

# EXAMINING ASPECTS OF COPPER AND BRASS CORROSION IN DRINKING WATER

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## ABSTRACT

### Examining Aspects of Copper and Brass Corrosion in Drinking Water

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As the water industry complies with the new arsenic standard and new treatments are installed, unintended consequences might be expected in relation to corrosion control when sulfate/chloride ratio, pH, phosphate, iron, aluminum, bicarbonate and organic matter levels are altered. In some cases, these changes will be beneficial and in other detrimental.

This research project is the first to systematically evaluate the effect of some key changes in the chemistry of the treated water in relation to copper and brass corrosion control. A 1.25 year pipe rig experiment was executed to anticipate effects of arsenic treatment on copper pinholes in 10 representative waters. The control water will mimic a synthesized version of Potomac River that is extremely aggressive to copper. Consistent with prior research that pitting is driven by free chlorine in this water and inhibited by phosphate, substitution of chloramine for chlorine or dosing of phosphate completely eliminated deep pits on tubes for the duration of the experiment. Chlorine caused serious pitting if NOM was less than 0.3 mg/L over a range of Cl:SO<sub>4</sub> ratio's. Pitting seemed to occur under deposits of iron or aluminum on the copper surface, and if anything, an equimolar amount of iron caused worse pitting than aluminum. Amendment of the aggressive water with 3 mg/L NOM eliminated growth of deep pits (> 0.05 mm).

While brass pipes (containing 0.09% lead, 63% copper and 36% zinc) was attacked non-uniformly by an aggressive water at high pH and with high Cl<sub>2</sub> content, no significant pitting occurred at any condition tested, even though pitting did occur for copper exposed to the exact same water. The implication is that zinc in the alloy may help to prevent non-uniform attack on copper and copper alloys.

The ban on lead-containing plumbing materials in the Safe Drinking Water Act (1986) and the EPA Lead and Copper Rule (1991) have successfully reduced lead contamination of potable water supplies. This part of the work carefully re-examined the lead contamination concern from the standpoint of existing performance standards for brass. The ANSI/NSF 61, Section 8 standard is relied on to protect the public from in-line brass plumbing products that might leach excessive levels of lead to potable water. Experiments were conducted to look at the practical strictness of these test-standards. In-depth study of the standard revealed serious flaws due from the use of a phosphate buffer and a failure to control carbonate dissolution from the atmosphere in the test waters. In order to help prevent undesirable outcomes in the future, standard's improvements are needed to assurance that brass devices passing this test are safe.

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Finally, thanks to my devoted family and friends, whose support has made all of my accomplishments possible.

This thesis is dedicated to Nestor Murray-Irrizarry and Carmen Iris Ramos...

## ATTRIBUTION

The three chapters of this thesis are presented as separate manuscripts according to specifications of Virginia Tech's journal article format. Chapter 1 and 2 were produced via collaboration between Nestor Murray (graduate student) and Marc Edwards (graduate advisor). As is typical for an M.S. thesis, Edwards provided the topic of study, direction during research procedures and grammatical corrections. Nestor Murray did work typical of a graduate research assistant on the project. Chapter 1 and 2 is an investigation of the pitting propensity of copper and brass corrosion, respectively.

Chapter 3 was produced via collaboration between Nestor Murray (graduate student), Abhijeet Dudi (graduate student), Marc Edwards (graduate advisor), and Michael Schock (Environmental Protection Agency researcher). Murray did the original experimental setup in the work and maintained the rigs for the first 3 months. Edwards and Schock provided intellectual input typical of graduate advisors and the paper was part of Dudi's thesis. Chapter 3 critically evaluates and examines the practical rigor of the NSF 61 section 8 testing procedure that is relied on to protect public health. The results highlight the need for an improved standard to certify lead bearing brass devices. The author of this thesis was fourth author on this publication. This study was presented at the AWWA Annual Conference in June of 2006 and part of it appears in the proceedings of that conference. A refined version of this chapter was published in *Journal American Water Works Association (JAWWA)*.

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# **CHAPTER 1: EFFECT OF ION EXCHANGE AND OTHER TREATMENTS ON NON-UNIFORM CORROSION OF COPPER**

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**ABSTRACT.** The pitting propensity of copper in a range of waters that might be produced via arsenic treatment examined in a 15 month experiment. In this water at high pH in which pitting is believed to be driven by free chlorine, important qualitative trends were obtained in relation to pitting propensity. Chloramine did not cause significant pitting either alone or in combination with orthophosphate. Chlorine caused serious pitting if NOM was less than 0.3 mg/L over a range of Cl:SO<sub>4</sub> ratio's. Pitting seemed to occur under deposits of iron or aluminum on the copper surface, and if anything, an equimolar amount of iron caused worse pitting than aluminum. Amendment of the aggressive water with 3 mg/L NOM or 1 mg/L orthophosphate eliminated growth of deep pits (> 0.05 mm).

## **INTRODUCTION**

Copper is the dominant tube used in homes and buildings, and while it has recently lost market share to PEX and PVC, as of 2001 it still accounted for most new tube installations as recently as 2001 (Marshultz, 2001). The net present replacement value of plumbing tube installed in U.S. buildings and service lines is on the order of 1 trillion dollars (Edwards, 2004a), which exceeds the net present replacement value of large pipe used in potable water distribution by a considerable margin (Brongers, 2002 ). This valuable asset is therefore deserving of protection.

It has long been understood that certain water treatments can increase the likelihood of pinhole leaks in copper tube (Edwards et al., 1994), and it is believed that such treatments have contributed to epidemic levels of pinhole leaks in a few areas of the country (Edwards et al., 2004b; Rushing et al., 2004). One outbreak at a large utility in Maryland ultimately caused leaks in 20-50% of the homes (Edwards et al., 2004b). In 2004, it was unambiguously proven that water alone could eat a pinhole leak in copper tube, and that imperfections in the tube or poor installation and other factors are not required (Marshall,

2004a). This does not mean that these other factors do not sometimes exert a significant influence or even control pitting.

The effective changes to treatment that are believed to have caused outbreaks of leaks include removal of organic matter, higher pH, higher chlorine residuals in water, and increased concentration of aluminum residuals (Edwards, et al., 1994; Rushing et al., 2004). It is suspected that a switch to chloramine can also sometimes contribute to the problem. Prompted by a few serious outbreaks of pitting, several research projects are underway to assess the frequency of pinhole leaks and to develop methods of monitoring for aggressive water.

Although the arsenic regulation is still in its infancy and pinholes might take years to eat through a pipe wall in some cases, there have already been two reported cases in which it was believed that new arsenic treatments caused pinhole leaks in copper. The first reportedly occurred in a medical facility fed water from anion exchange treatments. A building riddled with copper leaks had to be completely replumbed at a cost of tens of thousands of dollars. The second instance involved point of use installation of activated alumina, which is believed to have caused leaks in both brass and copper plumbing materials under a deposit of aluminum on the tube surface. In the latter case, we speculate that higher aluminum residuals in the water from the activated alumina likely contributed to the problem, along with higher pHs and moderate free chlorine (e.g., Rushing et al., 2004). In the former case with anion exchange the altered levels of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , bicarbonate, pH and natural organic matter are likely contributors. It is currently believed that there are many forms of pitting, some of which occur at low pH and some of which occur at high pH (Edwards et al., 1994), so effects of treatment changes are expected to vary from water to water.

Given the devastating economic consequences of pinhole leaks, which can cost over hundred thousand dollars per building after considering water damages, replumbing, insurance implications and mold growth (Edwards et al, 2004b), it was deemed desirable to develop some preliminary information on some impacts of arsenic treatment in longer

term experiments. This work therefore examines effects of modifications to water chemistry that might occur from arsenic treatments on non-uniform copper corrosion tendencies.

### EXPERIMENTAL METHODS AND MATERIALS

The general experimental approach involved exposing 10 different waters to plumbing materials in a re-circulating pipe rig (Figure 1.1). Most of the tube used in the rig was copper since pitting was a primary focus of the study, but smaller sections of brass, lead, stainless steel and other materials were also tested. The copper pipe included 3' long sections of 1/2" type M, L, and K pipe (i.e., varying wall thickness) as well as 1/2" brass pipe specifically manufactured for this experiment by the copper industry. This brass is the same type most commonly installed in home faucets although it only contains 0.07% lead.

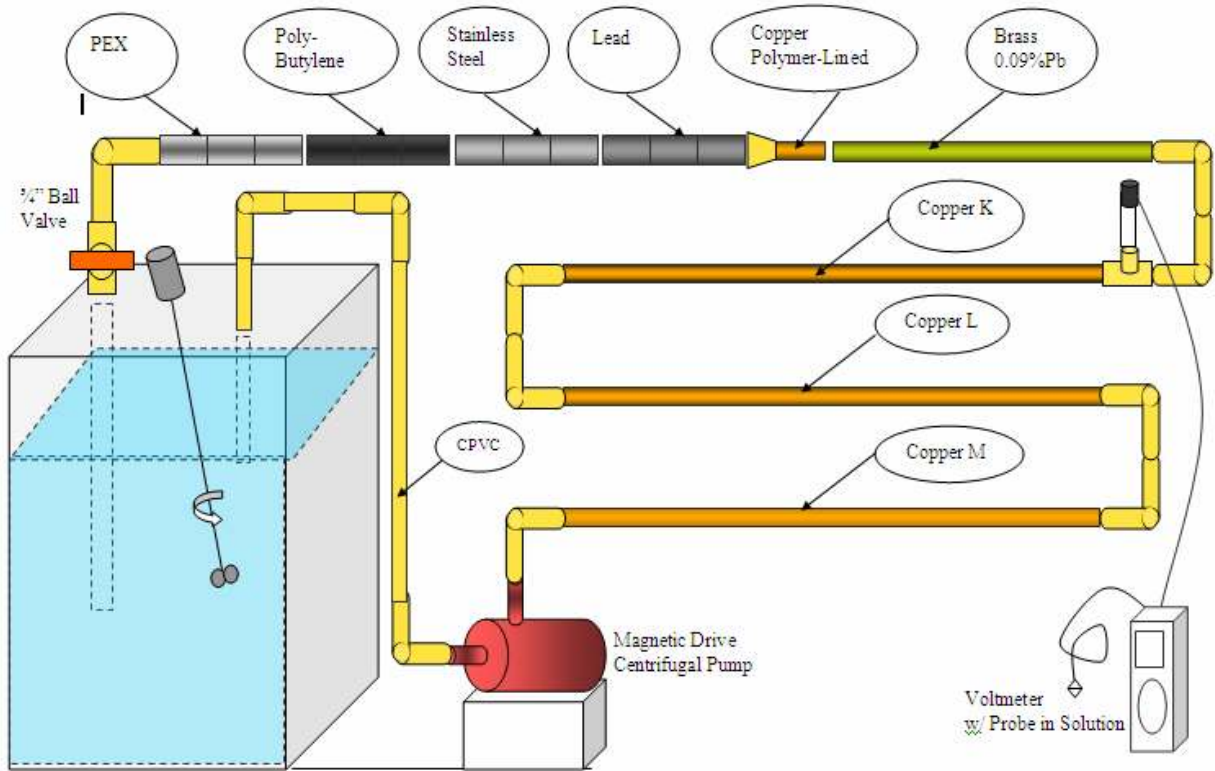


Figure 1.1: Basic pipe rig for experimental testing. Ten rigs were used in this testing.

The 10 waters were derived from a recipe described by Marshall (2004b) which had been proven to cause fully penetrating pinholes (8 leaks per foot) in Type M copper tube within 11 months. The control water for the current work had about 33% higher meq/L of  $\text{SO}_4^{-2}$  and 33% lower meq/L  $\text{Cl}^-$  than the Marshall water, and was constituted by adding 6.26 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 4.89 g of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and 10.75 g of  $\text{NaHCO}_3$  to 50 gallons of distilled water. The pH was raised to 9.2 using 10 mL of 5 M NaOH).

The other nine waters are modifications of the control and were designed to represent a wide range of waters that might be produced by anion exchange arsenic treatment (Table 1). To represent partial anion exchange treatment of the control water, the meq/L  $\text{Cl}^-$  was increased 25% and the meq/L sulfate was decreased 25%, thereby producing a water virtually identical to the Marshall recipe that had been proven to cause severe pitting. To represent complete anion exchange treatment of the control water, all the meq/L  $\text{SO}_4^{-2}$  was replaced with  $\text{Cl}^-$ . In other words, the sum of the  $\text{Cl}^-$  and  $\text{SO}_4^{-2}$  remain constant in each test, as would occur during anion exchange. All test waters also had 0.86 meq/L of  $\text{Ca}^{+2}$  and alkalinity of 34 mg/L as  $\text{CaCO}_3$ . The target pH was 9.2 and chlorine was dosed to 4 mg/L using reagent grade bleach. Aluminum was also added to the water as a catalyst for initiation of non-uniform corrosion as specified in initial experiments.

The tests in which different levels of NOM were added to the control were designed to simulate a range of NOM concentrations that might occur after activated alumina (AA), ion exchange (IX) or granular ferric hydroxide (GFH) treatment since these treatments can remove NOM. Other tests were conducted with an iron residual in the water instead of an aluminum residual, to compare different possible effects of iron and aluminum deposits on non-uniform copper corrosion. Finally, still other tests were conducted with 4 mg/L chloramine instead of chlorine, chloramine plus phosphate, and chlorine plus phosphate (Table 1.1).

Table 1.1: Water qualities selected for long term loop testing of copper pitting and lead leaching. Cl<sup>-</sup> and SO<sub>4</sub><sup>-2</sup> are varied by adjusting the amount of CaCl<sub>2</sub>\*2H<sub>2</sub>O or CaSO<sub>4</sub>\*2H<sub>2</sub>O added. All rigs also had aluminum as described in later text, except for the rig with iron instead of aluminum.

<b>Descriptor of water to be used throughout the report</b>	<b>SO<sub>4</sub><sup>-2</sup> Meq</b>	<b>Cl<sup>-</sup> meq</b>	<b>NOM mg/L as C</b>	<b>Comments on practical reason for modification</b>
Control	0.30	0.56	0	Water known to cause pitting
Higher Cl <sup>-</sup> and Lower SO <sub>4</sub> <sup>-2</sup>	0.16	0.70	0	Partial anion exchange treatment*
All Cl <sup>-</sup>	0	0.86	0	Complete anion exchange treatment
0.05 NOM	0.30	0.56	0.05	Removal of most NOM by As treatments
0.3 NOM	0.30	0.56	0.3	Removal of some NOM by As treatments
3 NOM	0.30	0.56	3	Water with high NOM for comparison
PO <sub>4</sub>	0.30	0.56	0	Determine if 1 mg/L PO <sub>4</sub> -P can prevent lead leaching or pitting relative to control
Iron	0.30	0.56	0	Dosing of 2 mg/L iron (and no aluminum) simulates effect of GFH fines on pitting and lead leaching
NH <sub>4</sub>	0.30	0.56	0	Monochloramine formed by adding ammonia
NH <sub>4</sub> & PO <sub>4</sub>	0.30	0.56	0	Determine effects of dosing phosphate and chloramine on lead leaching and pitting.

\*This water is virtually identical to that used by Marshall et al., 2004.

**Aluminum Dosing.** After changing the water every other week, aluminum was added to a final concentration of either 2 mg/L (as Al) using freshly prepared Al(OH)<sub>3</sub> solids or 1 mg/L aluminum salts as specified. When the aluminum was dosed in a “soluble” form, AlCl<sub>3</sub> was added directly to the water and stirred until it dissolved. The aluminum probably precipitated rapidly in the water as Al(OH)<sub>3</sub> or similar solids. When the aluminum was added as a solid, an Al(OH)<sub>3</sub> (s) stock solution was created by raising the pH of a 1,500 mg/L AlCl<sub>3</sub> solution to pH 9.0 using NaOH, followed by repeated rinsing/decanting of water over settled solids until the conductivity of the solution

dropped below that of the experimental water. After rapid mixing aluminum solids were dosed from this stock solution.

**Chloramine Dosing.** In the case of the two rigs with chloramine as a disinfectant, ammonia hydroxide (1M  $\text{NH}_3\text{OH}$ ) was added first, followed by addition of diluted chlorine while stirring rapidly. A dose of 4:1  $\text{Cl}_2/\text{NH}_3\text{-N}$  was achieved as confirmed via total chlorine and total ammonia measurements.

**NOM Dosing.** Prior to water changes, natural organic matter (NOM) was pre-chlorinated as would often occur in water treatment. It was determined that a dose of 30 mL of reagent grade  $\text{NaOCl}$  added to 38 mL NOM concentrated stock solution, diluted to a total volume of 200 mLs gave a residual of about 1 mg/L  $\text{Cl}_2$  after 24 hours. This meant that the vast majority of the chlorine demand of the NOM stock solution was met through pre-chlorination, and that the NOM was similar to that occurring in many distribution systems since it was pre-chlorinated. The pre-chlorinated NOM was then filtered through a 5  $\mu\text{m}$  pore size filter before dilution as needed for experiments.

**Electrochemical Measurements.** A variety of electrochemical measurements were made for the copper pipes. The corrosion potential ( $E_{\text{corr}}$ ) was obtained using a multimeter and a  $\text{AgCl}$  double junction reference electrode. These values are reported in millivolts (mV) versus  $\text{AgCl}$ . The  $\text{KCl}$  reference electrodes were checked and maintained regularly to ensure accuracy.

**Water chemistry measurements.** Dissolved and total metal concentrations in the water were tracked during the experiments using ion exchange (IC), inductively coupled plasma mass spectroscopy (ICP-MS) and TOC sampling before and after each water change.

**Visual Observations of Pipes.** Originally 3' long sections of ½" type M, L, and K pipe were included in the rig (Figure 1.3). The copper type M and L pipes were exposed for the whole experiment, whereas the K pipe was taken out at 12 months to check for depth



of pits and SEM analysis. Other very small sections (e.g., up to 3") were removed from the rig during the experiment.

**Analysis of Pipes.** After the experiment pipe samples were dried, weighed and then cut lengthwise to preserve separate top and bottom sections for inspection of pit density and pit depth. Overall weight loss was determined by measuring the pipe segment weight before the experiment, the pipe segment weight after the experiment, and the amount of scale removed from the pipe after cleaning with a felt-tipped Dremel tool (i.e., Weight Loss = Initial Pipe Weight – Scale – Final Weight). The extent of pitting was determined by visual counting of pits, determining pit depth (i.e., Pit Depth = initial wall thickness - final wall thickness at pits), and using a 0-25 mm caliper to measure wall thickness with an accuracy of 0.01 mm. Scanning electron microscopy and ESCA were used for detailed analysis of the surfaces.

