

Evaluation of Multiple Analytical Techniques in the Study of Leaching from Brass Fixtures

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Abstract

Lead has been found to leach from brass plumbing fixtures. Since leaching into drinking water might pose a health hazard, the Canadian Standards Association (CSA) carries out routine leaching tests on plumbing fixtures. Some fixtures have been found to be significant lead sources and the data suggests an initial leach rate, increasing somewhat with time followed by a long decline. Several analytical techniques were used to identify the distribution of lead in brass as well as the corrosion processes involved in lead leaching. In high zinc brasses, it was found that dezincification contributes significantly to the lead leach rate.

Keywords: Brass, Pb, De-alloying, Intergranular Corrosion, Passivity

Résumé

On a trouvé que le plomb est relâché de la plomberie de laiton. Puisqu'un tel relâchement dans l'eau potable peut poser un risque à la santé, l'Association Canadienne de Normalisation (ACN) conduit des tests de mesure routiniers sur les équipements de plomberie. Certains d'entre eux ont été identifiés comme des sources significatives de plomb et les données suggèrent un taux initial de relâchement qui semble augmenter avec le temps et qui est suivi d'un long déclin. Plusieurs techniques analytiques ont été utilisées pour identifier la distribution du plomb dans le laiton ainsi que les processus de corrosion impliqués dans le relâchement du plomb. Dans les laitons à haute teneur en zinc, nous avons trouvé que la dézincification contribue significativement au taux de relâchement du plomb.

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Introduction

Since the introduction of plumbing, lead contamination of drinking water has been a problem (1). While the first plumbing fixtures were manufactured from lead, brass has now become the most widely used alloy. The Canadian Standards Association has supplied data from Pb leaching tests which suggests at least two mechanisms are active during leaching.

Of all brasses used, leaded brasses (~7-1 % Pb) are the most widely utilized because they are easier to machine. The increased machinability comes from the presence of lead inclusions in the alloy that act as a cutting tool lubricant during manufacturing (2, 3).

Although brass generally has excellent corrosion resistance, even very small amounts of Pb leached from the alloy can be considered to be toxic (1). Lead poisoning mainly affects children; severe lead poisoning can lead to brain damage (4). The levels of Pb in blood required to cause symptoms are as low as 0.1 ppm (5). Much research has been done to determine the leaching mechanism of Pb and other metals from brass so that a way of inhibiting their removal could be determined. Agencies such as The Canadian Standards Association (CSA) and the Environmental Protection Agency (EPA) of the United States of America have devised strict guidelines for the amount of Pb that can be leached from brass plumbing fixtures to ensure safe levels in drinking water. The current maximum concentration of leached lead allowed by the CSA in drinking water is 0.015 ppm (6).

Lead is thought to leach into drinking water from brass by galvanic corrosion (wet corrosion). One theory is that the anode half reaction is the oxidation of lead while the cathode half reaction is the reduction of dissolved oxygen in water to form hydroxide. This electrochemical reaction forms lead hydroxide ($\text{Pb}(\text{OH})_2$) which is soluble in water under both slightly acidic or basic

conditions (6). Although this report discusses lead and lead leaching, it should be noted that other forms of corrosion can effect brass (leaded or not) causing elements such as Cu, and Zn to be leached into drinking water as well as the eventual failure of the plumbing fixture (7). Both Cu and Zn are found naturally in the body but high concentrations can be considered toxic and the CSA has developed maximum allowable concentrations in drinking water of 13 ppm for Cu and 30 ppm for Zn (8). Although the specific leaching of high concentrations of Cu from brass is not chemically favoured since Cu resists oxidation, Zn can be readily corroded and leached when its overall concentration is greater than 15 % by weight (7). The method by which Zn corrodes is referred to as dezincification which is a form of de-alloying. Two theories have been developed to explain its occurrence. The first suggests that Zn is selectively leached from the alloy leaving a porous metallic Cu residue while the second suggests that all of the brass dissolves and the Cu immediately re-deposits at sites close to where the brass was removed (7).

The CSA used a standard leach test to determine the amount of Pb leached from brass(9). This is a “dump and fill” process that is repeated over a 19 day period with the water being analysed on days 3-5, 10-12, and 17-19. The analysis for Pb is generally performed using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) or Atomic Absorption Spectroscopy (AAS). This test method is based on the American National Standards Institute (ANSI)/National Sanitation Foundation (NSF) 61 Section 9 Standard.

During this project, the CSA tested two samples (A and B), which had been treated using a base bath by the manufacturer to remove as much Pb located at the water contact surface as possible prior to testing. Once the samples were received, they were combined to form a single faucet set before the test was performed (figure 1). The water used during the CSA test was deionised and contained 0.01 mol sodium bicarbonate, 0.0003 mol sodium hypochlorite and 0.00013 mol HCl with the resulting pH of the solution being 8 (mimics normal tap water). This water tends to be more corrosive since the higher concentrations of carbonate species (CO_3^{2-}) normally found in tap water act to form corrosion passivity layers (6). Four additional untested brass samples were included in the study (C to F) both as controls and to provide further data on brass composition and structure.

