to stabilize. The highest orthophosphate dose (2.8 mg/L) caused lead levels to drop rapidly and stabilize in all brasses. The lead levels by the end of the test run were generally low (< 10 μg/L) and in some cases less than analytical detection limits (2 μg/L). Reducing the orthophosphate concentration to 0.5 mg/L, increased the time for lead levels to stabilize by as much as 50 days, but had little impact on final lead concentrations. In most cases, lead levels leached from coupons exposed to the control water (0.0 mg PO_4/L) appeared to still be decreasing after 140 days. Interestingly, lead levels leached from the yellow and free-machining brasses eventually dropped to approximately the same stabilized lead levels observed in the test runs where orthophosphate was added (Figures 9, 13, and 14). Although this observation did not quite hold true for all of the red brasses (Figures 10 to 12), their lead leaching trends were still decreasing at the termination of the test run. If the test runs were carried out longer, lead levels may have eventually dropped to the stabilized levels observed in the phosphate test runs. It was concluded that the biggest role of orthophosphate on lead leached from brass was as an "aging accelerator".

The alloy composition also impacted the amount of time required for lead levels to stabilize. Generally, the more lead in the alloy, the longer time required for lead levels to

stabilize. Brass composition had little impact on final lead levels (levels observed at the termination of the test runs) when orthophosphate was present at 0.46 and 2.8 mg/L.

Lead levels measured when phosphate was present were similar to those observed for the same alloy at pH 8.5. Based on results of the control test run, the impact of pH (7.5 versus 8.5) on lead levels leached from the brasses lessened relative to pH 7.0 test run results.

The impact of orthophosphate on pure lead was different than the brasses. Lead response was more typical of that described by lead solubility relationships.[14,67,68] Orthophosphate clearly reduced lead levels leached from pure lead (Figure 15). The highest orthophosphate dose was most effective in reducing lead concentration, lowering lead levels to near 100 μg/L by the end of the test run. The 0.5 mg/L orthophosphate dose was also effective at reducing lead levels, but to a lesser degree than the higher orthophosphate dose (final lead levels were about 200 μg/L). This result demonstrated the importance of sufficient orthophosphate dosing in obtaining optimal lead control benefits. Without orthophosphate addition, lead levels were near 300 μg/L at the end of the test run (130 to 140 dasys). Orthophosphate concentration did not have the same impact on stabilization time of the brasses. Orthophosphate had an immediate impact on lead reduction and stabilization, while without orthophosphate lead levels started high and dropped to stabilized levels by approximately 60 days.

Similar observations were made with lead leached from the 60:40 Sn:Pb solder coupon (Figure 16). The final lead levels were not as high and the benefit of orthophosphate was not as dramatic, but trends and patterns were nearly identical to the results of the pure lead test.

The impact of orthophosphate on copper leached from the brasses was more difficult to interpret (Figures 17 to 22). Copper levels leached from red brass C83600 and C84400 were 0.2 to 0.4 mg/L lower when orthophosphate was present. Copper leached from similar copper containing C84500 brass, however, was not impacted by orthophosphate. Copper leached from the yellow brasses and the C36000 coupons was lower by as much as 0.1 mg/L when orthophosphate was not present. Orthophosphate had little impact on copper leached from pure copper (Figure 23). The results are confusing but do suggest that in some cases orthophosphate (at pH 7.5) can provide some benefit in reducing copper dissolution from brass. Some insight into the observations can be found in recent work suggesting that orthophosphate is most beneficial at reducing copper levels at lower pH values (< 7.0) on new materials.[60] The research shows that minimal reduction in copper solubility at pH 7.5 is realized from the addition of orthophosphate.