**Experimental Timeline.** During the first few months of the experiment, it became clear that the electrochemical behavior of the rig was not consistent with that which had been observed by Marshall, even for the water that had virtually identical initial chemistry. Specifically, very high levels of  $E_{\text{corr}}$  ( $> 1$  V versus AgCl reference electrode) believed to be consistent with rapid pitting that were observed in the Marshall test were not observed in this experiment. Since the primary goal of the experiments was to replicate copper pitting and to judge relative effects of water chemistry changes by comparison, several attempts were made to try and determine the factors that might be preventing very rapid pitting in the current work.

A list of potential differences between the current rig relative to that of Marshall was compiled. Differences included 1) presence of brass and other metals in the rig, 2) initial dosing of aluminum from soluble salts instead of  $\text{Al}(\text{OH})_3$  particles, 3) use of internal velocity of 8 feet per second flow rate instead of 2 feet per second, 3) use of 1/2" diameter pipe instead of 3/4" pipe, and 4) free  $\text{Cl}_2$  restored to 4 mg/L once per day in the current work versus constant 4 mg/L achieved via continuous dosing.

During the timeline of this experiment a systematic attempt was made to restore very rapid pitting conditions similar to those that had been observed by Marshall by making changes to the base experiment (Figure 2). First, velocity was reduced. Thereafter, pre-formed aluminum particulates were dosed directly as per Marshall instead of soluble aluminum, and the concentration was increased from 1 to 2 mg/L. After 1 year without an electrochemical indication of severe pitting, materials other than copper were removed from the rig, since it was suspected that zinc leaching coming from brass pipe may have been inhibiting pitting corrosion on the copper pipe. Also, chlorine was dosed twice per day instead of once per day. None of these factors restored the severe electrochemical indications of pitting (as tracked by  $E_{corr}$ ) that were observed by Marshall.

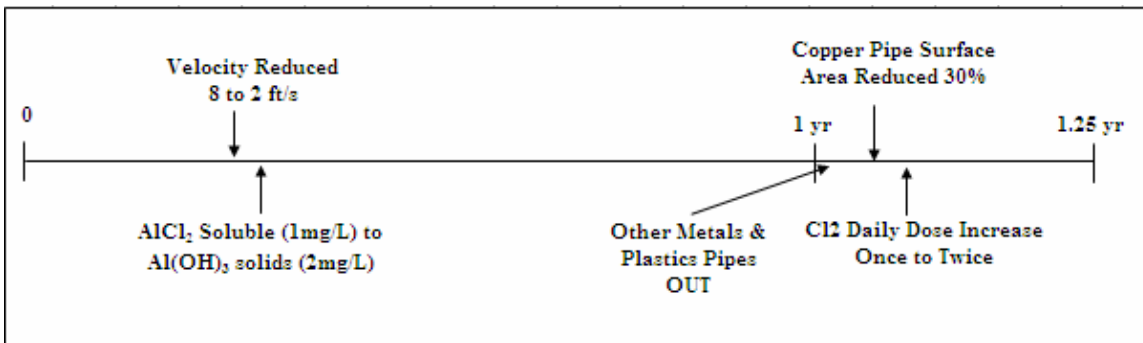


Figure 1.2: Substantive changes in test conditions during the experiment.

## RESULTS AND DISCUSSION

Experimental results are discussed in five sections including 1) analysis of copper surface after treatment through visual observation, 2) characterization of pitting in terms of appearance of the tubes, pit depth, pit density and weight loss, 3) scaling and scale identity, 4) kinetics of chlorine decay, and 5) electrochemistry of pitting. Thereafter key conclusions are reiterated relative to arsenic treatment.

### Visual Analysis of Copper Surface

After 15 months the type M and L pipes were examined (Figure 1.4 to Figure 1.8). The scale colors varied markedly dependent on exposure conditions. For the most part the pipes were covered with a dark brown-black scale, but conditions with 3 mg/L NOM,

chloramines plus phosphate, chloramines, and chlorine plus phosphate had green/white scale with dark/black spots. The iron scale was dark orange-black.

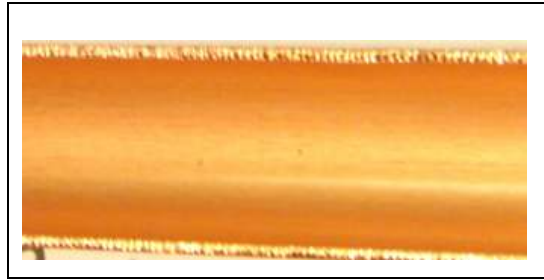


Figure 1.3: Photo of copper pipe type L uncontaminated surface.

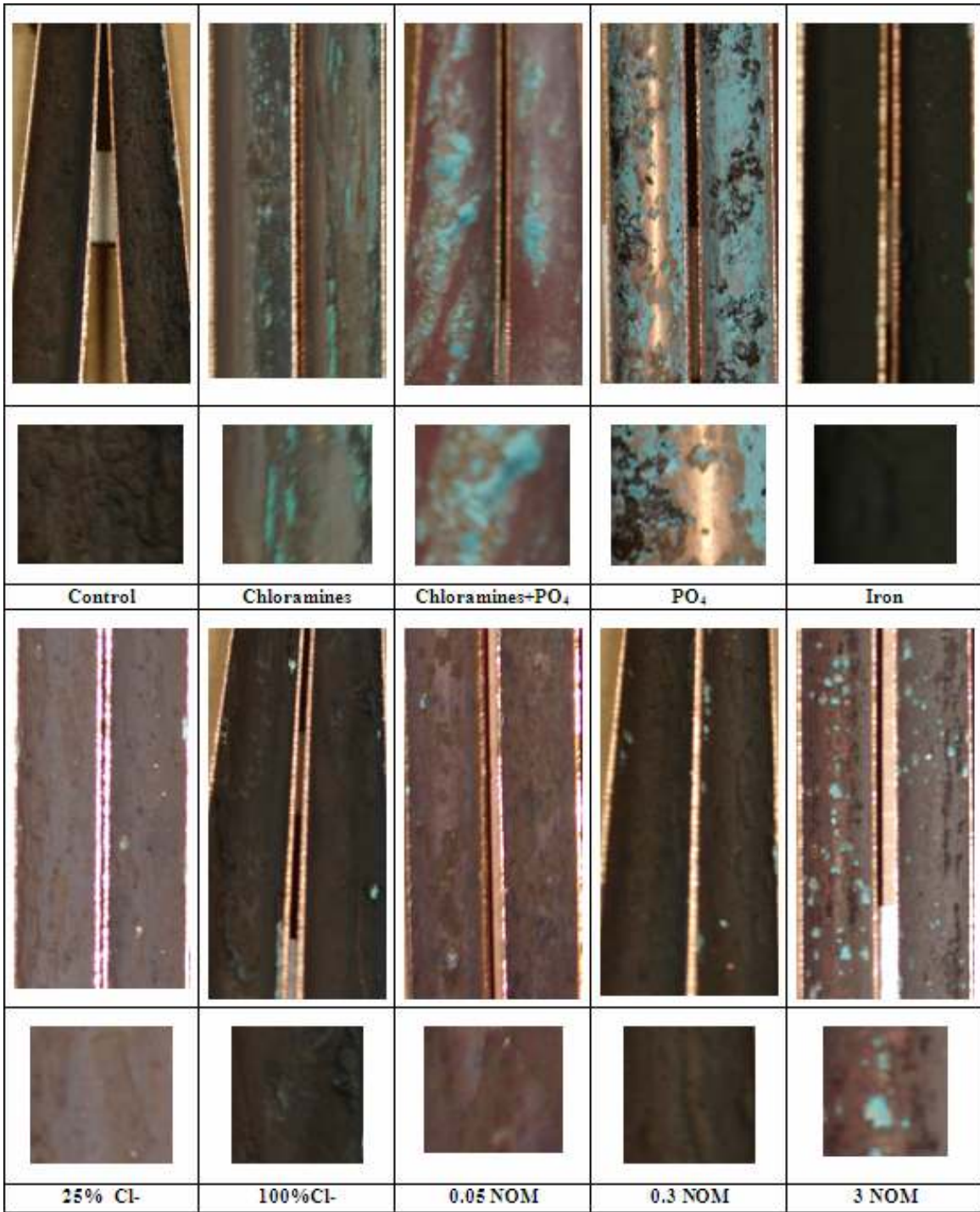


Figure 1.4: Copper type M after 15 months.



Figure 1.5: Copper type L after 15 months.



Figure 1.6: Copper type M for the last 5 months after all metals other than copper were removed from the rig.



Figure 1.7: Copper type M after the last 3 months and removal of the other metals.

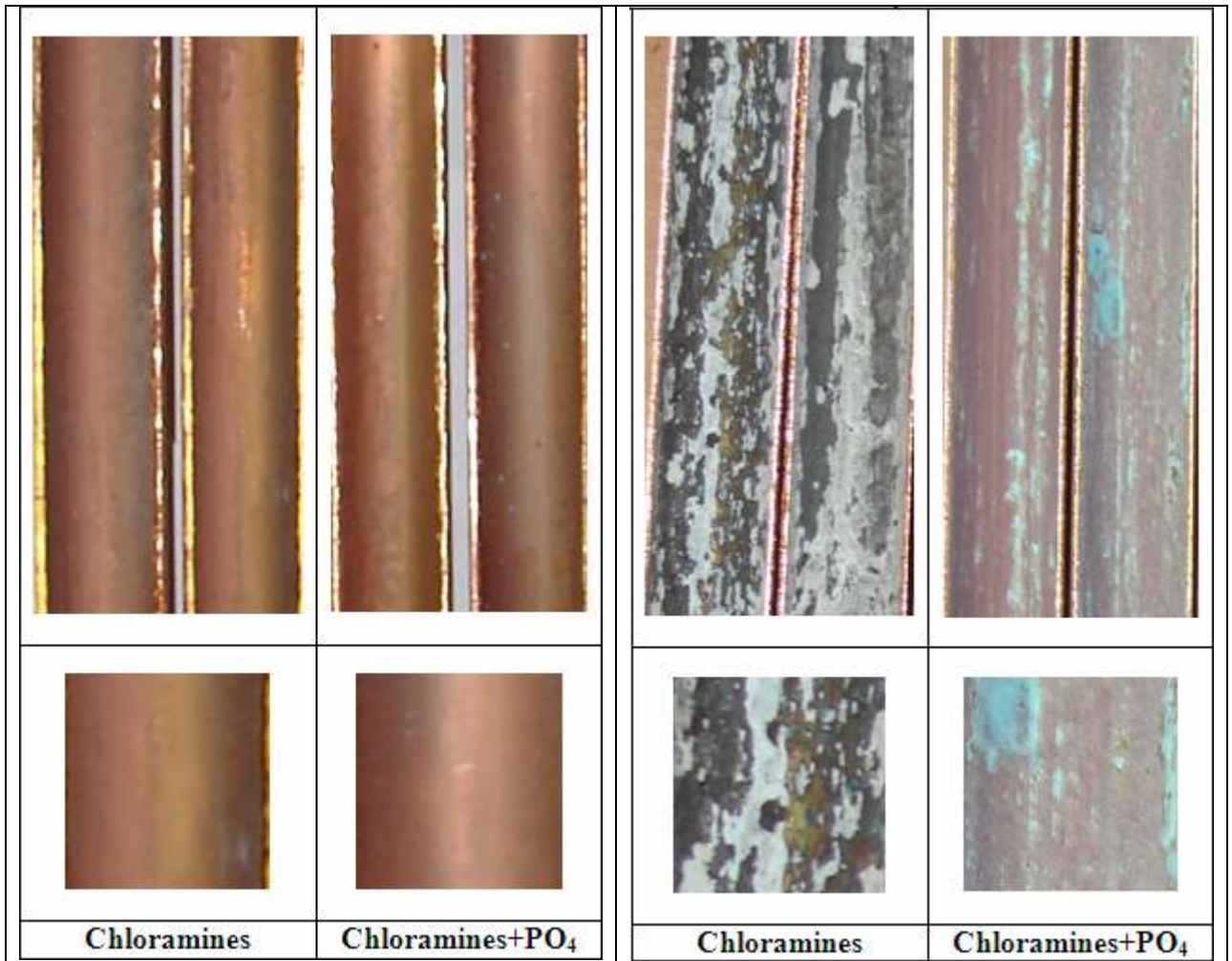


Figure 1.8: Copper type L ran for first 5 months (left) and copper type M ran for last 10 months (right).



### **Characterization of Pitting Propensity**

Even though no pinholes developed in the copper pipes after 15 months of experimentation, very serious pitting was nonetheless observed in many of the pipes. Two sets of tubes were subject to detailed analysis at 11 and 15 months. Tubes exposed to chloramine, chloramine plus phosphate, chlorine plus phosphate, and chlorine plus phosphate had no pits deeper than 0.05 mm. This is completely consistent with Marshall's prediction based on electrochemistry that pitting in this water is driven by chlorine and is inhibited by orthophosphate (Marshall et al., 2006). In contrast, all of the other tubes had at least 5 pits that had eaten through more than 15% of a Type M pipe wall thickness after just 11 months (Table 1.2). Indeed, the deepest pit on a tube exposed to chlorine and iron had eaten through 55% of a Type M pipe wall in just 15 months. Thus, while the experiment was a failure in terms of reproducing leaks and the extremely rapid pitting described by Marshall, the test waters were still very aggressive to copper and the analysis can support highly significant relative comparisons of pitting propensity

For a summary analysis of pitting and pit depth, the 5 worst pits on the 3' sections of tube were identified, and the range and average pit depth of these 5 pits were determined (Table 1.2). After 15 months, the average depth of the 5 worst pits on the tube exposed to iron particles were 96% deeper than the corresponding pits formed in the presence of aluminum. Thus, iron particles were more detrimental than an equimolar dose of aluminum in relation to pitting in this water.

With respect to NOM, levels of 0 mg/L (control), 0.05 and 0.3 mg/L had about the same average pit depth (Figure 1.9). However, 3 mg/L NOM virtually eliminated pitting in the first 11 months of the experiment and reduced pit depth by about 50% after 15 months. Thus, while NOM did not completely stop pitting corrosion in this extremely aggressive high pH water, it was still effective at slowing the rate of pit growth. It should be noted that NOM tends to sorb to metal surfaces more weakly at higher pH than at lower pH, so the current water is a situation in which effects of NOM on pitting are likely to be minimized.

Finally, waters representing complete anion exchange treatment were worse than the control water in terms of average pit depth, but better than the control water in terms of maximum pit depth. In contrast, partial anion exchange treatment was worst of all. This is consistent with a notion of an “optimally bad” ratio of Cl:SO<sub>4</sub><sup>-2</sup> in a given water (Figure 1.9). Certainly all three waters were highly aggressive, but in this case it was an intermediate ratio of Cl:SO<sub>4</sub><sup>-2</sup> that was most aggressive in terms of the number of deep pits.

Table 1.2: The range and average of 5 deepest pits on 3 feet long samples exposed for the indicated experimental time.

	Penetration Range and average of 5 worst pits in parenthesis						
Copper	Control	+25% Cl	100% Cl	0.05 NOM	0.3 NOM	3 NOM	Iron
11 months	0.14-0.25 (0.16)	0.25-0.25 (0.25)	0.15-0.22 (0.19)	0.14-0.22 (0.16)	0.12-0.21 (0.14)	All < 0.05	0.27-0.35 (0.29)
%depth	21	33	25	21	19	<	38
15 months	0.17-0.26 (0.19)	0.24-0.35 (0.28)	0.20-0.27 (0.24)	0.18-0.27 (0.21)	0.17-0.25 (0.18)	0.06-0.12 (0.09)	0.33-0.41 (0.37)
%depth	25	37	32	28	24	12	49

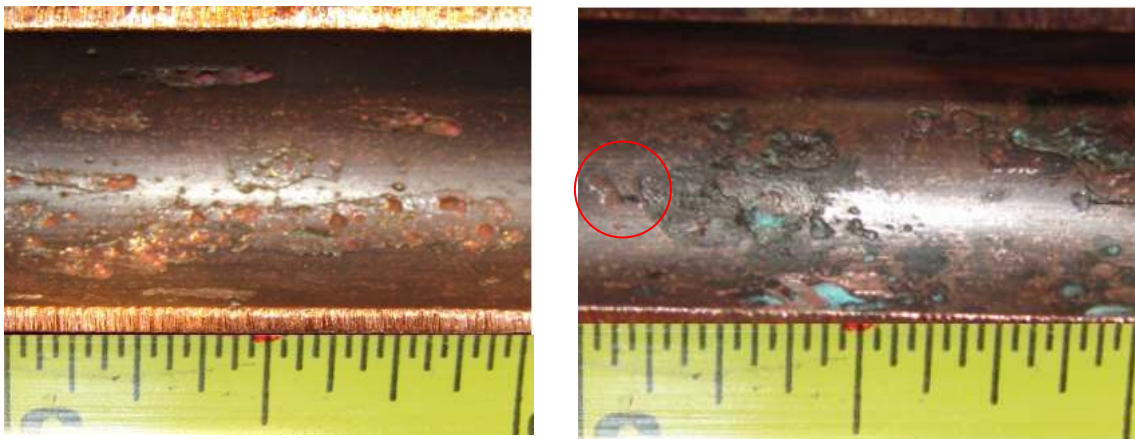


Figure 1.9: Photo of copper (type M) pipe surface (1 inch long) for 25% Cl- condition on the left and 0.3 NOM condition on the right.

### Pit Location and Density

In addition to the important parameter of pit penetration, the number and location of pits is also important. Each pipe was cut into three segments lengthwise and these segments were termed entrance, middle and exit sections. With sections all cut into top and bottom, six segments total were characterized.

For all pipes the front section had the greatest density of pits, the middle the second most and the exit the least (Figure 1.10). Of the pipes with pits, the pipe exposed to NOM had the fewest pits whereas the pipe exposed to iron particles had the most. Otherwise there were relatively few differences in pit density amongst the conditions. Again, the water dosed with orthophosphate and chlorine, with chloramines, and with orthophosphate and chloramines did not exhibit significant pitting and that data is not shown.