Pb leaching results from sample A and B found by the CSA are presented in figure 2. As is indicated in the graph, the concentration of leached lead declined rela-

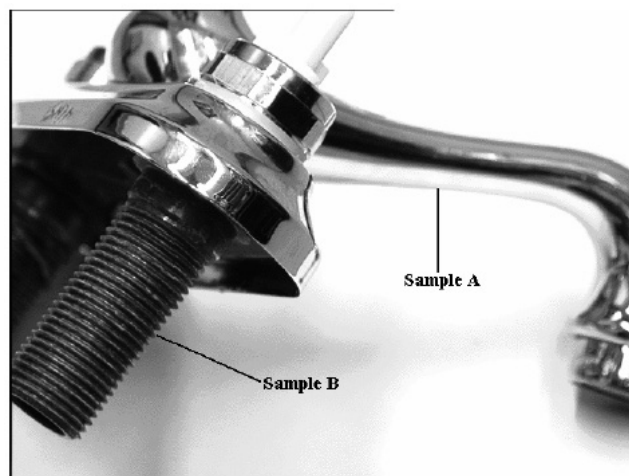


Figure 1: Sample A and B used during leach test.

tively linearly with a concentration spike being observed on day 11 ± 1 . After the spike in concentration occurred, the amount of leached Pb continued to decline. It should be noted that at no time did the quantity of leached Pb exceed the maximum amount allowed by the CSA.

This paper outlines the use of selected analytical techniques to determine the mechanism by which Pb leached from brass. The techniques that will be discussed include: optical microscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), electron microprobe-wave dispersive X-ray spectroscopy (microprobe-WDX), and inductively coupled plasma-mass spectrometry (ICP-MS). The role of dezincification inhibitors in limiting the amount of Pb leached from brass will also be discussed.

Experimental

Materials Tested

Table 1 lists observations of each of the six samples tested after being received from the CSA.

Procedures

When received, samples of appropriate size for analysis by SEM, microprobe, optical microscopy and ICP-MS were cut from the fixtures using a hacksaw. The areas that were cut were selected based on visual signs of corrosion, if corrosion was not apparent in the sample then areas were selected based on their geometry.

After cutting, the cross sectioned samples to be analysed using SEM, and microprobe were mounted in an epoxy resin and allowed to cure in air at room temperature. Once the resin had set, the samples were polished using sandpapers of various grits (180, 320, 500, and

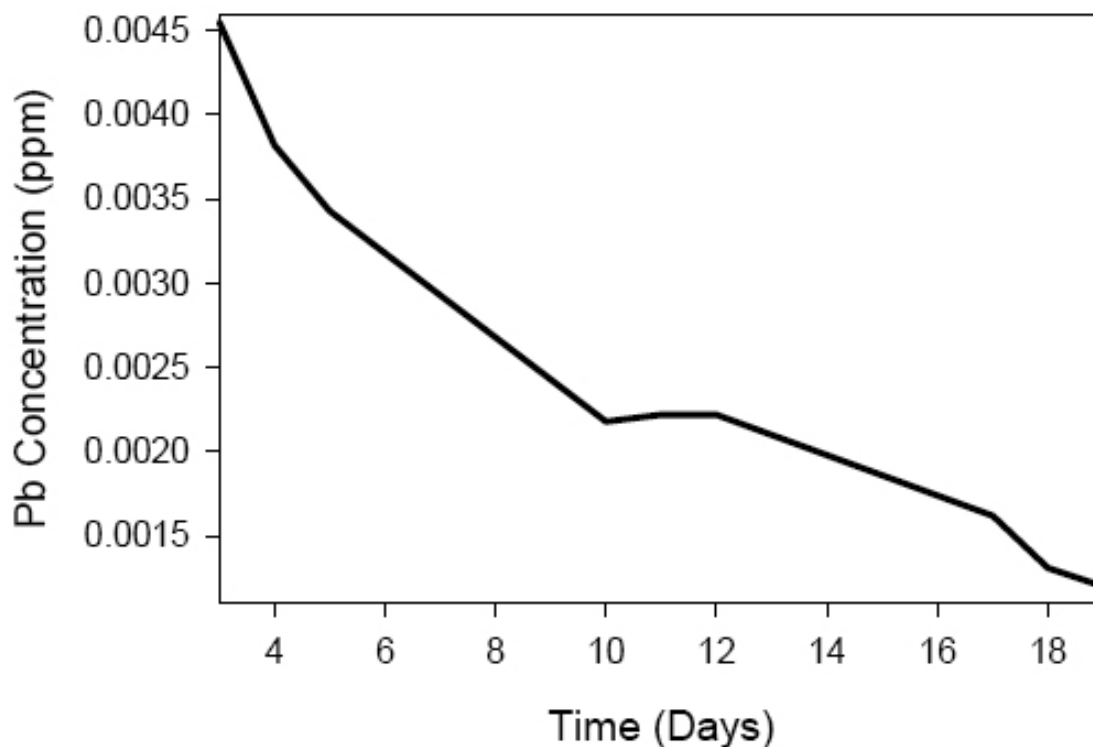


Figure 2. Results found during the CSA leach test of samples A and B. Results were determined using ICP-MS.

Table 1: Physical observations and information from each sample after being received from the CSA. As is apparent, many observations can be made by visual inspection which can help lead to the identification of possible corrosion processes that could affect the sample.