The impact of orthophosphate on copper at pH 6.5 was briefly explored as an extension to test run 5. After 142, days the pH was lowered from 7.5 to 6.5 for 23 days. Copper leached from the pure copper coupon immediately increased to more than 1 mg/L and averaged 1.2 mg/L over the period. At 182 days, 3.0 mg/L orthophosphate was added. The run was continued for an additional 17 days. The copper levels were initially sporadic, jumping between 0.67 and 2.3 mg/L, but averaged only 0.36 mg/L for the last two sampling events. This brief investigation was

not conclusive, but certainly suggests that more exploration into the impact of orthophosphate on copper corrosion is needed.

The impact of orthophosphate on zinc leached from the brasses was also difficult to interpret (Figures 24 to 29). Zinc leaching trends from brass coupons C36000, C83600, and C84400 showed small reductions in zinc levels when orthophosphate was present, and the remaining brasses exhibited no benefit. Red brasses did not benefit more from orthophosphate than the yellow brasses. Orthophosphate appeared to extend the time for zinc levels to stabilize, but did not impact final zinc concentrations (Figure 30).

Impact of stagnation time on metals leached

The effect of stand time on metal levels leached from the coupons was investigated by comparing 24- to 72-hour standing samples. As a point of clarification, the same coupon was used for both test times; 24-hour samples were taken on weekdays and 72-hour samples were taken over the weekend. Rather than discussing the influence of stand time on metals leached from each brass, one representative red (C84500) and yellow (C85400) brass will be used to demonstrate the general trends of each brass type group.

At pH 7.0 and 8.5, lead leached from red brass, coupon C84500 appeared to be slightly higher (10 to 25 μg/L) after 72 hours while yellow brass was not affected by stand time (Figures 31 and 32). Lead leached from the pure lead coupons in pH 7.0 water were clearly impacted by stand time, leaching as much as 100 μg/L more lead after 72 hours standing than 24 hours (Figure 33). At pH 8.5, however, no difference between 24- and 72-hour standing samples was observed (not graphically represented), suggesting water quality plays an important role on the rate of lead dissolution.

At pH 7.0, copper leached from red brass was generally higher (by as much as 0.5 to 1.0 mg/L) after 72 hours (Figure 34). This trend was also observed with the pure copper coupon (Figure 35). Yellow brass was affected by stand time in a completely unexpected way. Initially copper levels were lower at 72-hour than 24-hour standing time, however after 125 days the trend reversed (Figure 34). At pH 8.5, stand time had a small impact on copper levels. 72-hour samples tended to be 0.01 to 0.05 mg Cu/L higher at 72 hours for both brasses (not graphically represented). Once again, copper leached from the pure copper coupon after 72 hours followed the same pattern as 24 hours.

At pH 7.0, zinc leached from red brass was significantly higher (by approximately 1.0 mg/L) after 72 hours, more than doubling the zinc concentration (shown in Figure 36). Yellow brass was also effected by stand time in the same fashion but at a higher scale. By the end of the study, zinc levels leached from the yellow brass in 72 hours were more than double the levels at 24 hours (approximately 2.0 mg/L to 4.0 to 4.5 mg/L). Very small differences between 24- and 72-hour zinc concentrations leached from pure zinc were observed (shown in Figure 37). During the first 125 days, zinc was actually lower in 72 hours, however, the trend reversed thereafter.

Differences in trends never exceeded 0.25 mg Zn/L. Figure 38 shows that at pH 7.0, yellow brass leached the same amount of zinc as the pure zinc coupon at 72 hours (which is not different from 24 hours). This suggested that the dissolution rate of zinc from brass was slowed by factors such as surface area or alloy structure. At pH 8.5, stand time also had a significant impact on zinc levels of coupon C85400 (shown in Figure 39) but at a lower magnitude than pH 7.0 (approximately 0.15 mg/L). The red brass did not appear to be significantly impacted by pH. The pure zinc coupon was not affected by stand time at pH 8.5.