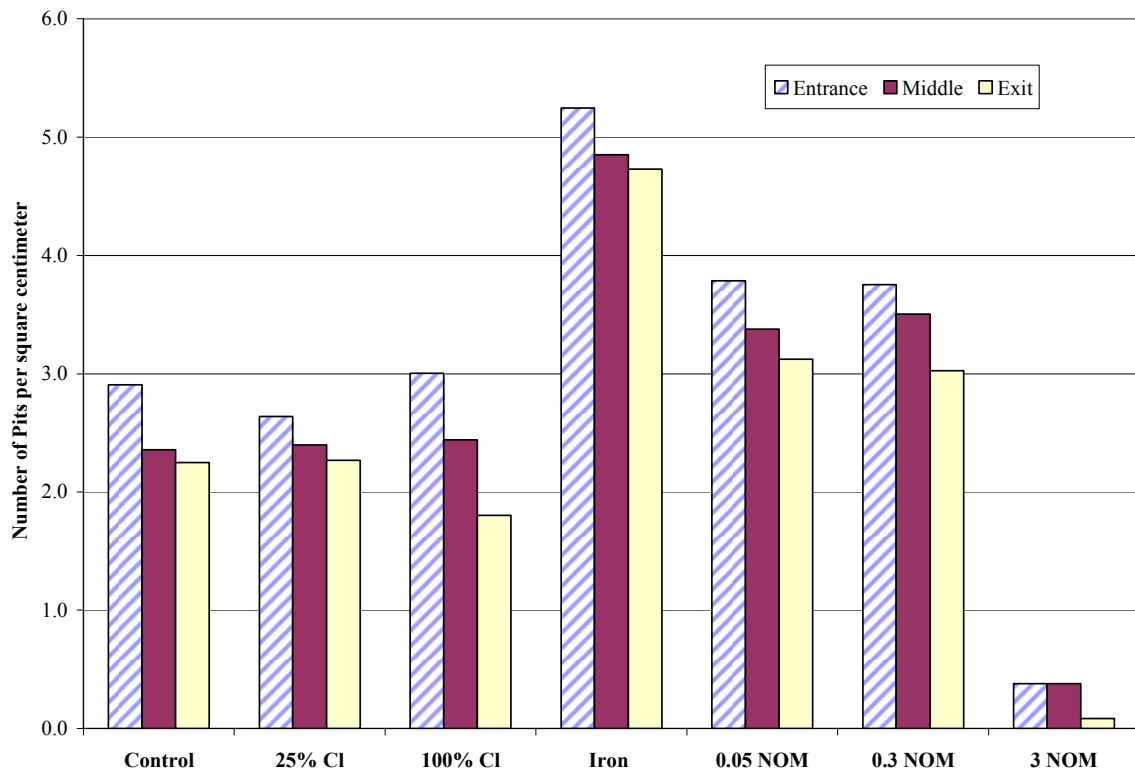


Figure 1.10: Average Copper Pipes # of Tubercles – Entrance, Middle versus Exit

Another clear tendency was a greater density of pits along the top segment of the pipe relative to the bottom in all conditions (Figure 1.11). As before, the copper pipe exposed to iron had the greatest number of pits whereas the pipe exposed to 3 mg/L NOM had the least (excluding the conditions without pitting).

Overall all copper pipes demonstrated greatest pit density at the entrance (relative entrance, middle and exit) and the top (relative to the bottom) when a 90 degree elbow was prior the pipes entrance. These tendencies may be due to water flow, electrochemistry, or air bubbles. (Figure 1.12)

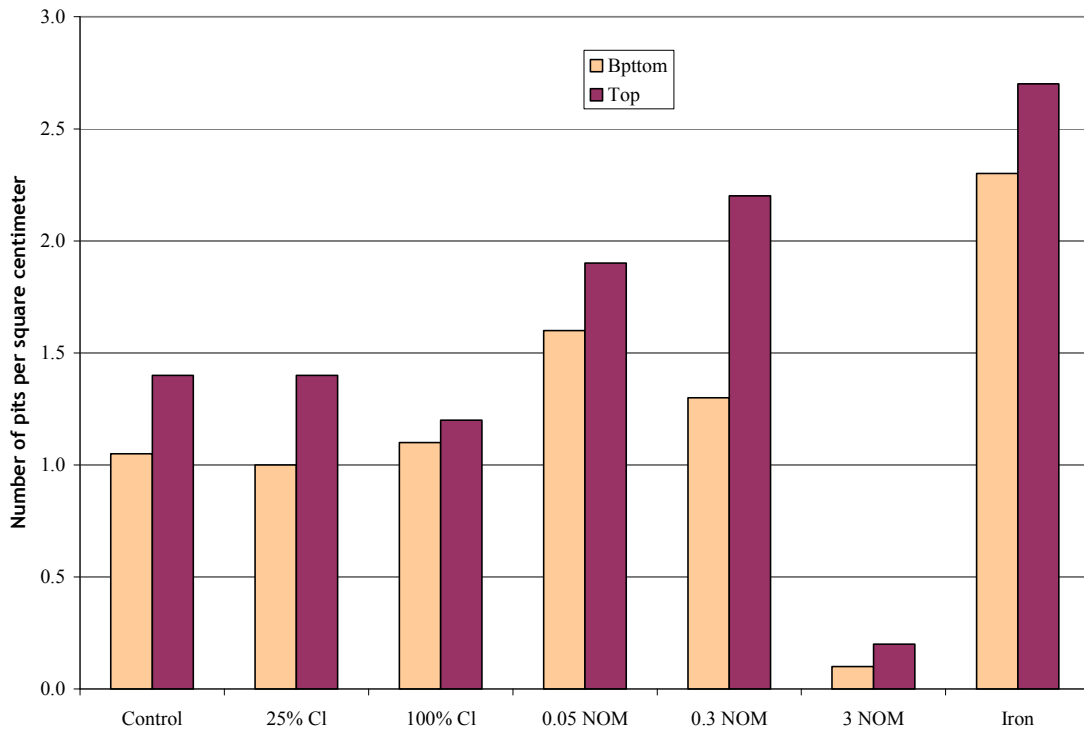


Figure 1.11: Average Copper Pipes Number of Pits on Copper Pipes - Bottom versus Top

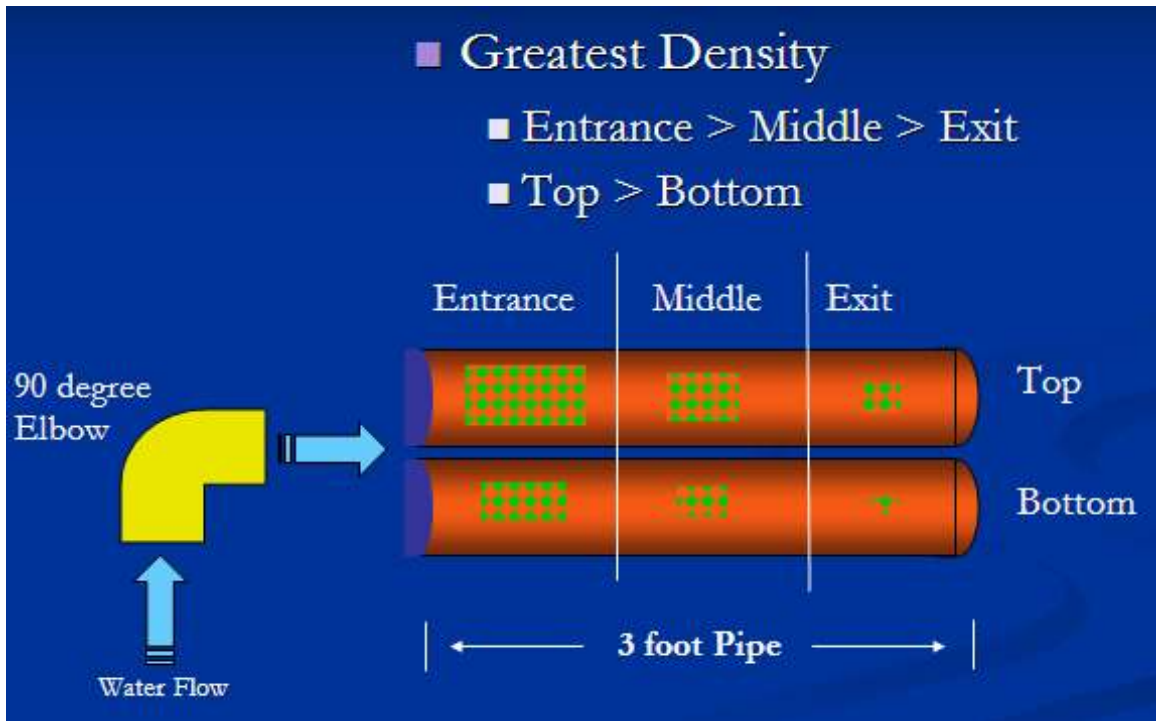


Figure 1.12: Overall pit density tendencies along a 3 foot copper pipe section.

### Weight Loss and Leaching

The copper that corrodes from the pipe can either become incorporated into scale or can leach into the water. In general, the concentration of copper leached into the water after 2 weeks of recirculation at this high pH was low. Perhaps the biggest difference observed arose when the aluminum was dosed as a soluble salt versus pre-formed aluminum hydroxide. Copper in the water was lowest during the time when aluminum was dosed as a soluble salt at 1 mg/L as Al and was much higher when aluminum was dosed as  $\text{Al}(\text{OH})_3$  at 2 mg/L as Al (Figure 1.13).

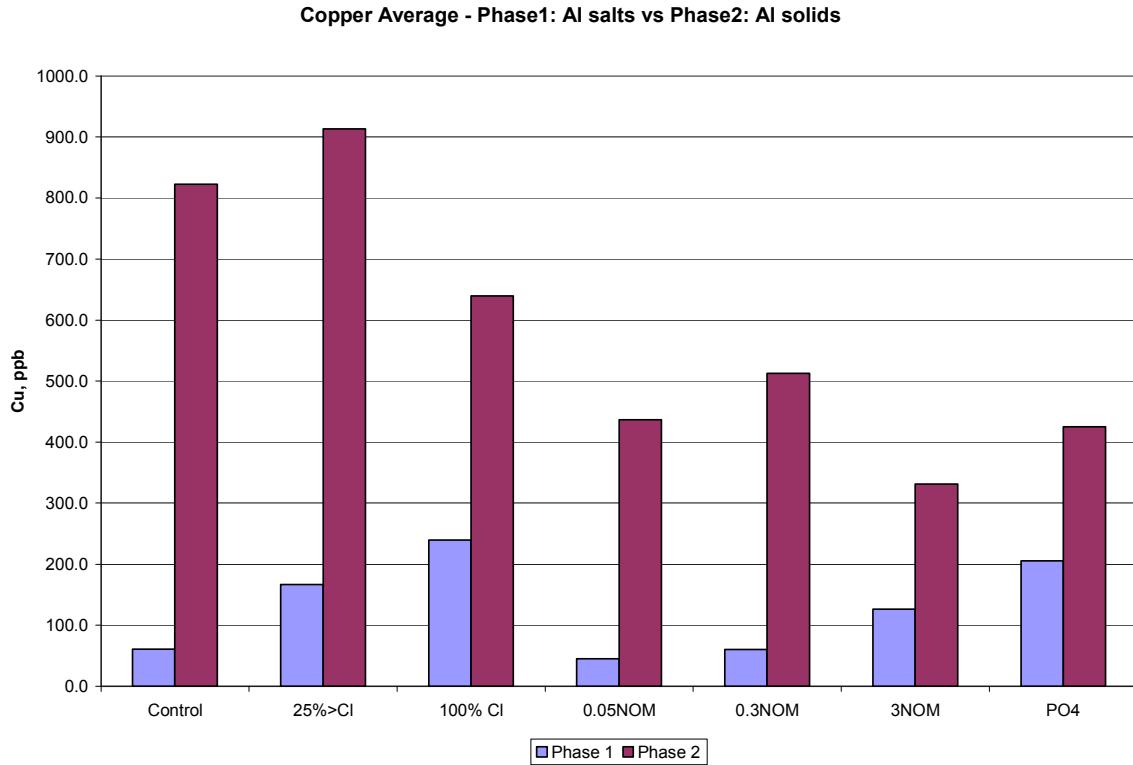


Figure 1.13: Copper was highest when aluminum was dosed as Al(OH)<sub>3</sub> solids.

Weight loss of the copper pipes was very low at less than 0.3% of the total mass in all cases (Figure 1.14). This is consistent with the fact that these waters actually have very low overall corrosion rates-- the devastating corrosion from pitting is attributable to a small amount of corrosion focused at a point on the surface. For example, the copper pipe exposed to iron particles had one spot penetrated to more than 50% of its depth, but less than 0.3% of the tube mass had been corroded away.

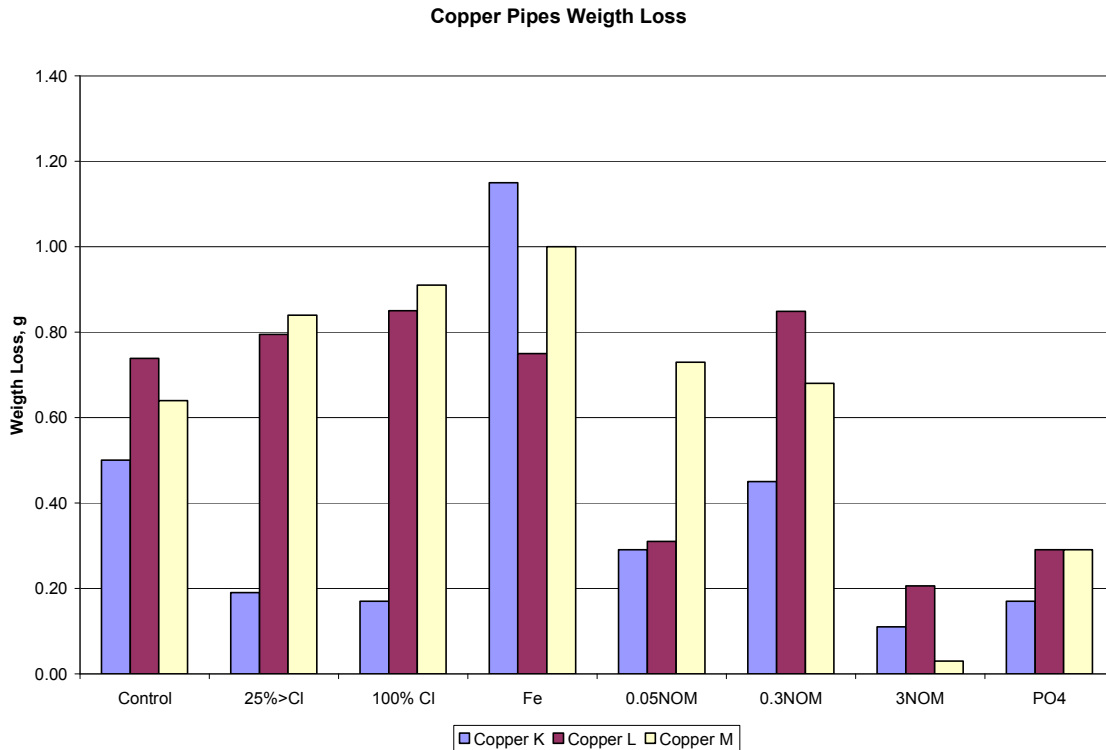


Figure 1.14: In all cases weight loss of the copper pipe was less than 1.15 g, which translates to less than 0.3%.

### Scaling and Scale Identity

There were marked differences between the systems in terms of aluminum and iron uptake. That is, the iron and aluminum added to the system sometimes disappeared from the water due to deposition on the pipes or to the experimental apparatus. Metals measurements were made just before the water was changed and then just afterwards to capture changes in iron and aluminum concentration with time. In the system dosed with chloramines, during the first 120 days when aluminum was dosed as a soluble salt, aluminum was about 1 mg/L immediately after the water change and dropped off to very low levels just before the water was changed (Figure 1.15). Both chloramines and chlorine exhibited this pattern, although the control with chlorine had greater uptake of aluminum when dosed with soluble salts.

As the meq/L of Cl<sup>-</sup> increased and sulfate decreased, more aluminum deposited to copper and less stayed in the water. As NOM increased from 0.3 and then to 3 mg/L, less

aluminum deposited to the pipe and more stayed in the water (Figure 1.16). This might reflect NOM's role in dispersing colloids. Finally, dosing of phosphate also prevented aluminum deposition, consistent with orthophosphates ability to stabilized colloids. During the second part of the experiment the aluminum was dosed as a particulate and at twice the initial concentration, resulting in more aluminum in the water and more aluminum depositing to the pipe and other surfaces.

For iron an interesting trend was observed in terms of deposition. When iron was dosed in a soluble form in the first phase of the research, 1.4 out of 2.0 mg/L iron remained in the water after two weeks of recirculation. Thus, only about 30% of the iron was being removed from the water. However, when the same 2 mg/L iron was dosed to the pipe as iron particles, about 75% was removed from the water after two weeks (Figure 1.17).

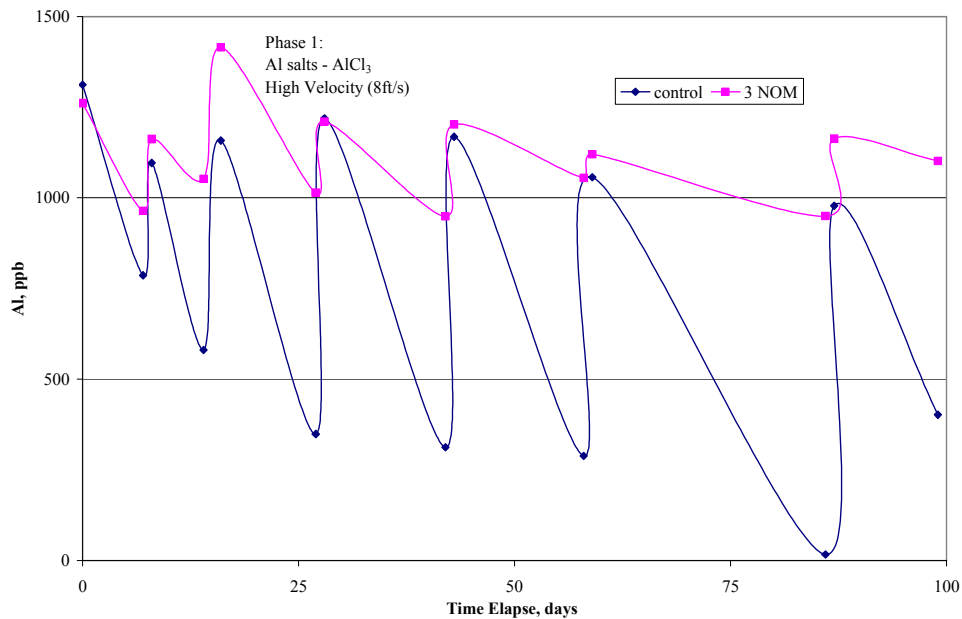


Figure 1.15: Illustrative patterns of aluminum deposition – soluble salt versus Al(OH)<sub>3</sub> solids.