Sample Identification	Fabrication Process	Underwent CSA Leach Tests	Colour of exterior	Coating on Outside of Material Present	Roughness of Water Contact Surface
A ‡	Permanent mould	Yes	Silver	Yes (Ni/Cr) ¶	Slightly rough
B*	Sand cast	Yes	Dark yellow	No	Rough
C*	Sand cast	No	Dark yellow	No	Very rough
D †	Forged	No	Light yellow	No	Smooth
E ‡	Permanent mould	No	Bright yellow	No	Slightly rough
F §	Tube forming	No	Light yellow	No	Smooth

* Samples B and C both represent fixtures used to connect a faucet containing two separate hot and cold water taps to the appropriate water pipes.

† Sample D represents a fixture used to connect a faucet containing a single hot/cold water tap to the water pipes.

‡ Samples A and E both represent faucets.

§ Sample F represents a brass tube used to manufacture faucet spouts.

|| The rougher the surface is, the more surface area is exposed to the water and therefore the more material is available to be corroded.

¶ The composition of the coating was determined by SEM and found to be Ni with a Cr overlayer

1000) and an Engis Kent 3 automatic polishing unit. After polishing, the samples were buffed to produce a mirror finish using $0.3\ \mu\text{m}$ $\alpha\text{-Al}_2\text{O}_3$ and $0.05\ \mu\text{m}$ $\gamma\text{-Al}_2\text{O}_3$ in sequence. When this was complete, samples for optical microscopy (as well as some for SEM analysis) were etched for approximately 30 seconds using an etchant containing NH_4OH , H_2O , 3% H_2O_2 (2:1:1) to reveal the grain structure by promoting attack at the grain boundaries. The epoxy mounted samples to be used for SEM or microprobe analysis were also coated with a conductive medium (C for microprobe, C or Au for SEM) so as to increase the conductivity of the samples.

After sample preparation was complete, etched cross sectioned samples were examined using a Zeiss Axioplan optical microscope with a Hitachi HV-C20 digital camera and Northern Eclipse imaging software at various magnifications (50, 100, 200, 500, and 1000 \times .) This analysis was performed to determine the grain structure of each sample and to look for any evidence of microstructural defects or corrosion of the samples that had been tested by the CSA.

After initial optical examination, SEM-EDX was performed on all samples to study their grain structure, corrosion processes (if any), and composition. Samples were examined using SEM-EDX since it is a fairly easy instrument that can be used to get a detailed picture of the composition of the sample of interest as well as images at very high magnifications.

The SEM used for this project was a LEO Stereoscan 440 Scanning Electron Microscope with a Gresham light element detector and Quartz XOne EDX microanalysis software system. The instrument used a tungsten-hairpin filament electron gun as well as an integrated secondary electron detector. The samples (both cross sections and surface samples) involved in this project were analysed for concentration of Cu, Zn, Pb and any other elements that could be found in various brasses to determine a relative elemental composition. EDX maps were also employed to determine the locations of any inclusions in relation to the water contact surface and the distribution of inclusions throughout the samples. All SEM analyses were performed using a 20 kV accelerating voltage and a magnification appropriate to each sample. The detection limit of the SEM used was 0.5 weight % for all elements.

During microprobe analysis, a Japan Electron Optics Laboratory (JEOL) JXA-8600 Superprobe with four WDX detectors and an accelerating voltage of 25 kV was used. Before use, the instrument was calibrated for Bi, Pb, Cu, and Zn using pure elemental samples of

Bi, Cu, and Zn while Pb was calibrated with $\text{Pb}(\text{CO}_3)$. Images were also taken of each cross sectioned sample using the back scatter electron detector. The detection limit was as low as 0.03 weight % for Cu (0.06 weight % for Pb).

To determine the trace element concentrations in the samples, ICP-MS analysis was performed. Before being analysed, 100 – 300 mg portions of each of the six samples tested were digested in concentrated nitric acid (HNO_3) and then diluted to 50 mL using deionised water. Samples were then given to Ms. P. Edmonds of the London Health Sciences Centre, UWO Campus, for ICP-MS analysis of the trace elements. The ICP-MS used during this project was a Finnigan MAT Element Ultratrace system with a detection limit of 1 ppt (part per trillion).

Results and Discussion

Optical Microscopy

The grain structure of each of the six samples was determined using optical microscopy. Although all of the samples were manufactured from brass, various grain structures were found which were attributed to the use of different solidification rates (10). When rapidly cooled (108 – 106 K/s), a single α phase grain structure can be produced (grains are generally rhombohedral in shape, see figure 3.) At lower cooling/solidification rates ($< 102\ \text{K/s}$), high Zn containing brasses can form an α - β grain structure (Figure 4) where the β phase contains a higher concentration of Zn than the α phase does (10). When a two phase grain structure is formed, the α phase is generally in the form of dendrites (long, thin, sometimes branched grains) that are uniformly distributed in the β phase matrix (does not have grain structure, resembles amorphous material) (10). The formation of the two phase grain structure is thought to involve solute enrichment of the β phase areas by Zn compared to the α phase (10).

Apart from the grain structure, the presence of Pb could be easily determined at moderate magnification since Pb inclusions are blue/grey in colour while the surrounding brass is generally yellow. The evaluation of the cross sections was also able to show the presence of lead inclusions at or near the water contact surface. Inclusions located at the surface are candidates for removal into solution when exposed to drinking water compared to those located well beneath the surface.