A preliminary study was conducted to further address the impact of stand time on the metals leached from brass alloys. The study, operated identically to protocol previously established, used test water described under the NSF faucet test protocol (pH= 8.19, DIC= 113.6 mg C/L, alkalinity= 501.7 mg $CaCO_3$/L, free chlorine= 1.9 mg/L, and sodium= 220.0 mg/L). Two brasses, yellow brass C85200 and red brass C84400 were each evaluated in duplicate. Stagnation profiles were developed from samples taken following 30 minutes, 1, 2, 4, 6, 8, and 15 hours. Lead results suggested that stagnation profiles varied with alloy composition. Figure 40 shows that lead levels reached maximum levels as early as 30 minutes (following 2 months of operation or "conditioning") for the yellow brass. This observation may have been associated with the overall low amount of lead leached from the alloy. Figure 41 shows that lead leached from red brass, however, was very much impacted by stagnation time. Lead levels appeared to still be increasing up to 15 hours. These results suggest that the dissolution rate of lead is slowed down by factors such as surface area or diffusion barrier films. These observations agree with observations made between 24- and 72- hour standing samples.

Stagnation profiles for copper leached from both brasses (Figures 42 and 43) show that the most rapid increase in copper levels occurred over the first 6 hours. The copper levels appeared to still be slightly increasing after 15 hours. Similar observations were made with zinc stagnation profiles, but continuing increases of zinc levels after 15 hours was not as apparent (Figures 44 and 45).

The results of this portion of the study showed that the dissolution rate of metals from brass and pure metals is dependent on a combination of factors. Alloy characteristics and water quality are clearly important. In terms of corrosion or dissolution rate, brasses likely will differ from pure metals based on diffusion considerations. It is also reasonable to assume that for a given corrosion rate, longer stand times would be required to reach higher metal levels in more corrosive waters. But the question arises as to what happens to corrosion rates under changing water qualities. For example, how does a change in pH, and subsequent distribution in chlorine species, affect corrosion rates? Further, under typical drinking water conditions (and in this study), two oxidants are present, dissolved oxygen and a disinfectant. How do the oxidants interact and what happens to the corrosion rate when one is depleted? If both are depleted, dissolution would cease. On the other hand, if an unlimited supply of oxidant and time were available, metal levels leached from brass coupons would theoretically reach levels leached from the pure coupons and chemical equilibrium. Unfortunately, it was impossible to determine oxidant levels in the cells at the end of stagnation periods due to the small sample volumes used.

But, one could theorize how the results would be affected if one or both oxidants were depleted. Clearly the results pointed out the complexities of the role of stagnation time, and oxidant type and levels on metal levels. Also, the results demonstrated the difficulty associated with comparing metal levels measured in corrosion control studies and field samples under non-equilibrium conditions to each other and solubility model predictions based on equilibrium conditions.

Evaluation of low-lead alloy

An evaluation of the lead and other composite metals leached from a low-lead containing brass[a] was made during test run 5 (pH=7.5). The nominal composition of the alloy as reported by the manufacturer was 85% copper, 4% tin, 3% bismuth, and less than 0.2% lead. Figure 46 shows that despite low lead composition, significant amounts of lead leached from the coupon initially. However, within a short period of time, lead levels dropped to near instrumental detection limit (2 μg/L). No detectable bismuth was leached from this coupon at any stage of the test run. The instrumental detection limit for bismuth was 0.025 mg/L.

Impact of sulfate on copper dissolution

Although the impact of sulfate on copper corrosion was not stated as an objective of this study, background sulfate levels, theoretical considerations, and observations made over the test runs warrants brief discussion. Figure 47 (taken from Schock et al.[60]) shows copper levels (after concentrations were considered stable) leached from the pure copper coupons during all 5 test runs superimposed on a solubility diagram. The theoretical curves correspond to average DIC and orthophosphate concentrations during the respective runs. The figure also includes the computed solubility line for $Cu_4(OH)_6SO_4 \cdot H_2O$, which is in closer agreement to the experimental data at higher pH values. Although this observation was not made under controlled experimental conditions, it does suggest that sulfate may impact copper dissolution. Clearly more experimentation needs to be done to clearly identify the role of sulfate on copper corrosion.