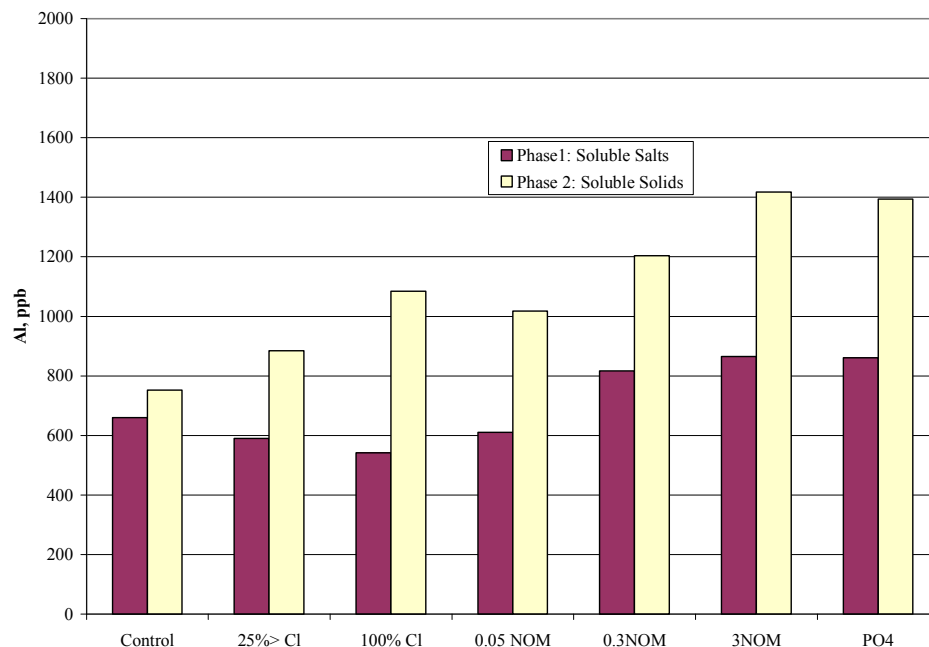


Figure 1.16: Average aluminum left in the water after two weeks of recirculation. During phase 1 aluminum was dosed as a soluble salt at 1 mg/L as Al, whereas in phase 2 aluminum was dosed as 2 mg/L as Al(OH)<sub>3</sub> solids.

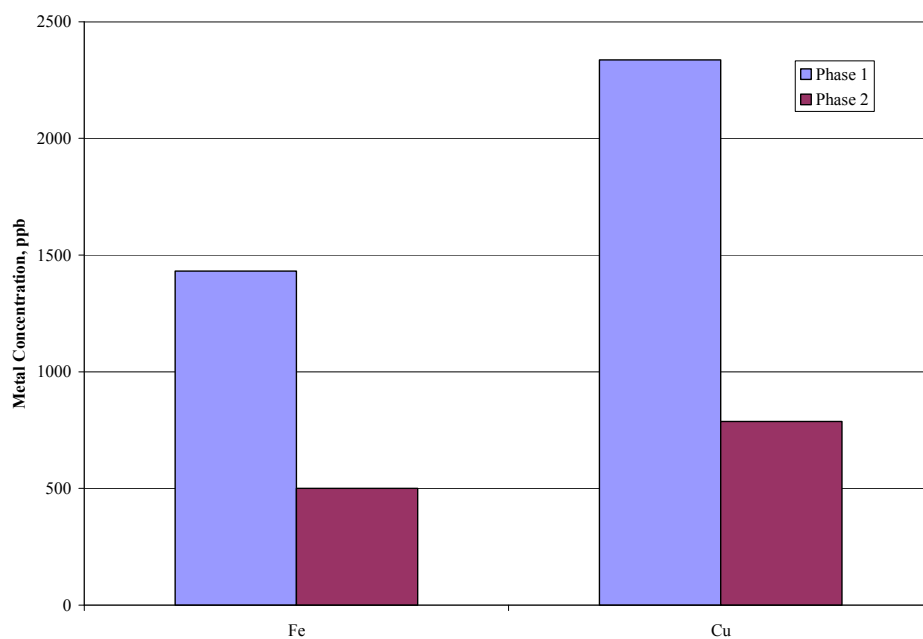


Figure 1.17: Average iron and copper in the water after two weeks of recirculation. During phase 1 iron particles were formed in-situ from a soluble salt whereas in phase 2 iron hydroxide was pre-formed.

Selected sections of each pipe were analyzed with a field emission scanning electron microscope (FE-SEM) equipped with electron dispersive spectroscopy (EDS) to determine the elemental surface composition of the pipe scale. The instrument determines the statistical quality of collected data by calculating a minimum detection limit (MDL) for each element during each surface site measurement. It is convention to report only data that is at least two times the MDL.

Each sample was analyzed for both uniform scale (smooth section of pipe) or for areas that were deemed to have been attacked by non-uniform corrosion (e.g., possible tubercles above pits). Many different individual surface measurements on each sample were taken (approximately 7-20 measurement sites). In some cases, an element was detected on a particular surface but also not present ( $< \text{MDL}$ ) at other spots on the same surface. (Figure 1.18)

After a careful surface examination key trends became evident (Figure 1.19 and Figure 1.20). Phosphate was only present in the rigs dosed with this inhibitor (Figure 1.19). Only 0.1 to 1.4% phosphate was present on the uniform areas of the rig with chloramines and chlorine, respectively. In contrast, 3.8-3.9% phosphate was present in scale over pits on the pipe, consistent with some theories that orthophosphate is more likely to act at anodic areas of the pipe.

Systems dosed with aluminum had between 1.1 and 8% aluminum in the scale of the pipe, whereas the system dosed with phosphate had between 0.6 to 1.5% iron deposits (Figure 1.19 and Figure 1.20). The chloramine condition, chloramine plus phosphate and the phosphate plus chlorine condition all had green/white scales.

Chloride was not found on the top layers of scale in non-uniform corrosion areas. However, it was present on pipe in both conditions dosed with chloramines, as well as in the NOM and high chloride condition.

Zinc was present on all pipes at levels between 0.7 and 16%. Thus, there is little doubt that zinc leached from brass located elsewhere in the rig could have influenced and inhibited corrosion to some extent in all the rigs. Traces of lead from the lead pipe, and sulfate, calcium and sodium from the water were also detected on some pipe surfaces.


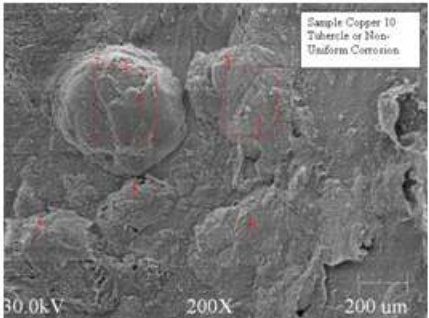
		True-Image (1" by 1/2")	SEM Photograph
		Water Chemistry Description of Copper Pipes	Control
0.05 NOM			

Figure 1.18: SEM of selected sections of copper pipe analyzed. Note that locations marked by a + represent a measurement area of  $1 \mu\text{m}^2$  and the entire surface within boxed areas were analyzed.

Water Chemistry	Uniform Corrosion Element %	Image	Non-Uniform Corrosion Element %
R1: Control, 14ppmCl ppmAl(s) 2 (total)	<p>Zn, 0.9 Al, 2.1 Cu, 83.3 O, 12.3</p>		<p>Zn, 0.7 Al, 2.0 Cu, 74.9 O, 20.8</p>
R7: 4Cl2:1NH4-N, 1ppmAl	<p>Zn, 1.2 Al, 5.1 Cl, 0.4 Cu, 69.3 O, 22.6</p>		<p>Zn, 16.4 Al, 8.0 Cu, 32.8 O, 38.9 S, 0.6 Na, 2.6</p>
R3: 4Cl2:1NH4-N, 1ppmAl, 3ppmPO4	<p>Zn, 0.8 Al, 4.3 Cl, 0.7 Cu, 83.6 O, 10.3 P, 0.1</p>		<p>Zn, 1.7 Al, 4.8 Ca, 0.4 Cu, 55.3 O, 32.9 S, 0.5 P, 3.8</p>
R9: 1ppmAl(s), 3ppmPO4 4ppmCl2 (total)	<p>Zn, 0.7 Al, 3.8 Cu, 83.9 O, 10.7 P, 1.4</p>		<p>P, 3.9 Al, 5.9 Ca, 0.8 Cu, 55.1 O, 32.0</p>
R5: 2ppm Fe & no Al 4ppm Cl2 (total)	<p>Zn, 0.9 Fe, 0.6 Cu, 82.1 O, 14.9</p>		<p>Zn, 0.8 Fe, 1.5 Cu, 76.0 O, 19.9</p>

Figure 1.19: Photo of each pipe surface and composition of uniform and non-uniform corrosion areas.

Water Chem Descip	Uniform Corrosion Element %	Image	Non-Uniform Corrosion Element %
R2: Cl- >25%			
R4: 100%Cl-			
R10: 0.05ppm preCl2-NOM			
R8: 3ppm preCl2-NOM			

Figure 1.20: Photo of each pipe surface and composition of uniform and non-uniform corrosion areas.

### **Kinetics of Chlorine Decay**

There were wide variations in the pattern of chlorine decay in the test waters during the experiment. To better characterize the science behind this chlorine decay four types of experiments were conducted including 1) beaker tests with the water but without pipes, 2) tests in the recirculation rig at the end of the experiment but with no pipes present, 3) circulation rig experiments with all the different pipe materials, and 4) circulation rig experiments with only copper pipes present. Also, representative chlorine decay data after 24 hours of circulation were obtained to characterize the trends of chlorine decay during the experimental course. (Figure 1.21)

The beaker test was performed using a 3 liter chemically resistant plastic beaker while slowly stirring at 250 rpm. Water was made up as described previously. The pH was maintained at 9.4 and chlorine was maintained at 4 mg/L. Chlorine demand in all the waters was very low, with less than 15% decay in 30 hours in all cases. There was some initial rapid chlorine demand in the water dosed with 3 mg/L pre-chlorinated NOM in this case. Kinetics were essentially zero order with constant loss of chlorine with time in all waters (Figure 1.23).

The same test was repeated in the rigs after 1.25 years of experiment but after all the metal pipes were removed. In this case the decay represents that observed in the water, plus decay from contact with any oxide deposits left on the apparatus during rapid flow. Results were similar to the batch test (Figure 1.23) with very low rates of chlorine decay. Overall, the system dosed with phosphate inhibitor had the most rapid decay.

When chlorine decay was characterized in the circulation rig with all the metal pipes present, the situation changed markedly. Specifically, most pipes exhibited a high chlorine demand and there were major differences amongst the rigs (Figure 1.23). Only the water dosed with phosphate had chlorine decay rates which were about the same as in the absence of pipes. Thus, decay rates in the presence of phosphate in the rigs without metal pipe were highest and they were essentially unchanged with the metal pipes present. However, the rig dosed with 3 mg/L NOM had the next lowest decay rate and

the rig dosed with iron particles had the highest rate. Clearly, the water was influencing the chlorine demand exerted by the metal pipe surfaces present in the rig. Comparison to the chlorine decay after all metal pipes but copper was removed from the rig suggest that virtually all the demand was from copper pipe. That is, the extent and kinetics of chlorine removal was about the same in this case versus the condition with all pipes, even though only 1/3 of the copper surface was present. This similarity in decay rates might be partly attributable to the presence of a new section of copper pipe in the rig at this time.

By drawing a tangent to the initial decay curve, these trends can be summarized for all four tests and waters tested, as illustrated in Figure 1.20 lower left graph (Figure 1.22).

Throughout the experiment trends in chlorine decay were tracked by measurement of residual chlorine after 24 hours (Figure 1.24). The control and lower levels of NOM (0.05 and 0.3 NOM) increased chlorine decay after dosing of aluminum solids (after 4 months), from an average residual of 3-3.5 mg/L down to 0.5-1 mg/L. In contrast, water conditions with the highest level of NOM or PO<sub>4</sub> stayed higher than the other conditions with an average of 3.5-4 mg/L during the entire course of the experiment.

In systems with variable Cl:SO<sub>4</sub> ratio, the short term trend was different than the long term trend. Early on, the highest amount of Cl<sup>-</sup> had a lower rate of chlorine decay, but by the end of the experiment the opposite trend occurred. The highest rates of chlorine decay were always observed in the rigs dosed with iron solids, and the decay rate in this rig seemed to increase after 6½ months.

After examining the chlorine decay kinetics and compared to the average pit depth (discussed early) a major tendency becomes clear. In general, waters with higher chlorine decay rates are more susceptible to greater depth of pits. (Figure 1.26)

## Electrochemistry of Pitting

Electrochemical potential, referred to simply as  $E_{\text{Corr}}$ , is currently the most widely applied and most successful means of tracking pitting propensity. An  $E_{\text{Corr}}$  measurement quantifies the electrical potential existing between a metal sample and a reference electrode such as a Ag-AgCl. Pourbaix determined that when a new copper was exposed into a water,  $E_{\text{Corr}}$  would typically rise to within 100 mV vs. Ag-AgCl after a period of days and then stabilize (Pourbaix, 1969). However, in waters that supported copper pitting,  $E_{\text{Corr}}$  would continue to rise over a period of months to a critical value at which point pit initiation and propagation would have occurred. This overall trend is collectively referred to as electrochemical rise. Mechanistically,  $E_{\text{Corr}}$  rise results from either acceleration of the cathodic reaction or a decrease in the anodic reaction. The fact that  $E_{\text{Corr}}$  rise is often correlated with pitting propensities offers support in favor of Nguyen's hypothesis that copper pitting reactions are under cathodic control; given that factors which accelerate the cathodic reaction or localize anodic areas of attack increase  $E_{\text{corr}}$  and tend to encourage pitting.

In this case neither  $E_{\text{corr}}$  rise and the absolute value of  $E_{\text{corr}}$  was completely consistent with trends in pitting. Specifically, as chloride content increased  $E_{\text{corr}}$  also increased (Figure 1.27), whereas pitting did not increase with the fraction of chloride in the water. However, the next highest  $E_{\text{corr}}$ , as well as a clear  $E_{\text{corr}}$  rise occurred in the presence of iron particles (Figure 1.27). For waters dosed with NOM, clear trends were not clear, although the  $E_{\text{corr}}$  in the presence of highest NOM tended to be lower than was observed for other conditions (Figure 1.27).  $E_{\text{corr}}$  in the presence of chloramines (not shown) and chloramine/phosphate (Figure 1.27) were also very low, and these conditions did not pit.

The  $E_{\text{corr}}$  was a strong function of the free chlorine content of the water (Figure 1.27). For this test, total chlorine was monitored at different time intervals while it decayed, and  $E_{\text{corr}}$  was measured at the same time. This raises the possibility that  $E_{\text{corr}}$  may be a good overall indicator of pitting propensity simply because it is related to and is largely controlled by the free chlorine concentration in the water. It is very clear that free



chlorine is necessary for pitting to occur in this water. However, it does not seem that  $E_{\text{corr}}$  or fluctuations in  $E_{\text{corr}}$  are closely related to pitting propensity.

$E_{\text{corr}}$  was stable at about 150 mV in the rig dosed with phosphate and chlorine, quite possibly because chlorine levels in this rig remained relatively constant. In the presence of NOM, as long as chlorine was above 2 mg/L,  $E_{\text{corr}}$  was constant at about 170-180 mV. In all other cases, as chlorine decayed,  $E_{\text{corr}}$  dropped by between 180 and 200 mV as  $\text{Cl}_2$  decayed.  $E_{\text{corr}}$  dropped most prominently as  $\text{Cl}_2$  dropped below 1 mg/L and down to 0 mg/L (Figure 1.27).

In addition, the current flowing between the sequential copper tubes in the rig was measured. In the Marshall experiment, the first copper pipe was highly anodic relative to the second and third pipes, but this did not occur to a significant extent in this experiment.

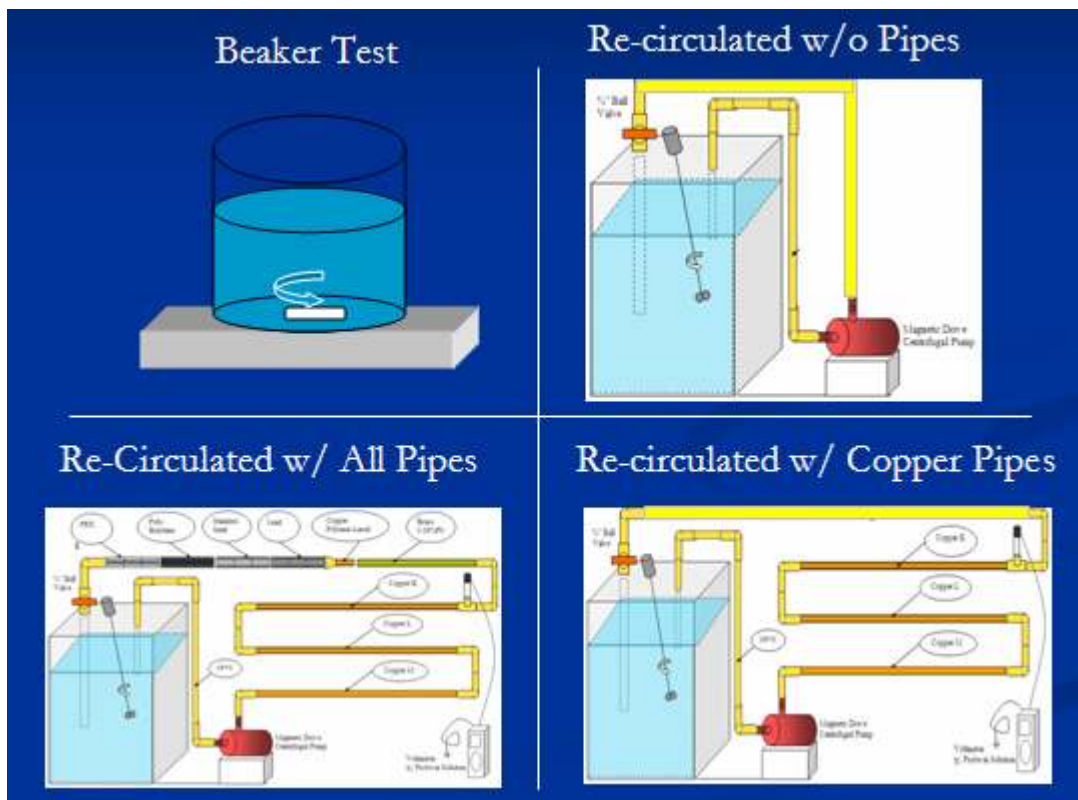


Figure 1.21: Short-term experiments to study the kinetics of chlorine decay.