Samples A and B showed clear evidence of corrosion. Although areas where Pb was leached were not

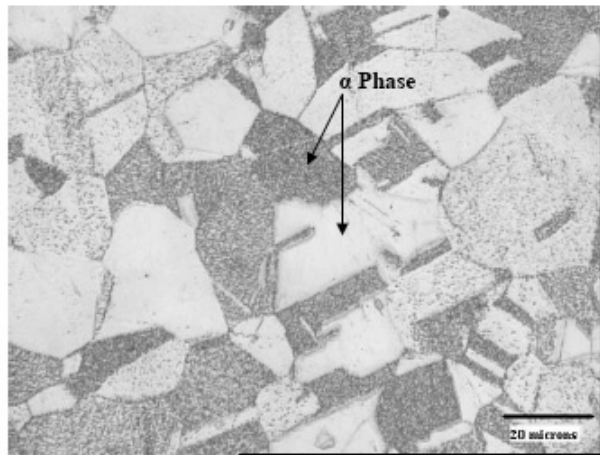


Figure 3: α phase grain structure as found in sample F. Size of scale bar is 20 microns.

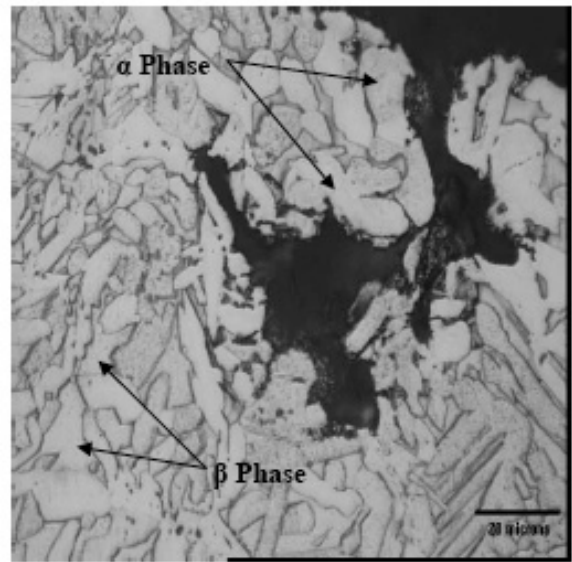


Figure 4: Two phase α - β grain structure as found in sample A as well as area corroded via dezincification. Corroded area is surrounded by α phase dendrites with the β phase having been selectively removed first. Size of scale bar is 20 microns.

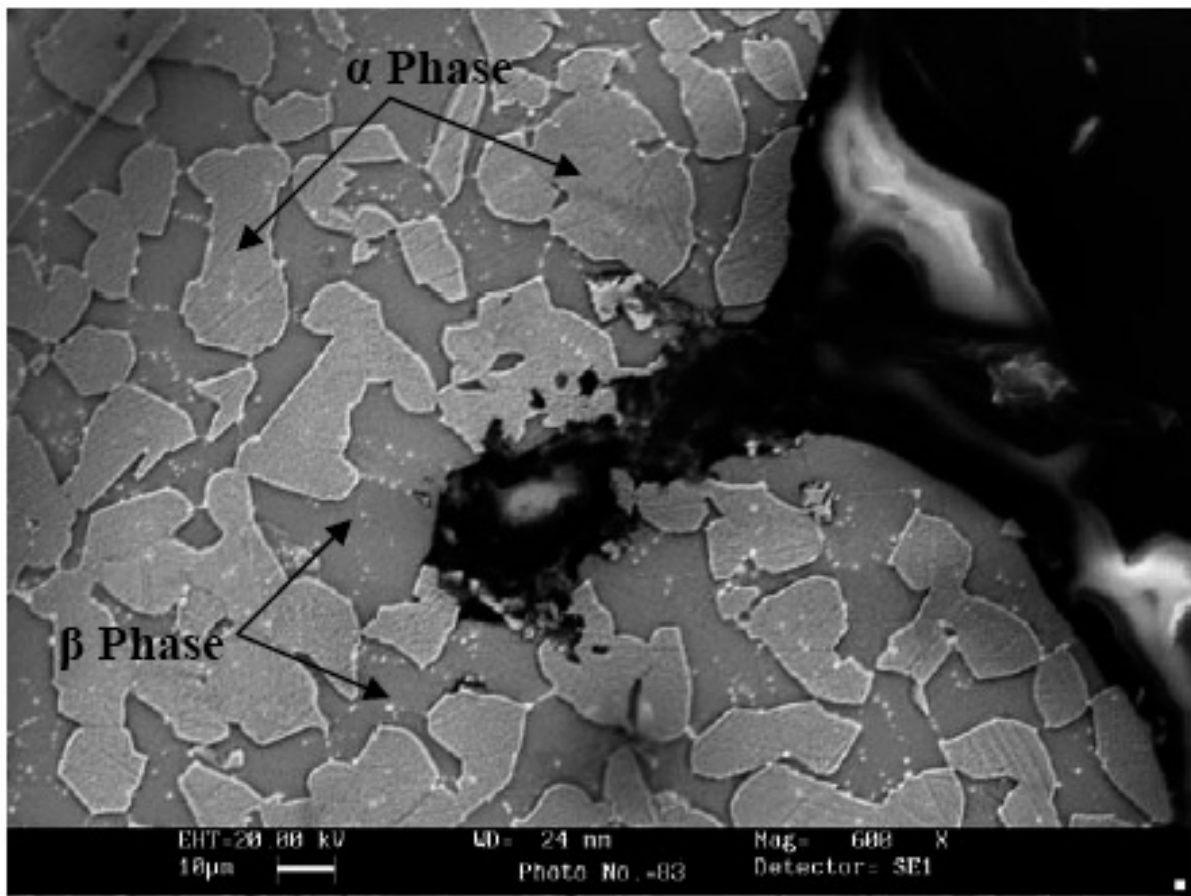


Figure 5. SEM image of a cross section from sample B showing area where intergranular corrosion occurred. Note that the vacant area is surrounded by both α and β phase grains whereas in dezincification corroded areas are generally surrounded only by α phase grains. Size of scale bar is 10 microns.