DISCUSSION AND CONCLUSIONS

The results of this study showed that the amount of lead leached from brass was generally dependent on the amount of lead in the brass from pH 7.0 to 8.5. The more lead in the alloy, the greater amount of lead leached from the alloy. In nearly all cases, the highest lead levels leached from the brasses during the first two weeks of exposure and decreased at the fastest rate during this period. New coupon surfaces and a thin layer of excess lead smeared over the coupon surface as a result of coupon machining were believed to contribute to this observation. At pH 8.5, the concentration of lead leached from the brasses "leveled off" after 60 to 70 days. Under more corrosive conditions (pH 7.0), lead levels were still decreasing slightly at the end of the test run (155 days). The pure lead coupon leached considerably more lead than the brasses which

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[a] Nibco, Inc., Elkhart, IN.

suggested that corrosion rates of brass were hindered. Slight fluctuations in leaching trends were often associated with pH fluctuations in the extraction water.

The impact of pH on the amount of lead leached from brass was dependent on the amount of lead in the brass. In higher lead containing red brasses, more lead leached from the brasses at pH 7.0. This observation followed expected lead solubility response to pH and was also observed with the pure lead coupon. As the amount of lead in the alloy decreased, however, the impact of pH on the amount of lead leached from the alloy decreased to the point were there was little or no impact on the yellow brasses.

Orthophosphate tended to act as an "aging accelerator" in that it's most significant role on lead leached from brass was to reduce the time required for lead levels to stabilize. This was clearly the case with the yellow brasses and was believed to eventually be the case for red brasses given longer time or usage. Lead levels dropped and stabilized most rapidly with 3 mg/L orthophosphate followed by the 0.5 mg/L dose, and the 0 mg/L dose. The pure lead and solder coupons responded to orthophosphate more according to solubility predictions (orthophosphate reduced final lead levels). Lowest lead levels were observed at 3 mg/L, followed by 0.5 and 0 mg/L. The amount of lead in the alloy impacted the time required for lead levels to level off as well. As the amount of lead increased, the trends shifted to the right or took longer to stabilize. The role of alloy composition on final lead levels also decreased when orthophosphate was present.

The amount of copper leached from the brasses at pH 8.5 was also clearly related to alloy composition. It appeared that red and yellow brasses acted as two groups. The red brasses leached the most copper and by the end of the study were leaching as much copper as the pure copper coupon. It was hypothesized that at some critical copper content, the alloy takes the leaching properties of pure copper. Copper levels were relatively stable throughout the entire study. At pH 7.0, copper levels were sporadic and difficult to order. Copper levels increased over the first 60 days of the study and leveled off. Once again, some red brasses leached as much copper as the pure copper coupon. The amount of copper leached from the alloys was strongly influenced by relatively small fluctuations in pH.

The impact of pH on copper levels increased with increasing pH. Largest differences in copper levels between pH 7.0 and 8.5 were observed with pure copper and the red brasses. The difference decreased as the copper composition decreased. Lower copper levels were observed at pH 8.5.

The impact of orthophosphate was obvious. In some cases, copper levels leached from some alloys when orthophosphate was present were slightly lower, however the opposite observation was made in other cases. It was believed that pH 7.5 was borderline to receive copper benefits with orthophosphate. Preliminary investigation suggested that orthophosphate may provide benefit to copper corrosion at pH 6.5.

The amount of zinc leached from the brass coupons at pH 8.5 and 7.0 was dependent on the amount of zinc in the alloy. The highest zinc levels were observed at the start of the study, dropping slightly to approximately 60 days were leveled off. By the end of the test runs yellow brasses leached more zinc than the pure zinc coupon. This suggested that critical zinc composition exists when the brass takes on the leaching properties of pure zinc. Zinc levels were sensitive to pH fluctuations.