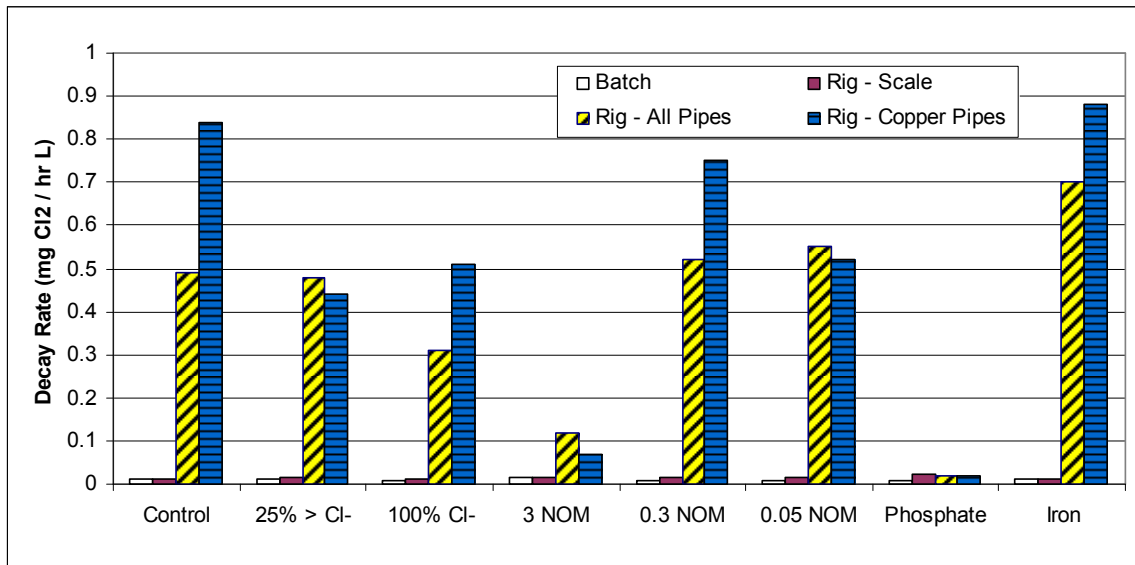


Figure 1.22: Short-Term Experiments Chlorine Decay Rate

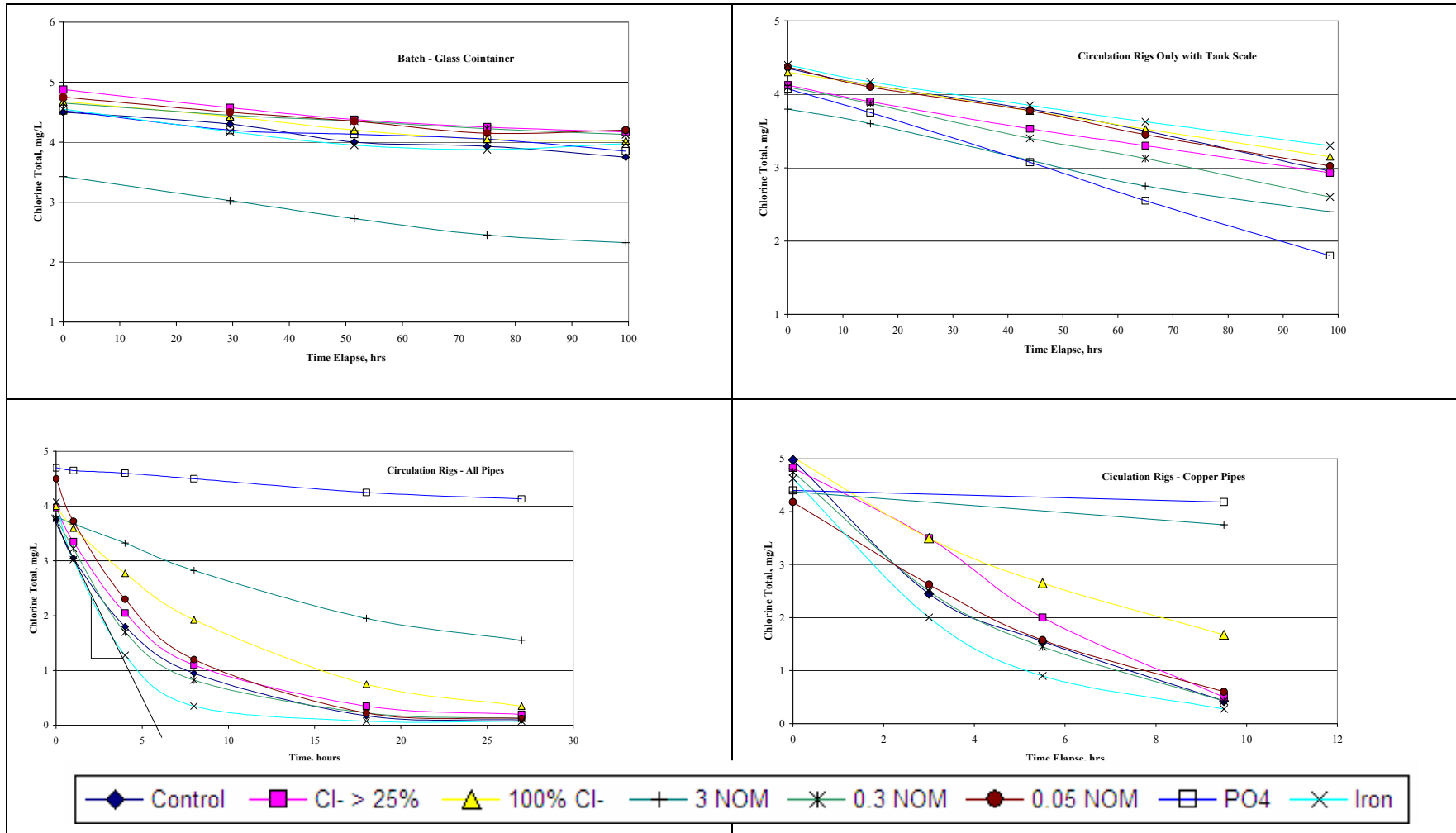


Figure 1.23: Chlorine uptake in beaker tests (upper left), rig tests without pipe (upper right), in the rigs with all pipe present (lower left), and in circulation rigs with copper only (lower right).

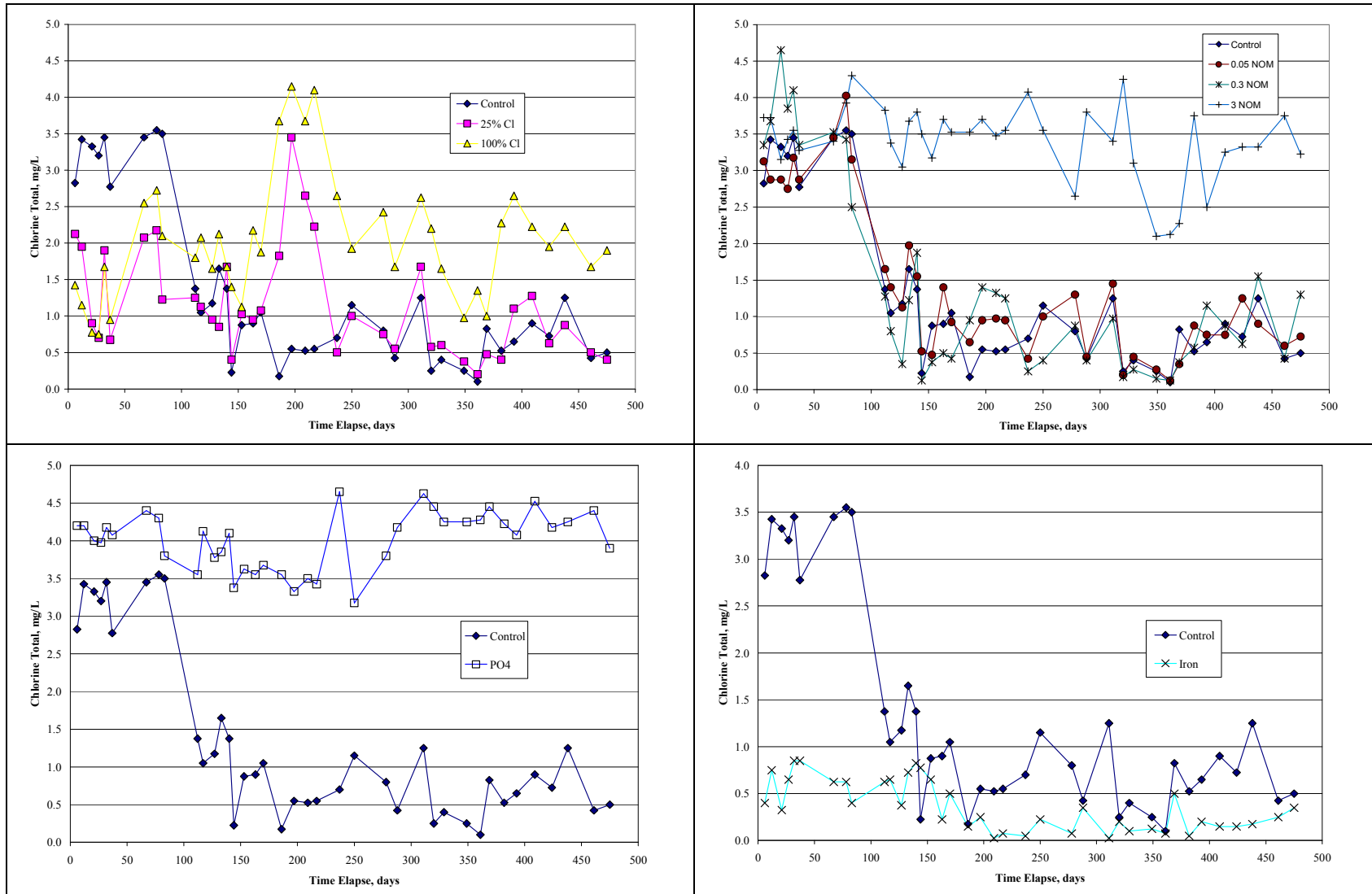


Figure 1.24: Total Chlorine measure 24 hours after raising it to around 4 mg/L for all water conditions.

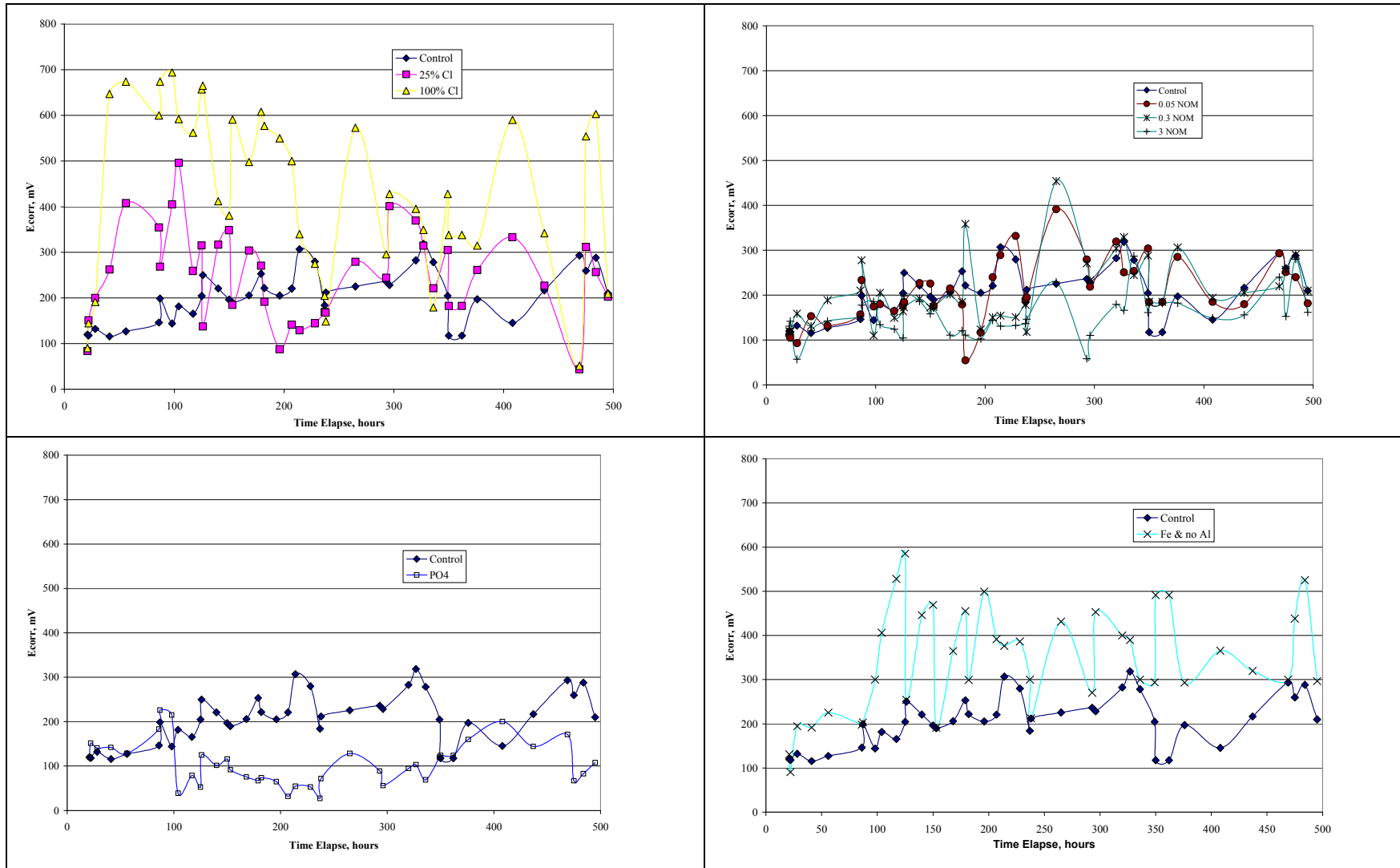


Figure 1.25: Electrochemistry - Copper M ( $E_{corr}$ )

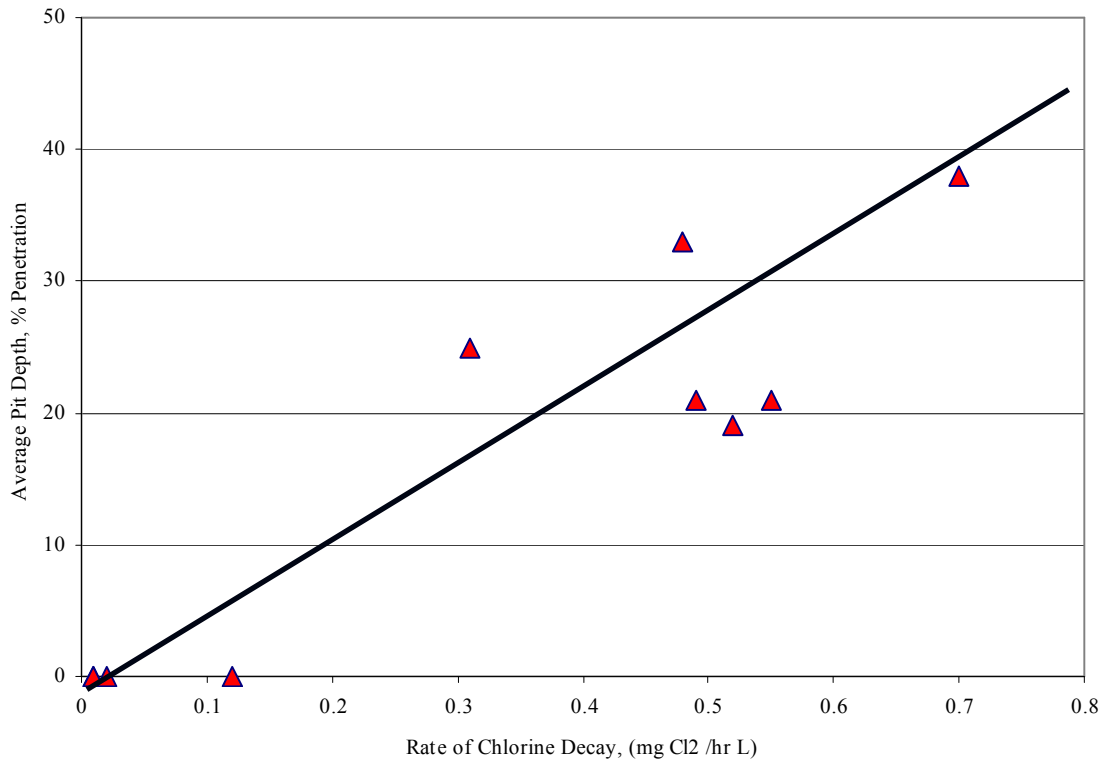


Figure 1.26: Relationship of chlorine decay and average pit depth.

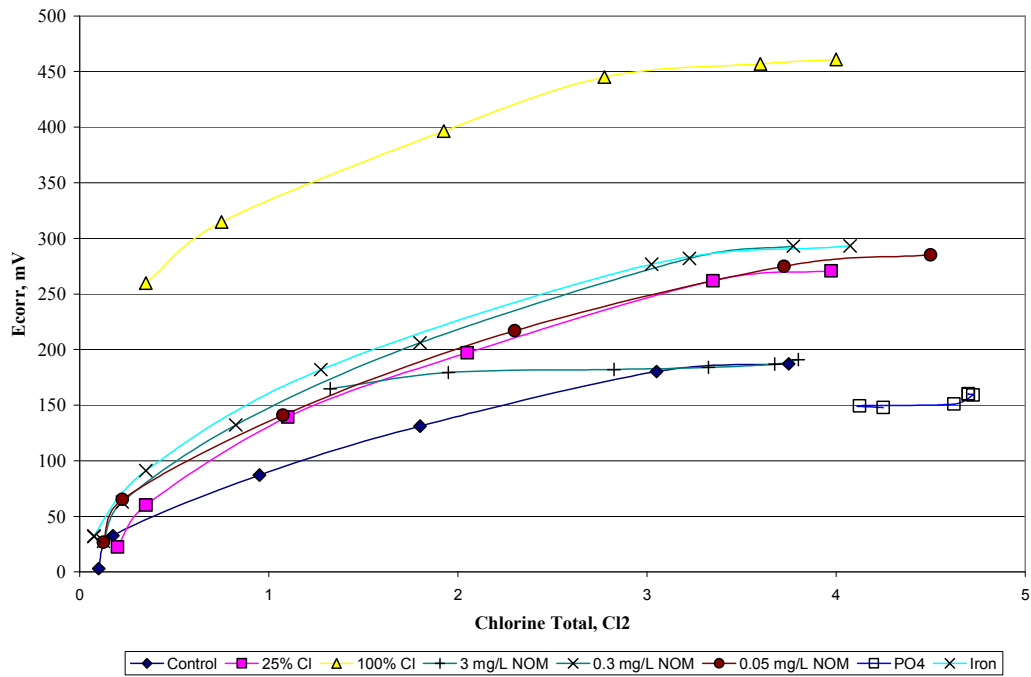


Figure 1.27: E<sub>corr</sub> as a function of chlorine concentration

## DISCUSSION

Further consideration was given to the failure to produce very rapid formation of pinhole leaks. To elaborate, no holes were created in any rig in the current work with 9' of pipe present in each, whereas the first of three 1' sections in the Marshall study developed 8 leaks/ft. Moreover, overall tube weight loss in the current work was < 0.3%, whereas the front tube in the Marshall study lost nearly 3% of its mass in 11 months. Thus, while the current work reproduced severe pitting, it is believed that the overall corrosion conditions were at least an order of magnitude less aggressive in this study than in the Marshall study.