observed, dezincification was found at multiple sites in both samples (figure 4). Another form of corrosion called intergranular corrosion was found to have occurred in sample B as well (see SEM image, Figure 5). This form of corrosion involves the selective corrosion of grain boundaries allowing the intact grains to be dislodged into solution, leaving vacant areas that are surrounded by both α and β phase grains (10). In both samples, areas with a thickness greater than 70 μm were found to have been affected by at least one type of corrosion. When dezincification or intergranular corrosion occurs, it should be noted that lead inclusions originally located beneath the water contact surface are exposed to water, causing an increase in the concentration of leached Pb. In samples containing a two phase grain structure, dezincification affects the higher Zn containing β phase first with the lower Zn containing α phase being corroded second (11). This last observation is characteristic of dezincification and allows for its easy identification using an optical microscope. Observations of the samples made by optical microscopy are presented in table 2.

SEM Analysis

The majority of this research was carried out with the

use of SEM-EDX analysis due to its ability to collect both qualitative (images using secondary electron detector) and quantitative (EDX-spectra) data. Although it generally has a high detection limit (0.5 weight % in our case), SEM still provides a good picture of the concentration of the major elements and morphology/topography of alloy samples. Table 3 gives the concentrations of all major elements found in the six samples by SEM-EDX analysis. Results were taken from cross sectioned samples at areas away from the water contact surface. The areas analysed were square with dimensions of approximately $150 \times 150 \mu\text{m}$.

All of the samples tested except for C were found to contain high concentrations of Zn ($> 15\%$) indicating that they would be susceptible to dezincification. The analysis also confirmed the presence of inclusions in each of the samples which were originally identified during optical microscopy. The concentration of Pb found in samples A to D were all within the typical range found in most leaded brasses (7-1%) with samples C and D having the highest concentrations. The included matter found in sample E turned out to be Bi rather than Pb. Some manufacturers have recently begun to use Bi rather than Pb to

Table 2: Observations from samples after being observed by optical microscopy.

Sample	Grain Structure	Presence of Inclusions (Type)*	Size of Inclusions	Form of Corrosion Visible	Depth of Corrosion
A	Two phase α - β system	Yes (Pb)	$< 5\mu\text{m}$	Dezincification	$\leq 80 \mu\text{m}$
B	Two phase α - β system	Yes (Pb)	$< 5\mu\text{m}$	Dezincification/ Intergranular	$\leq 70 \mu\text{m}$
C	Single α phase	Yes (Pb)	1 – 15 μm
D	Single α phase	Yes (Pb)	$< 5\mu\text{m}$
E	Two phase α - β system	Yes (Bi)	$< 4 \mu\text{m}$
F	Single α phase	No

*Composition of inclusions was confirmed by SEM and microprobe analysis, see below.

Table 3: Concentration (weight %) of all elements with concentrations greater than 0.5 weight %.

Element	Sample*					
	A	B	C	D	E	F
Cu	60.0 ± 1.5	58.0 ± 1.0	84.0 ± 0.6	58.0 ± 0.6	60.0 ± 0.0	69.0 ± 0.0
Zn	37.0 ± 1.0	38.0 ± 2.3	8.5 ± 0.6	39.0 ± 0.6	38.0 ± 0.0	31.0 ± 0.0
Pb	0.9 ± 0.1	2.2 ± 0.7	4.1 ± 0.2	3.5 ± 0.2	ND	ND
Bi	ND	ND	ND	ND	0.8 ± 0.1	ND
Al	1.2 ± 0.1	0.8 ± 0.3	0.9 ± 0.1	1.0 ± 0.1	1.2 ± 0.1	ND
Sn	ND	ND	2.0 ± 0.2	ND	ND	ND
O	0.9 ± 1.2	0.7 ± 0.8	ND	ND	ND	ND

*An entry of ND, Not Determined, indicates that the value found during analysis was below the detection limit of the instrument.

increase the machinability of brass. It has been found that Bi acts like Pb in brass, segregating as a pure phase within the microstructure causing weak points. As well, Bi is generally considered non-toxic (3). Unfortunately, Bi inclusions have been known to cause increased tool wear, thus raising manufacturing costs (3).

As is apparent from table 3, the presence of O in samples A and B indicates that oxidation occurred when they were exposed to water. It should also be noted that the standard deviation of each of the measured elemental concentrations was larger for the CSA tested samples than for the control samples. This increase could be due to the collection of impurities at the surfaces containing metal oxides. More likely, the difference resulted from inhomogeneous corrosion. It should be noted that the analyses presented in this article are of cross-sectioned samples. Analysis of the surfaces directly exposed to water (water contact surface) showed larger concentrations of oxygen and then are presented in table 3.