The impact of pH on zinc levels increased with increasing pH. Largest differences in zinc levels between pH 7.0 and 8.5 were observed with pure zinc and the yellow brasses. The difference decreased as the zinc composition decreased. Lower zinc levels were observed at pH 8.5.

Orthophosphate did not appear to significantly impact zinc levels. In some cases, zinc levels were slightly lower when orthophosphate was present. However the opposite observation was made in other cases.

The impact of stagnation time based upon 24- and 72-hour standing sample comparisons showed that there was little impact on lead leached from red brasses and no visual impact on the yellow brasses. There was, however, significantly more lead leached from the pure lead coupon after 72 hours than at 24-hours at pH 7.0 only. In the case of copper, higher levels leached from the red brasses and pure copper after 72 hours at pH 7.0. Stand time did not impact copper leached from the yellow brasses. Little difference between copper levels leached from all of the coupons was observed at pH 8.5. Zinc leached from the brass coupons was most strongly impacted by stagnation time. The largest differences were observed at pH 7.0. The pure zinc coupon was not impacted by stand time. The impact of stagnation time decreased at pH 8.5. The results clearly showed that the impact of stagnation time was dependent on the alloy composition and "corrosiveness" of the water. Stagnation profiles conducted over 15 hours also suggested that the alloy composition can also influence profiles.

How does data collected in this study apply to the "real world"? The data suggest that when all other variables remain constant, the amount of lead leached from brass plumbing products such as faucets can be reduced by reducing the amount of lead in the alloy. Highest lead contributions will occur when the brass devices are newly installed. Appropriate precautions can be taken to limit the lead exposure during this time such as flushing the device before consuming the water. Although lower-lead containing brasses are a benefit in that they leach less lead, zinc and copper dissolution must also be considered. Of particular concern is susceptibility of higher zinc-containing yellow brass alloys to dezincification and associated plumbing failures. In addition casting and machining considerations which were not specifically addressed in this report must be considered. Truly low-lead containing brass alternatives to leaded brass such as the bismuth brass evaluated in this study may serve to eliminate the lead contribution by brass. Other issues such a production cost and practicality, and the dissolution of bismuth are still issues to resolve. Orthophosphate appears to be effective at reducing lead levels when brass materials are relatively new. The benefit appears to decrease with age and as other mechanism become more

predominant. The exposure time required to receive the greatest lead exposure from brass depends on the alloy composition and water quality. In "corrosive" water and with red brasses, highest lead levels may not be obtained until beyond 15 hours of stagnation. Lead and Copper Rule requires at least 6 hours standing time, which does not necessarily represent the worst case scenario. In addition poor metal level reproducibility in samples taken from the same location could be attributed to differences in stagnation time.

It is important to stress that the conclusions of this study were based on tightly managed laboratory experiments with identically machined coupons in several closely controlled waters using consistent, reproducible operating procedures. Extrapolation of the results to field conditions where alloys are subjected to the distribution system should be done with some caution. For example, brass faucets encounter mechanical operation which may effect metal levels by influencing leaching trends or physically dislodging protective films. Physical features of alloy fixtures are also likely to play a role in the degree which metals leach from them in the distribution system. While results of this study suggest that reducing the amount of lead in a brass faucet or other plumbing fixture or valve will reduce the lead levels at the tap, the significance of the reduction will likely depend on the role of these other parameters.

FUTURE NEEDS

More research is needed on exploring the degree variables other than metal solubility influence the metals leached from alloys. Specifically, the variables that should be studied are: alloy machining and finishing techniques; faucet structure; water flow pattern, velocity, and pressure through faucet structures; mechanical operation; fixture age; and stagnation time. Kinetic issues related to the impact of oxidants (type and concentration) on metal dissolution rates also needs to be further addressed. This study focused on the impact of 24- and 72-hour stand times on metal levels, but more work at lower stand times would be more relevant to home occurrence of metals in tap water samples and the Lead and Copper Rule monitoring program.

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