A retrospective analysis suggested at least 4 factors which have been involved either alone or in part. First, zinc leaching from the brass in the rig may have inhibited pitting on copper. Zinc is often cited as a cathodic inhibitor of non-uniform copper corrosion, and its deposition on copper surfaces may have therefore reduced the growth rate of pits. Even after the brass was completely removed from the rig at the end of year 1, deposits of zinc from within the apparatus continued to dissolve, as evidenced by levels of 6-50 ppb  $Zn^{+2}$  measured in the recirculated water months after the brass had been removed. The potential inhibition of corrosion by zinc addition is a promising subject for future research.

Secondly, in the current work, the first set of copper tubes in the flow path was almost at the same  $E_{corr}$  as the second and third samples. This is in marked contrast with the experiment of Marshall and other recent tests conducted in this type of water, in which the first section of copper tends to become highly anodic relative to the last sections. We term this phenomenon "flow electrification," and we suspect it tended to drive pitting in the front section of copper in the Marshall study. Some preliminary experiments have indicated that the presence of zinc in water stops flow electrification, which in turn, might explain reduced rates of attack on copper in this work.

A third factor is that  $\text{Cl}_2$  levels dropped relatively rapidly in this apparatus (Figure 1.22) when compared to the approach of Marshall, who maintained constant chlorine of 4 mg/L. Using the example with iron as illustrative, at  $t = 0$  and 4 mg/L  $\text{Cl}_2$ , the initial chlorine decay rate is about 0.7 mg/L  $\text{Cl}_2$  per hour in this work. But because the  $\text{Cl}_2$  was not replenished until 24 hours later and it often reached nearly 0  $\text{Cl}_2$ , the average rate of  $\text{Cl}_2$  decay was 4 mg  $\text{Cl}_2$ /L over 24 hours or 0.16 mg  $\text{Cl}_2$ /L/hour. Thus, if the depth of pits were directly proportional to  $\text{Cl}_2$  decay rates, pits would grow at  $0.70/0.16 = 4.4$  times slower rate using the  $\text{Cl}_2$  dosing scheme in this work versus holding the  $\text{Cl}_2$  constant at 4 mg/L. This is clearly an important contributor and it might even be the only critical difference. However, replenishing  $\text{Cl}_2$  twice each day during the last phase of the experiment still did not reproduce rapid pitting as tracked by  $E_{\text{corr}}$ .

Finally, it is possible that initial exposure of the copper to the higher flow rate or initial use of soluble rather than particulate aluminum may have formed a protective layer on the copper. It is possible this protective layer was somewhat resistant to pitting attack even after aggressive conditions were restored.

## CONCLUSIONS

In a water with a high pitting propensity attributable to free chlorine at high pH:

- 1) iron residuals caused more serious pitting than an equimolar level of aluminum residuals
- 2) the form of the iron or aluminum, either initially soluble or initially particulate, can lead to differences in deposition and might influence pit initiation
- 3) complete replacement of sulfate with chloride does not dramatically worsen pitting, although it is believed that the ratio of chloride to sulfate is one key factor in pitting
- 4) levels of NOM between 0 and 0.3 mg/L NOM exhibited similar pitting severity; however, the presence of 3 mg/L NOM in the water inhibited pitting
- 5) the addition of orthophosphate reduced pitting propensity dramatically
- 6) substitution of chloramines for chlorine in water of this type reduced pitting severity

Relative to results from previous research using water of the same approximate composition, less severe pitting was observed. This may be due to:



- 1) a different form of aluminum dosed in initial phases of testing (soluble instead of particulate)
- 2) presence of zinc inhibitor in the current test from corroding brass
- 3) lower levels of chlorine overall in the current experiment

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## **CHAPTER 2: EFFECT OF ION EXCHANGE AND OTHER TREATMENTS ON NON-UNIFORM CORROSION OF BRASS.**

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**ABSTRACT.** Although brass was attacked non-uniformly by an aggressive water at high pH and with high  $\text{Cl}_2$  content, no significant pitting occurred at any condition tested, even though pitting did occur for copper exposed to the exact same water. The implication is that zinc in the alloy may help to prevent non-uniform attack on copper and copper alloys.

### **INTRODUCTION**

Plumbing products made from brass and other alloys are frequently used in valves, pumps and other precision plumbing products. These materials also can legally contain up to 8% lead by weight provided that they also pass certain performance standards. This study examined the effects of water treatment on non-uniform corrosion of brass in an aggressive high pH water with aluminum. The fraction of chloride and sulfate in the water, amounts of natural organic matter (NOM), iron instead of aluminum, and chloramines disinfectant were also examined as part of this evaluation.

### **Experimental Methods and Materials**

The experimental setup, modifications to the waters and experimental timeline were detailed in Chapter 1. The brass used in this work contained 0.09% lead, 63% copper and 36% zinc.

During the experiment in the rig with chloramines and chloramines plus phosphate, nothing of significance appeared to be occurring with respect to non-uniform corrosion early in the experiment. Therefore, in these two rigs significant deviations in the protocol were tested including 1) very high levels of chloramines and 2) lower pH (Figure 2.1). The molar ratio of chlorine to ammonia was always 4 to 1. However, the total chlorine

concentration was 4 mg/L during the first 11 months and then raised to 16 mg/L during the remainder of the experiment (Figure 2.2). Chlorine decay rates were low and these levels of residual were stable.

In addition, during the first 7 ½ months (Phase 1) the pH was kept in the range of pH 8.8-9.2, but thereafter the pH was lowered to pH 8-8.2.

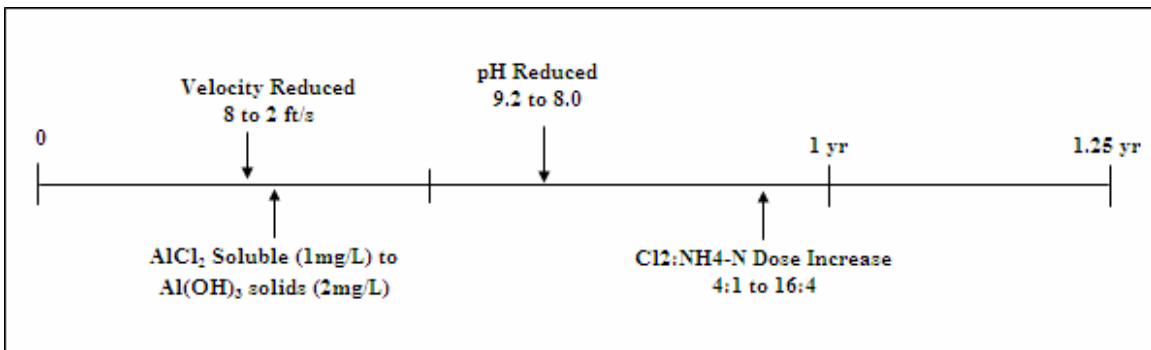


Figure 2.1: Substantive changes in test conditions during the chloramines experiments.

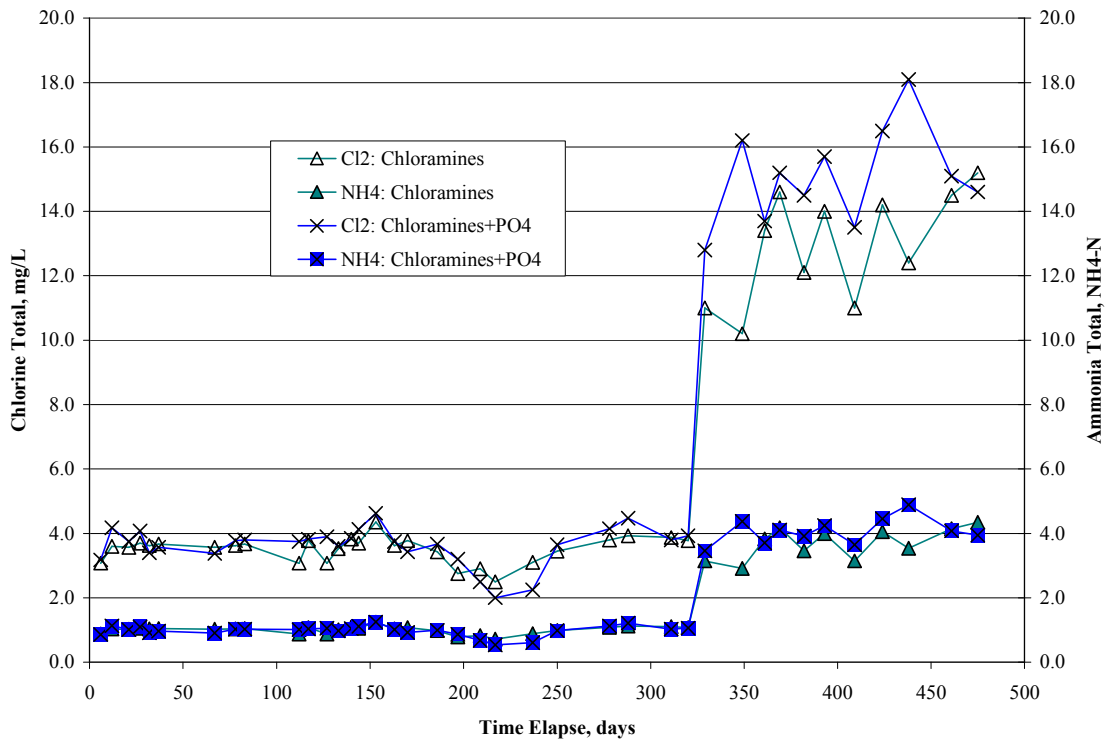


Figure 2.2: Total Chlorine and total ammonia as nitrogen measured 24 hours for the chloramines conditions.

## **RESULTS AND DISCUSSION**

Experimental results are discussed in four sections including 1) analysis of copper surface via visual observation, 2) weight loss and dezincification, 3) scaling and scale identity, and 4) electrochemistry relative to copper. Thereafter key conclusions are drawn relative to treatments that might modify these constituents.

### **Visual Analysis of Copper Surface**

The original pipe surface was photographed at the start of the experiment (Figure 2.3). In general results at 7 ½ months and 15 months were similar. From a superficial visual observation, attack on the brass pipe appeared to be non-uniform and highly variable (Figure 2.5). However, when the highly non-uniform surface scale was removed, surprisingly, no significant pits were detected on any of the brass samples. During high pH exposure for the first 7 ½ months in the system with chloramines the brass surface was new and shiny (Figure 2.4). After dropping the pH and increasing the chloramine concentration, much more significant attack was observed (Figure 2.5). The condition in which all the sulfate was replaced by chloride seemed to have more scattered mounds relative to the same conditions with lower chloride and higher sulfate. Similar effects were observed at 0.3 mg/L NOM or lower. The water with high levels of NOM (3 mg/L), PO<sub>4</sub>+ Cl, and chloramine + PO<sub>4</sub> had highly non-uniform scale but with large patches of the surface unaffected. The rig with iron particles seemed to form deposits non-uniformly along the bottom of the pipe.

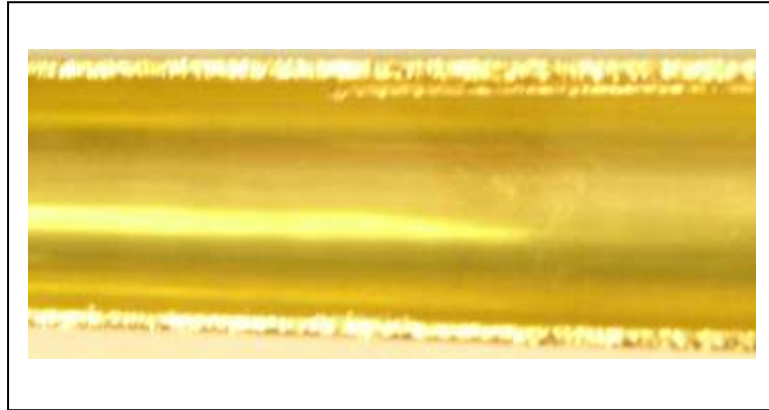


Figure 2.3. Brass tube uncontaminated internal surface.

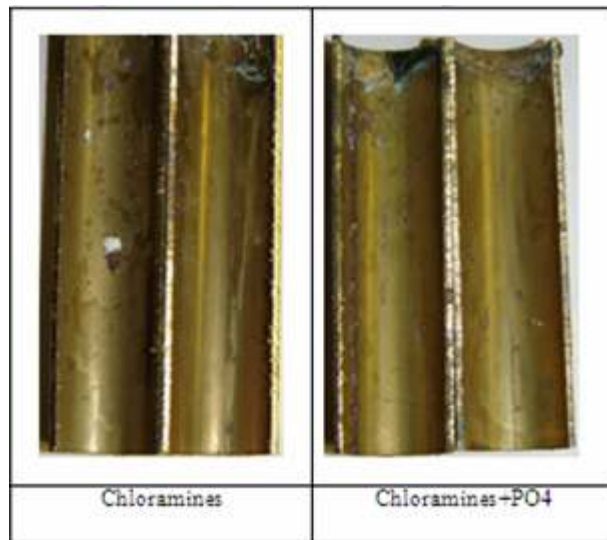


Figure 2.4: Brass photo for the first 7 ½ months, exposed mainly to high pH water and low chloramine residuals.



Figure 2.5: Brass photos after 15 months, after raising pH and Cl<sub>2</sub>:NH<sub>4</sub> concentration ratio.

### Weight Loss and Leaching

The zinc and copper that corrodes from the pipe can either become incorporated into scale or can leach into the water. In general, the concentration of zinc leached into the water after testing at pH 9.2 was high when compared to the second phase of experiments at slightly higher pH (Figure 2.6). The exception was the system dosed with PO<sub>4</sub>, in which zinc leaching markedly increased with the higher pH.

Despite the appearance of the samples which suggested an aggressive attack, only few of the conditions exposed to chlorine had detectable weight loss (Figure 2.7). This is consistent with the fact that these waters actually have very low overall corrosion rates.

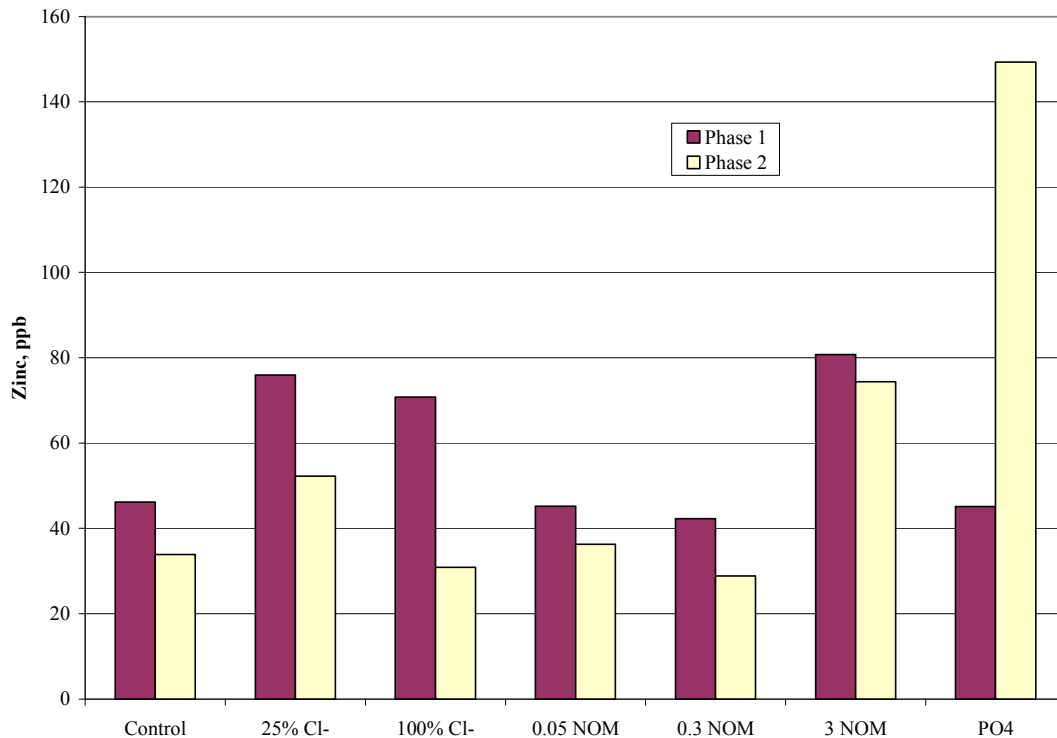


Figure 2.6.A: Zinc leaching for all water conditions. Phase 1 ran for the first 7 months in which the upper pH limit was kept at 9.2; phase 2 ran the rest of the experiment with an upper pH limit of 9.6.



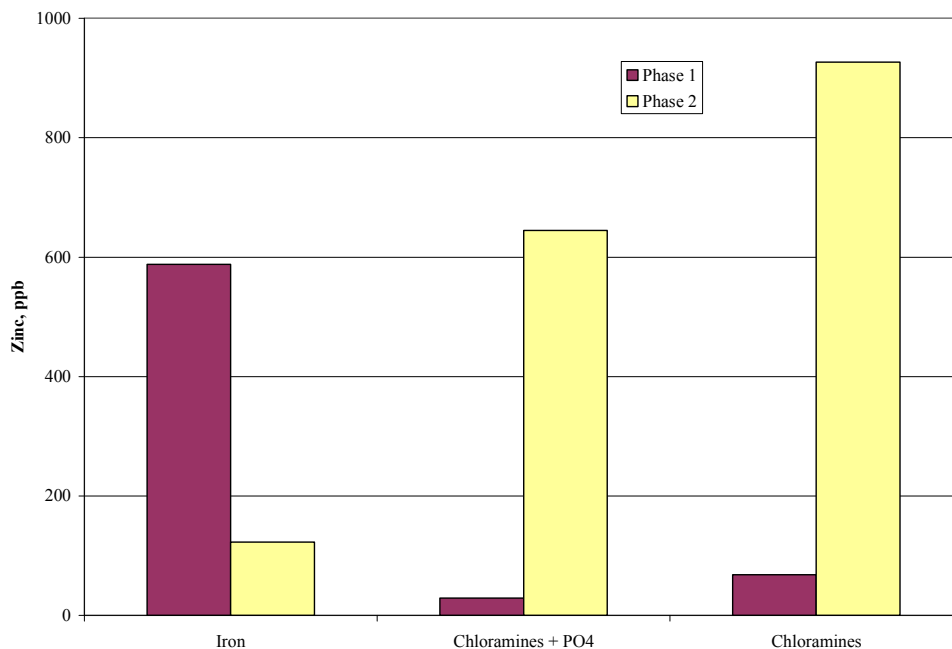


Figure 2.6.B: In the phase 1 for the iron condition iron soluble salts were added as in contrast with phase 2 were iron solids were added. In addition, for the chloramines conditions phase 1 had high pH (9.2) and phase 2 had low pH (8.0).