When samples A and B were examined by SEM for signs of corrosion, evidence that multiple forms of corrosion had occurred was found as previously discussed. Both samples were found to have undergone dezincification at areas which were in contact with the water. Sample B was found to undergo plug type dezincification (affects localized areas leaving surrounding material unaffected (figure 6) while sample A was found to experience layer type dezincification (affects a broad area, figure 7 – microprobe image) (11). These conclusions were made based on the presence of porous Cu layers at the corroded areas (figure 6, confirmed by EDX maps), areas where the β phase had been removed first leaving the α phase in tact (figure 4), and signs of corrosion in the surrounding brass. Since the testing conditions were the same and the two brass materials were found to contain approximately the same concentrations of Cu and Zn (see table 3), the differences in corrosion behaviour could be due to elements present with concentrations below the detection limit of the SEM used. These elements and their role in altering the type of corrosion that occurs are reported in the ICP-MS results section.

Apart from dezincification, SEM imaging of sample cross sections showed direct evidence that wet corrosion of the Pb inclusions had occurred. Empty pores found at the surface were found to contain no or very little Pb. This observation is consistent with wet corrosion where Pb is oxidized and removed leaving the surrounding Cu-Zn system intact.

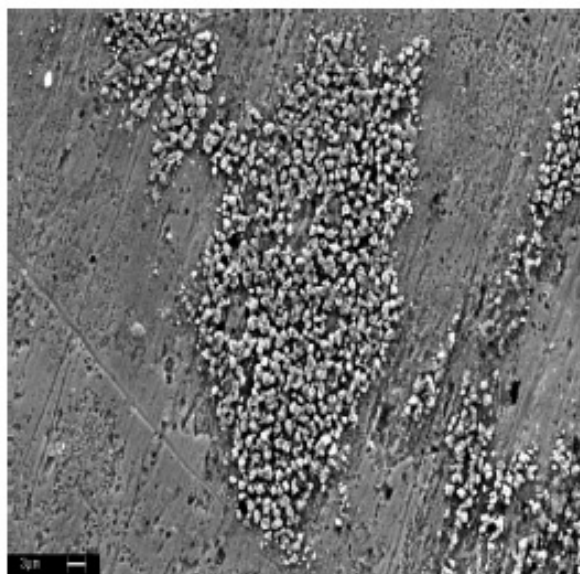


Figure 6: SEM image of water contact surface of sample B after leach test performed. Evidence that plug type dezincification had occurred during testing was found and is indicated in the image as the porous region. Size of scale bar is 3 microns.

Microprobe

The microprobe results are summarized in table 4. The detection limits were determined during calibration of the instrument using appropriate standards. The results are in good agreement with those obtained using SEM-EDX (particularly for Cu and Zn) and provided confirmation of the identity of inclusions. The results for Pb and Bi differed from the values found by SEM-EDX due to the smaller volume analysed by microprobe compared to SEM since the dispersion of the inclusions in the brass was found to be more heterogeneous than homogeneous (the heterogeneous dispersion of the inclusions in the material also accounts for the large error found for the Pb concentration from sample C). The detection limit was at least five times smaller than that for SEM, making it an extremely sensitive technique. This being said, SEM-EDX is still a more robust technique than microprobe-WDX due to its ability to collect high magnification images, EDX spectra, EDX maps with low acquisition times and to determine the concentration of more than four elements at any one time.

Figure 7 is an image of sample A taken using the back scatter electron detector. This particular image shows the large surface of sample A that was corroded by layer-type dezincification as well as the presence and location of Pb inclusions (white spots). Many of the Pb inclusions normally located beneath the water contact surface of the brass came into direct contact with the water after

Table 4: Microprobe-WDX results for all six samples. Values are reported in weight % and the detection limit for each sample is listed in brackets beside the results.

Sample	Element*					Main Component of Inclusions†
	Cu	Zn	Pb	Bi		
A	61.1 ± 0.49 (0.03)	37.5 ± 0.45 (0.03)	1.38 ± 0.21 (0.07)	ND (0.08)		Pb/67.0 %
B	57.8 ± 0.67 (0.03)	41.5 ± 0.60 (0.03)	0.70 ± 0.08 (0.07)	ND (0.08)		Pb/85.3 %
C	90.2 ± 1.72 (0.03)	8.59 ± 0.22 (0.03)	1.20 ± 1.56 (0.06)	ND (0.09)		Pb/93.0 %
D	59.4 ± 0.35 (0.03)	39.5 ± 0.17 (0.03)	1.12 ± 0.28 (0.07)	ND (0.08)		Pb/83.0 %
E‡	56.6 (0.03)	43.4 (0.03)	ND (0.06)	ND (0.09)		Bi/87.7 %
F§	69.0±0.15 (0.03)	30.9 ± 0.15 (0.03)	ND (0.06)	ND (0.09)		None

* A value of ND represents Not Determined, ie. the results were below the detection limit of the instrument.

† The diameter of the electron beam was larger than the inclusion allowing for material directly surrounding the inclusions to be analysed at the same time as the inclusions resulting in a lower concentration of the included matter being determined than is actually present.

‡ Analysis of the overall composition was only determined once with the focus being placed on the identification of the included matter.

§ Sample F was found not to contain inclusions, see optical microscopy section.

dezincification, thus allowing an increase in the Pb leach rate, as observed during the CSA test.