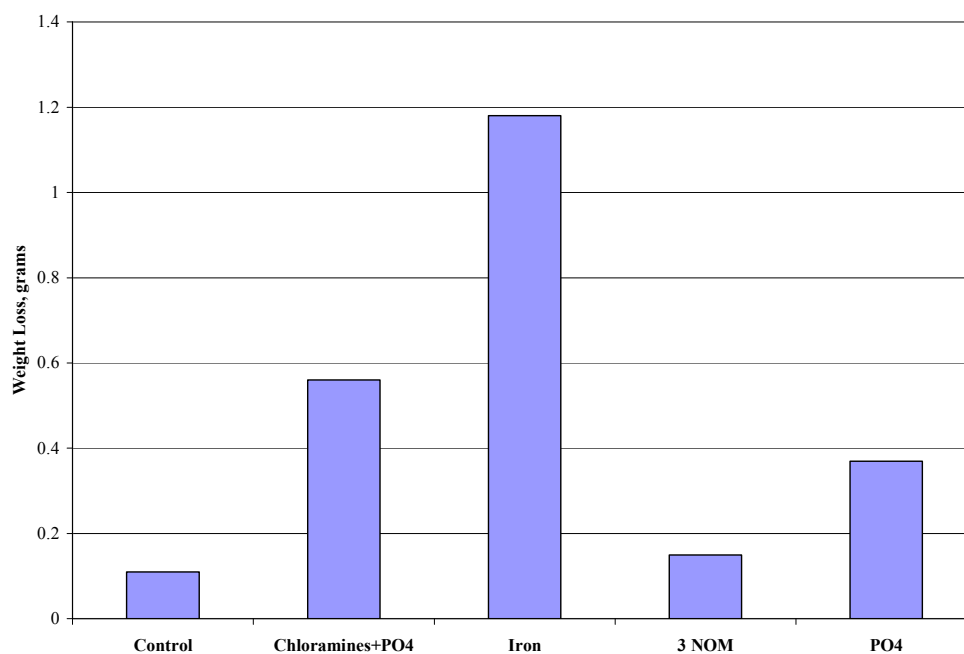


Figure 2.7. Weight loss of the brass pipes exposed to free chlorine at the end of the entire experiment. In all cases weight loss of the copper pipe was less than 1.2 g, which translates to less than 0.3% of the pipe mass.

### **Scaling and Scale Identity**

Selected sections of each pipe were analyzed with a field emission scanning electron microscope (FE-SEM). The scale deposition was analyzed by acquiring a picture and ESCA was used to identify major constituents (Figure 2.8).

Key trends became evident after a thorough evaluation (Figure 2.9 and Figure 2.10). Areas of the pipe with scale were highly enriched in zinc relative to the alloyed metal, whereas areas of the pipe without scale were deficient in aluminum.

Systems dosed with aluminum had between 6.2 and 8.4% aluminum in the scale of the pipe, whereas the system dosed with phosphate and high NOM had 4.9 to 1.8% aluminum deposits, respectively (Figure 2.9 and Figure 2.10). In contrast, systems dosed with iron had only a small amount of iron 1.6% in the scale of the pipe. In the case of non-uniform corrosion, aluminum traces were present in all conditions (2.7 to 7.2%) as well as iron in the iron condition.

In both systems dosed with aluminum and iron, zinc (18.8 to 27%) and copper (39 to 54.7%) were important components of scale over the pipe surface. Conversely, iron and chloramine conditions had higher zinc (40.8 and 33.3) and lower copper (19.7 and 23.4%) when compared to the rest of the conditions.

Chloride was found on the top layers of scale in non-uniform corrosion areas between 0.6 to 1.8%. However, it was not present on pipe in chloramine and low NOM (0.05 NOM) conditions. Sulfate was found in the control, 25% chloride and chloramine conditions ranging from 1.1 to 2.0%.

Lead was present only as a scale in the iron, PO<sub>4</sub> and chloramine conditions as a trace ranging from 3.4 to 11.4%. However, did only play an important a role on the non-uniform scale for 100% chloride and iron conditions (3.5 and 5.4%).

Traces of sulfate, calcium and sodium from the water were also detected on some pipe surfaces.


Water Chemistry Description for Brass Pipe	True-Image (1" by 1/2")	SEM Photograph
	PO4	

Figure 2.8: Example of the SEM selected sections of brass pipe analyzed. Note that locations marked by a + represent a measurement area of  $1 \mu\text{m}^2$ .

Water Chem.	Uniform Corrosion %	Image	Non-Uniform Corrosion %
R1: Control	<p>Zn 19.5 O 19.2 Na 5.2 Al 7.0 Cl 1.5 Cu 49.3</p>		<p>Zn 48.2 O 29.1 Na 10.6 Al 6.4 Cl 1.8 S 1.1 Cu 1.7</p>
R7: Chloramines	<p>Pb 3.4 O 27.9 Zn 33.3 Na 6.9 Al 6.2 Cu 23.4</p>		<p>O 26.4 Zn 52.2 Na 8.0 Al 5.9 S 2.0 Cu 6.2</p>
R9: PO4	<p>Pb 11.4 O 10.8 Na 4.2 Al 1.8 P 1.5 Cl 0.6 Cu 0.5 Zn 27.0</p>		<p>O 32.1 Zn 44.2 Na 8.4 Al 6.4 P 3.9 Cl 0.6 Ca 1.3 Cu 2.1</p>
R5: Iron	<p>Pb 6.6 O 24.8 Zn 40.8 Na 7.4 Fe 1.6 Cu 19.7</p>		<p>Pb 5.4 O 22.4 Zn 57.1 Na 9.1 Cl 0.9 Fe 1.2 Cu 5.8</p>

Figure 2.9: Photo of each pipe surface and composition of uniform and non-uniform corrosion areas.

Water Chem.	Uniform Corrosion Element %	Image	Non-Uniform Corrosion Element %
R2: Cl <sup>-</sup> >2.5%	<p>Zn 18.8 O 28.4 Na 4.4 Al 8.3 Cu 39.0</p>		<p>Zn 54.5 O 26.3 Na 12.5 Al 2.7 S 1.4 Cl 0.6 Cu 0.9</p>
R4: 100%Cl <sup>-</sup>	<p>Zn 20.0 O 27.4 Na 2.5 Al 8.4 Cu 39.7</p>		<p>Zn 43.8 O 31.8 Na 8.1 Al 7.0 Cl 1.0 Cu 5.9 Pb 3.5</p>
R10: 0.05 NOM	<p>Zn 18.8 O 16.8 Na 3.3 Al 6.2 Cu 54.7</p>		<p>Zn 50.9 O 28.8 Na 11.0 Al 5.7 Cu 3.7</p>
R8: 3 ppm NOM	<p>Zn 24.3 O 15.2 Na 3.1 Al 4.9 Cl 0.6 Cu 47.8</p>		<p>Zn 54.4 O 25.9 Na 7.8 Al 7.2 Cl 1.6 Cu 1.6</p>

Figure 2.10: Photo of each pipe surface and composition of uniform and non-uniform corrosion areas.

## Electrochemistry of Brass Corrosion

Several key measures of brass electrochemistry were tracked during the experiment.

$E_{\text{corr}}$  of the brass pipe relative to an AgCl reference electrode was, with few exceptions, either stable or in decline throughout the experiment. This is consistent with the fact that pitting did not occur.

The galvanic behavior of brass relative to copper was tested by connecting the brass pipe to a copper pipe and measuring the voltage drop and current between the two (Figure 2.11, Figure 2.12 and Figure 2.13). A higher amount of  $\text{Cl}^-$  relative to sulfate increased the magnitude of the current between copper and brass, with the current acting to sacrifice the brass. The presence of phosphate dramatically reduced the current, and while NOM did not matter in the first part of the test, more NOM decreased the galvanic current in the second part. The presence of iron increased currents relative to aluminum (Figure 2.11). Trends in voltage were consistent with the current trends, in that a greater voltage drop resulted in a greater current as described.

Chloramine results are discussed separately and in relation to the control with free chlorine (Figure 2.14). In general, the voltage drops between the copper and lead in the system with chloramine were very low throughout the experiment. Likewise, currents and voltage between the two metals were also low. In general, the galvanic corrosion between brass and copper seems to be driven by free chlorine and not chloramine, with the main difference arising from chlorines ability to increase  $E_{\text{corr}}$  of copper tube.

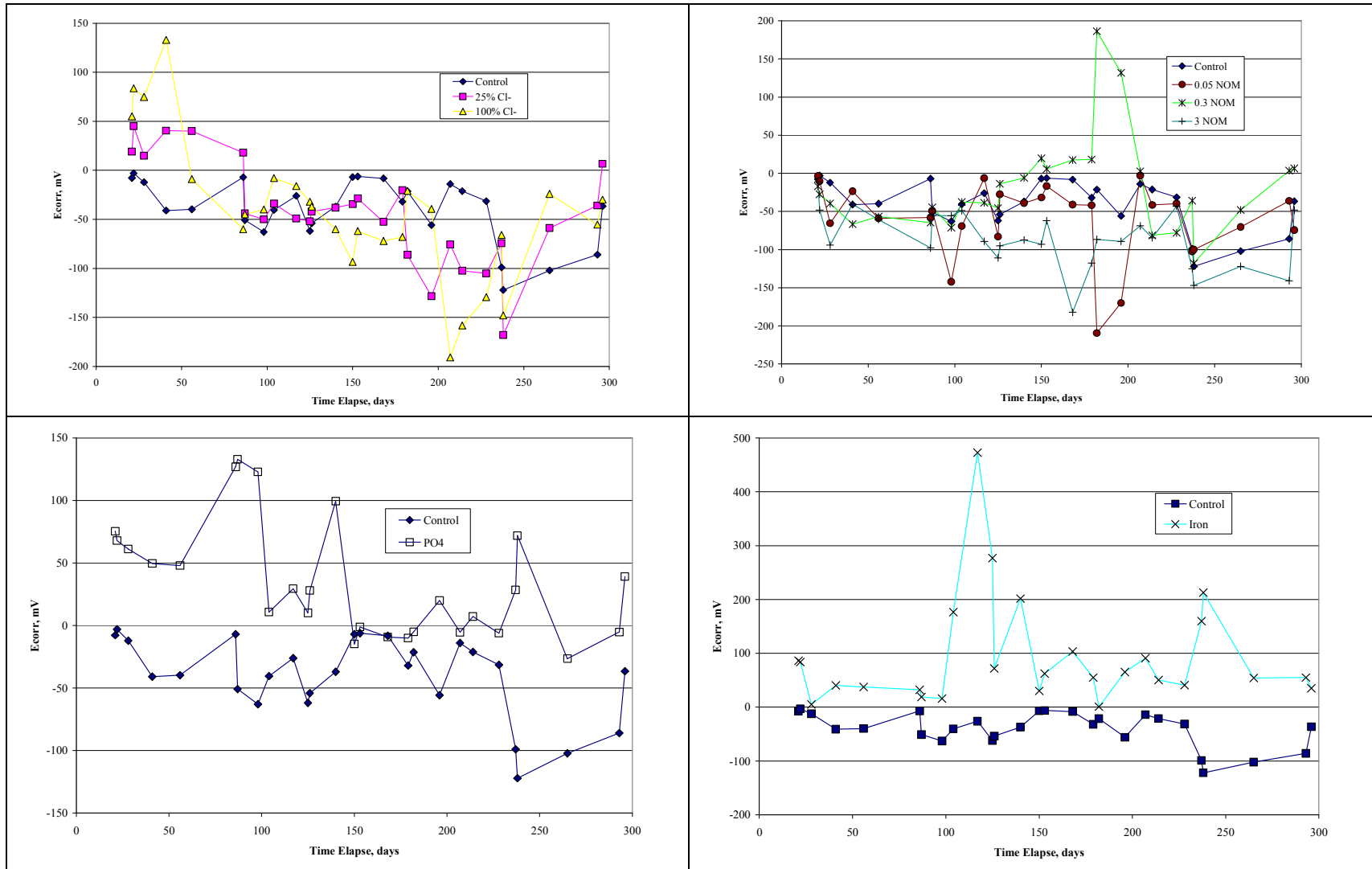


Figure 2.11: Brass pipe electrochemistry ( $E_{corr}$ ).

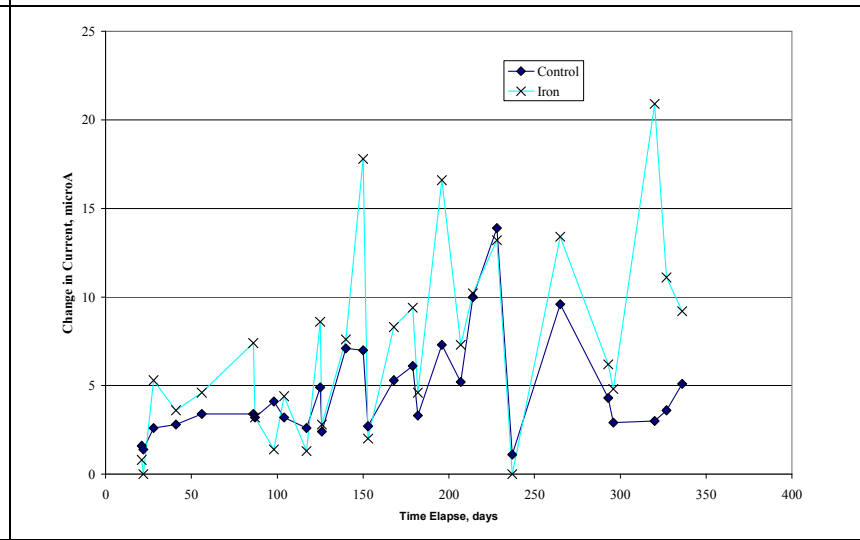
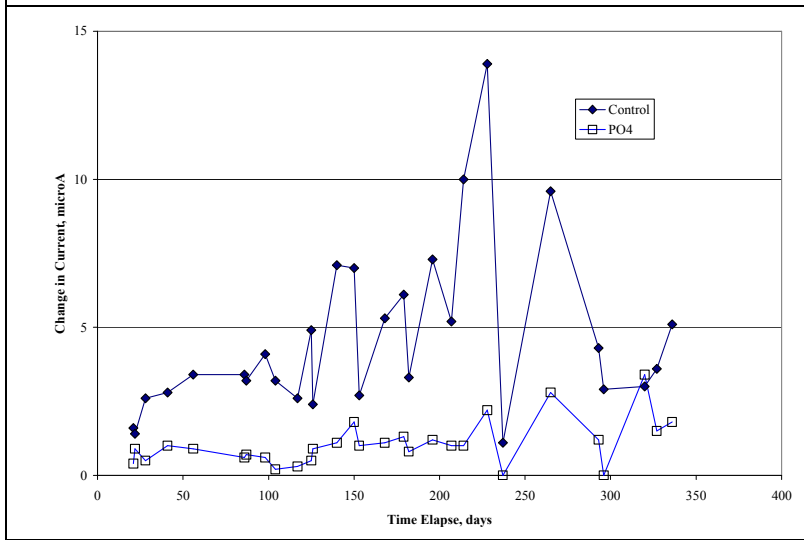
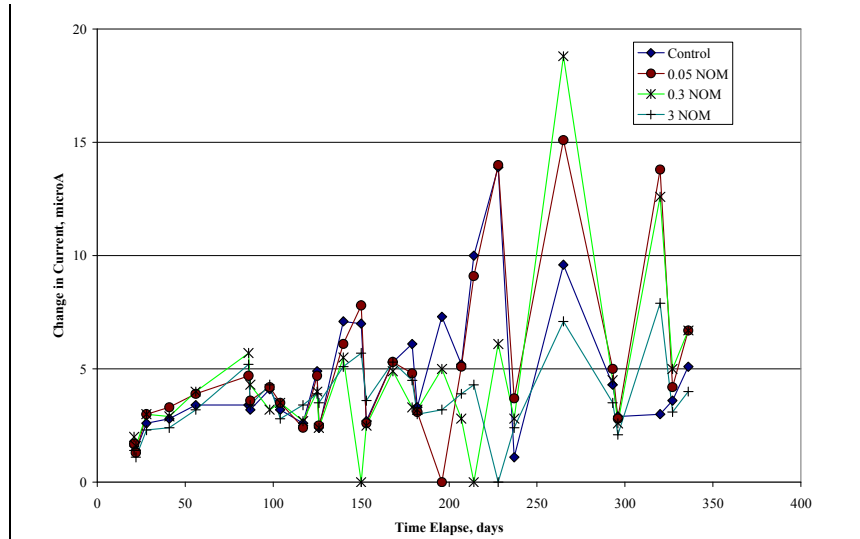
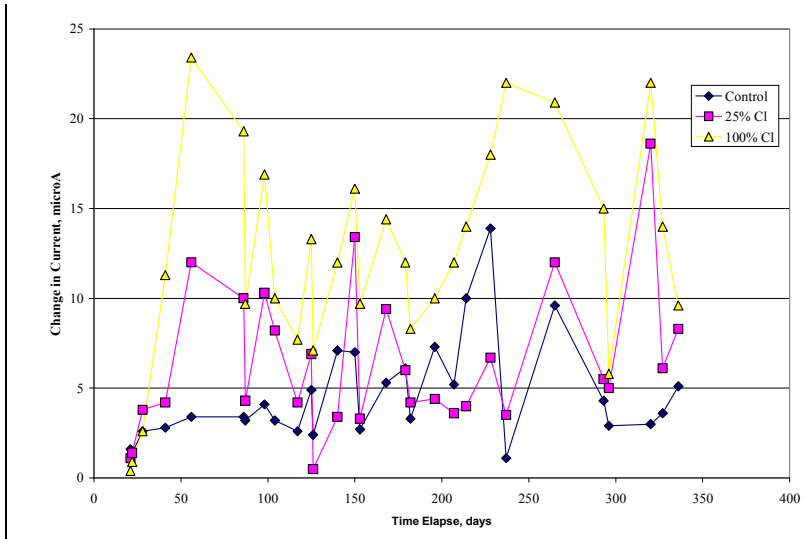