ICP-MS

Table 5 lists all elements found by ICP-MS except for Zn, and Cu, since these have already been thoroughly investigated using SEM and microprobe. The concentrations of Pb and Bi determined were very similar to those determined using both SEM-EDX and microprobe-WDX. During analysis, many elements were found to be present that are not common to brass even in small amounts. The presence of these unexpected elements

is the result of the manufacturing process in which both newly mined ore and scrap brass is used. It is commonly felt that the scrap material is the source of sundry trace elements (12). The principle importance of ICP-MS in this study was the identification of trace elements added as corrosion inhibitors. Elements of particular interest are As and Sn since they can be added to brass to inhibit dezincification (17, 18), which as discussed previously can greatly affect brass. Previous research has shown that As concentrations of < 0.1% and Sn concentrations of ~ 1% are effective in inhibiting dezincification, each of which by a differ-

Table 5: Concentration of all trace elements found by ICP-MS in the six samples. All results are in ppm.

Element	Sample					
	A	B	C	D	E	F
Sr	7.0×10^{-2}	1.3×10^{-1}	1.1×10^{-1}	2.3×10^{-1}	3.5×10^{-1}	3.3×10^{-1}
Pd	1.9×10^0	4.4×10^0	1.2×10^0	8.5×10^0	3.6×10^0	2.0×10^0
Cd	1.8×10^1	6.8×10^1	4.4×10^2	8.9×10^1	2.6×10^1	9.8×10^0
Sn	5.0×10^2	9.1×10^2	1.9×10^4	2.1×10^3	1.4×10^3	5.0×10^2
Sb	1.0×10^1	7.1×10^1	3.5×10^2	1.2×10^2	1.9×10^2	4.5×10^0
Ba	7.2×10^0	1.2×10^1	8.6×10^0	1.6×10^1	1.9×10^1	1.2×10^1
Hg	1.0×10^{-3}	6.0×10^{-2}	9.0×10^{-1}	5.0×10^{-1}	1.0×10^{-3}	1.0×10^{-3}
Al	5.8×10^3	2.0×10^3	6.0×10^{-1}	1.2×10^1	2.3×10^3	3.7×10^0
Cr	3.6×10^0	1.6×10^0	2.2×10^{-1}	8.4×10^0	4.0×10^1	5.5×10^{-1}
Mn	4.2×10^0	6.8×10^0	4.0×10^{-1}	4.2×10^1	8.0×10^1	2.7×10^0
Co	2.8×10^0	5.7×10^0	1.6×10^0	1.5×10^1	9.9×10^1	1.8×10^0
Ni	9.2×10^2	1.2×10^3	3.8×10^3	1.8×10^2	13×10^3	1.6×10^1
Se	1.4×10^2	1.4×10^2	4.0×10^1	1.4×10^2	9.8×10^1	8.2×10^1
As	7.6×10^{-1}	1.1×10^2	2.0×10^1	8.0×10^1	1.5×10^0	6.0×10^{-2}
Pb	1.2×10^4	1.5×10^4	6.5×10^4	2.3×10^4	3.5×10^2	1.9×10^1
Bi	2.4×10^0	7.8×10^0	1.2×10^3	2.0×10^1	8.5×10^3	9.1×10^0

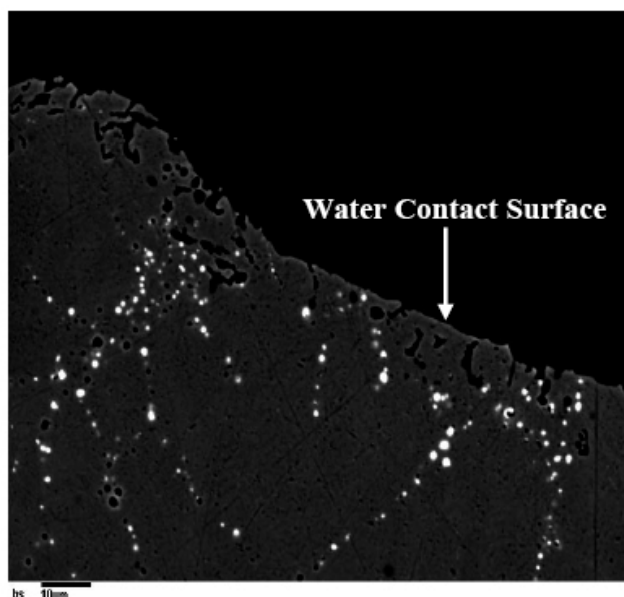


Figure 7: Microprobe image showing the water contact surface (top portion) from a cross section of sample A after the leach test was performed. As is apparent from the image, the water contact surface was grossly affected by layer type dezincification. Pb inclusions are indicated in the image as the bright white spots. Size of scale bar is 10 microns.

ent mechanism (13). Accordingly, the discussion of the ICP-MS results, table 5, will focus on the presence of As and Sn. The other elements found are probably due to contamination from the scrap material used during manufacture of the brass.

All six samples examined were found to contain either As and or Sn. The detection limit of the ICP-MS used was as low as 1 ppt (part per trillion) allowing for an accurate measurement of ultra-trace components. During dezincification, both the Cu and Zn are oxidized to the 2+ oxidation states. Arsenic (As) inhibition of this process might occur by the following mechanism: As present near the site of dezincification reacts with Cu^{2+} reducing it to Cu^{1+} while As is oxidized to form As^{3+} (7). The Cu^{1+} can then undergo hydrolysis (reaction with water) to form cuprous oxide (Cu_2O), a known passivity layer (6). The newly formed As^{3+} can also react with Cu metal forming As metal and Cu^{1+} which can then also be hydrolysed to form Cu_2O (7). The passivity layer located at the surface of the material then forms a barrier that decouples the cathode (dissolved O_2 , H_2O) from the anode (metal surface) and thus restricts dezincification. It should also be noted that current theories predict that in two phase α - β grain systems like those found in samples A and B, inhibition of dezincification by As will only occur for the α -phase while the β phase (richer in Zn) would still be susceptible (11).

The mechanism proposed for Sn inhibition is the following: Sn segregates in the grain boundaries forming a film which inhibits diffusion of Zn from inside the grain structures to the surface of the sample where dezincification occurs (14). Although Sn works fairly well as a dezincification inhibitor for single α phase grain structures, it is unable to prevent this form of corrosion from occurring in the β phase of samples containing a two phase α - β grain structure. This selective protection of the α phase grains with no or limited protection of the β phase may occur because the β phase is a continuous phase that does not exhibit grain boundaries. Therefore, since Sn resides solely in the grain boundaries which only completely surround the α phase, it would be unable to stop Zn diffusion to the corroding surface from the continuous β phase.

Sample A contained neither Sn or As in high enough concentrations to act as an effective inhibitor (table 5). On the other hand, sample B was found to contain enough inhibitor (As, $\sim 0.01\%$) to limit the occurrence of dezincification. This being said, the concentration of As found in B was low, which might explain why plug type dezincification was still found to have occurred. The amount of corrosion found and the distance between the corroded areas at the water contact surface along with the above value of the As concentration suggest that the surrounded unaffected areas contained enough As to form proper passivity layers that protected both the α and β phases rather than just the low Zn containing α phase as previously thought. This last observation was confirmed during SEM analysis by the fact that cross-sectioned samples showing plug type dezincification at the water contact surface did not show any corrosion of either phase in the surrounding material. It is felt that in the areas that did undergo corrosion, the concentration of As was too low to act as an inhibitor and no Cu_2O was formed allowing for the Zn to be selectively attacked and leached.

Current theory states that the occurrence of layer type dezincification occurs only in acidic waters at room temperature while plug type dezincification occurs in basic waters at temperatures slightly above room temperature (7). As discussed above, both layer type and plug type dezincification were found to occur when the samples (A and B) were exposed to deionised water with a pH of 8 at room temperature. Our results suggest that it is not specifically the pH or temperature of the water used but the presence of either internal or external corrosion inhibitors that determine which type of dezincification occurs. As well as elements added to the base material,

species found within the water (either added on purpose or naturally occurring) can form stable passivity layers with metal ions after initial oxidation has taken place (6). More surface sensitive techniques such as XPS (X-ray photoelectron spectroscopy) might be used to investigate this suggestion. For instance, one can determine the As and Cu_2O concentrations at and around the corroded areas found in sample B.

The results and discussion provided thus far support the following explanation of the CSA leach results. When samples A and B were exposed to water during the CSA test, electrochemical couples were set up at the water contact surface between the Pb inclusions and water and dissolved oxygen. As a result, Pb was removed via wet corrosion showing a linear decline in concentration (figure 2). As the test time increased, dezincification occurred and more and more Zn was removed via dezincification leaving a primarily porous Cu surface behind, particularly when uniform-layer type (sample A) rather than plug type (sample B) dezincification occurred. Water was then able to fill these pores and leach/corrode newly exposed Pb inclusions that are usually located beneath the water contact surface. The leached Pb caused an increase in the total concentration observed of leached Pb, which then decreased rapidly once all of the newly exposed inclusions had been removed.

The remaining four samples can also be discussed in terms of their ability to undergo dezincification and/or Pb leaching. As indicated in table 5, only sample C was found to contain a Sn concentration greater than 1%. Between the large quantity of Sn and it having only a single phase α grain structure as well as a Zn concentration that is well below 15%, this particular sample would most likely not undergo dezincification (of either type) at the water contact surface. This would therefore limit the amount of Pb exposed to water to that already found at the water contact surface.

Sample D was found to contain a concentration of As high enough to afford it some protection from dezincification. The concentration found in this sample was very low (lower than that found in sample B), meaning that plug type dezincification would most likely still occur in some areas causing some new Pb inclusions to be exposed to water. Since the amount of As in sample D is low, it might also be suggested that its presence is not due to addition by the manufacturer but rather to contamination by the use of scrap brass during production of the material. The other two samples, E and F, did not contain dezincification inhibitors but neither contained Pb as well. Even though E may undergo leaching of Bi,

it is non-toxic so it is not as worrisome as the fact that both E and F have no protection from the occurrence of layer type dezincification. Therefore, exposure of the samples to water for a long enough period of time could lead to the failure of both plumbing fixtures due to the creation of channels by dezincification leading from the water contact surface all the way to the exterior of the fixture.

Conclusion

The leaching of Pb from brass is a problem that can only be understood by use of sensitive analytical techniques. Results from all four techniques used allowed for the discussion of corrosion mechanisms which affect Pb leaching. Analysis of the samples using optical microscopy, SEM, microprobe, and ICP-MS showed that data obtained during Pb leaching tests by the CSA were consistent with the exposure of Pb inclusions by dezincification, which resulted in an increase in the leach rate which then decreased rapidly as the inclusions were removed. These results also indicated that the type of dezincification found depended on the presence and concentration of appropriate dezincification inhibitors, as well as the fact that the amount of Pb leached depended greatly on the type and amount of dezincification that occurred.

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