Figure 2.12: Brass pipe electrochemistry (change in voltage). Copper M versus Brass



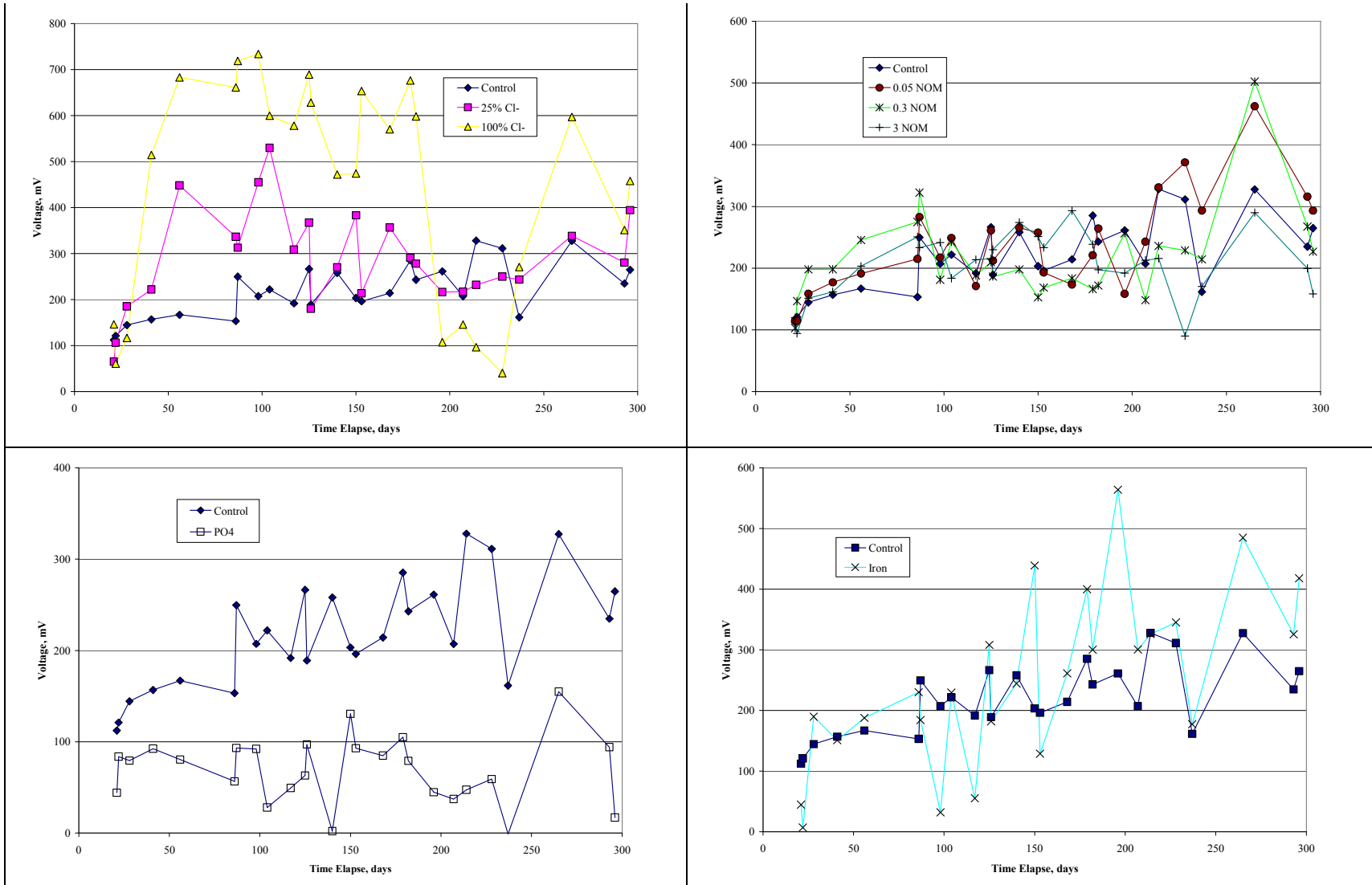


Figure 2.13: Brass pipe electrochemistry (change in voltage). Copper M versus Brass

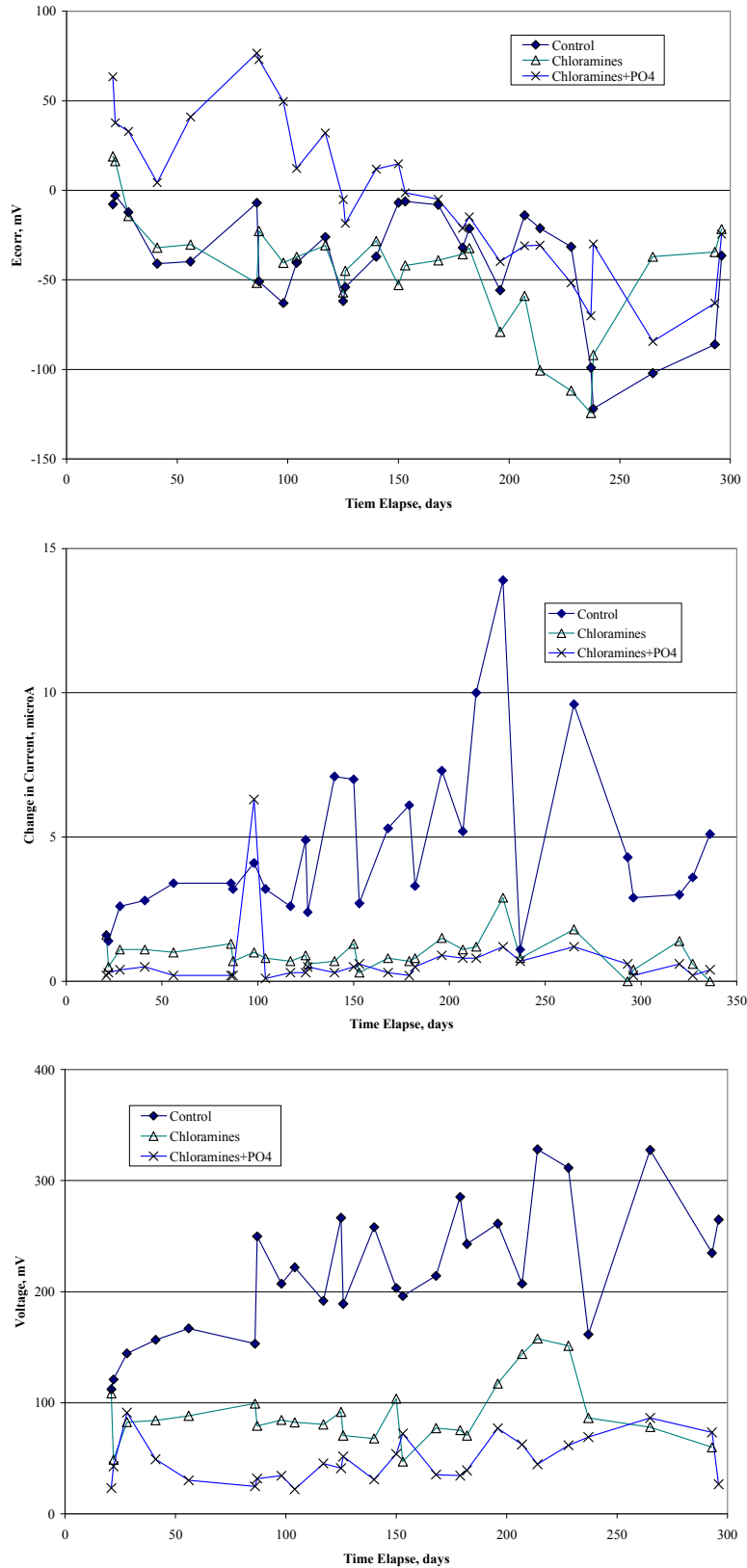


Figure 2.14: Electrochemistry of Brass: Ecorr (Top), Change in Current (Middle) and Voltage (Bottom) measure against copper type M.

## CONCLUSIONS

In a water with a high pitting propensity attributable to free chlorine at high pH:

- 1) brass was attacked non-uniformly, no significant pitting occurred at any condition tested
- 2) zinc in the alloy may help to prevent non-uniform attack copper alloys.
- 3) the galvanic corrosion between brass and copper seems to be driven by free chlorine and not chloramines

Key Conclusion: No significant pitting was occurred at any of the conditions.

## CHAPTER 3: LEAD LEACHING FROM IN-LINE BRASS DEVICES: A CRITICAL EVALUATION OF THE EXISTING STANDARD

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**ABSTRACT.** The ANSI/NSF 61, Section 8 standard is relied on to protect the public from in-line brass plumbing products that might leach excessive levels of lead to potable water. Experiments were conducted to examine the practical rigor of this test. Contrary to expectations, the test was not highly protective of public health. Rather, it was determined that small devices made of pure lead- which pose an obvious public hazard- can easily pass the leaching protocol. Reforms are needed to help prevent such unacceptable outcomes in the future. Brass devices passing the test can contribute to lead levels at the tap in residences, schools and other buildings.

### INTRODUCTION

A crisis of confidence arising from excessive lead in potable water of the nation's capital (*Nakamura, 2004, Edwards et al., 2004a,b*) has prompted a comprehensive national review of lead standards. It is widely accepted that minimizing the extent of lead leaching to drinking water from plumbing materials is a worthy public health goal and the EPA Lead and Copper Rule (LCR) has achieved great progress in this area (*Federal Register, 1991*). The amount of lead leached to public drinking water is a function of two key factors that are under societal control. The first factor is the type of plumbing material used, because some plumbing products have a relatively high tendency to contaminate drinking water with lead. The second factor is the corrosivity of the water supply that contacts plumbing products. Achieving the goal of very low lead in potable water requires progress in both areas.

The EPA LCR has been designed to assess the lead leaching tendency of public water supply in the context of existing plumbing. Lead present in the one liter "first draw" EPA LCR sample can come from: 1) lead present in the source water, 2) lead leached to water as it quickly passes through service lines at high flow rates, and 3) lead leached to water as it contacts the home plumbing system during prolonged stagnation (Figure 3.1). The EPA LCR also requires monitoring of lead leaving the treatment plant and has very limited sampling provisions to detect "spikes" of lead that might build up in water from prolonged stagnation in service lines (Edwards and Dudi, 2004b). If 90% of first draw samples are not below the 15 ppb lead action limit, the LCR prescribes steps to minimize corrosivity of the water. For example, by manipulating the chemistry of public drinking water through adjustment of pH, alkalinity, or by addition of corrosion inhibitors such as orthophosphate, it is often possible to greatly reduce leaching of lead to public water supplies at relatively modest cost (*Schock, 1989a; Schock et al, 1996; Edwards, 2002a*). Such corrosion control steps can often reduce lead leaching to water from many lead-bearing plumbing products including pure lead pipe, lead solders and brass.

Some progress has been made phasing out potentially harmful plumbing products. Pure lead pipe, leaded solders and brass with > 8% lead content were deemed such a potential hazard, they were explicitly banned in the 1986 SDWA as amended in 1996 (Federal Register, 2000). Recently, progress has been driven by Proposition 65 in California, which has led to use of very low lead brass residential water meters and required a more stringent standard for lead discharge from consumer faucets. Proposition 65 has also impacted standards for products that are available nationally (*Maas et. al., 2002a-e*). However, the definition of "lead free" brass still allows sale of devices containing up to 8% lead by weight as long as they are in compliance with performance standards established in accordance with 42 U.S.C. 300g-6(e) (EPA, 2005)

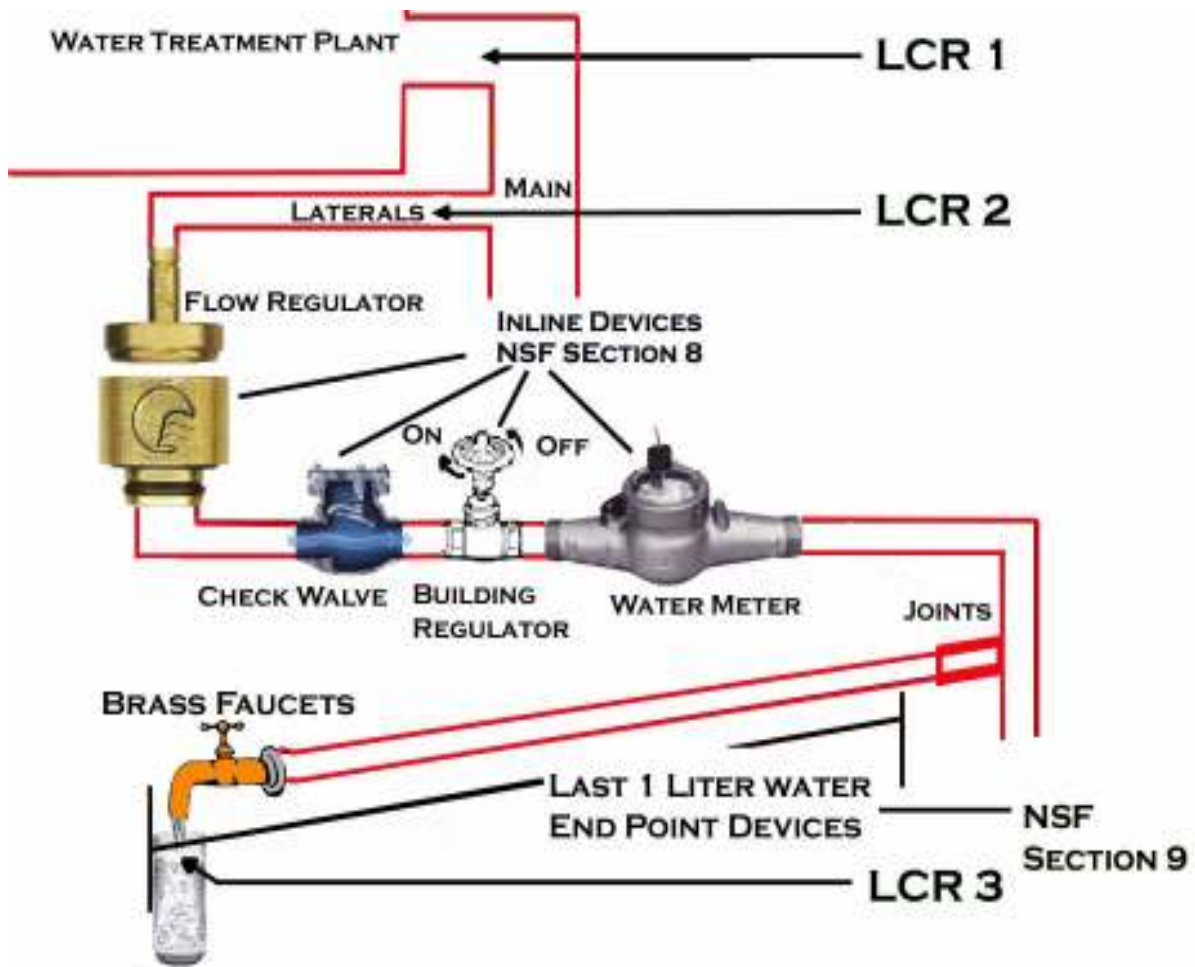


Figure 3.1: The lead and copper rule requires sampling at the treatment plant (LCR 1) and in first draw samples from consumers' tap (LCR 3). Some sampling is recommended of service lines (LCR 2). NSF section 8 and section 9 are performance standards that attempt to insure that plumbing devices do not have a tendency to leach high levels of lead to potable water.

To illustrate the potential magnitude of the problem, we note that a typical gate valve has at least 100 g of brass that could uniformly corrode away before the product failed. At 5% lead content, the lead leached to water from corrosion could contaminate every drop of water (e.g., increase the concentration to the 15 ppb action limit) that would be used by a typical family of four in a year. Of course, this amount of brass corrosion does not occur in a year, but is spread over the product lifetime. In typical domestic plumbing system configurations, multiple brass devices are often installed between the water main and the water taps in the home. Thus, there can be an additive effect. They also give potential for rather unpredictable “spikes” of lead in drinking water coming from the tap. These spikes could be attributable to a combination of the water that sat inside these devices during stagnation, plus sloughing off of particulate (precipitated or corroded) material during stagnation and flow.

These considerations illustrate a societal need for a test that prevents installation of brass products that could release excessive amounts of soluble or particulate lead to water. What are the desirable characteristics of a test? On the practical side, those selling plumbing products are correct to argue that the test should be of reasonable duration and expense. If the test was too expensive or required too much time, improved plumbing products could be excluded from market, which is not in the public interest. It is also critical that the test be reproducible in different product testing laboratories around the country and at different times. Finally, it is critical that the test be prospective, such that products leaching problematic levels of lead can be excluded from the pool of products that is installed in homes (or schools) before they pose a direct public health threat or difficulty with regulatory compliance. Obviously, many of the home or institutional plumbing products in question are not visible or even readily accessible once installed, so a “recall” of dangerous products would be practically impossible.

It must also be kept in mind that under the Lead and Copper Rule, for large water systems (serving over a population of 50,000), the target 90<sup>th</sup> percentile value is not 0.015 mg/L. Rather, the target is “optimization” or minimization of a lead release, which can be viewed as a more stringent goal. Nonetheless, standards that “allow” brass devices to contribute significant lead can cause corrosion control treatment burdens and difficulty in meeting LCR 90<sup>th</sup> percentile requirements for corrosion control.

Some have argued that the EPA Lead and Copper Rule (LCR) itself will protect the public from leaded brass products that are currently legal. This argument logically fails for many reasons. First, the EPA LCR would have to be modified extensively to quantify lead leaching from leaded brass devices, since at present the LCR does not 1) intend to make sure that homes are sampled with every possible type of plumbing product configuration, 2) attempt to document the presence of specific types of leaded brass products present in the homes which are sampled in the EPA LCR, and 3) purposefully detect spikes of lead that might occur from leaded brass installed near the service lines. Additionally, only a very small percentage of residences are sampled by the LCR, which leaves detection of unusual problems in homes up to individual consumers. Testing of new in-line products using something like the LCR would require installation of potentially dangerous untested products in consumers’ homes, sampling according to some new protocol as yet undeveloped, and exposing consumers to potentially harmful levels of lead throughout the test. In short, the LCR was not designed, nor can it rationally be modified, to protect the public from specific potentially harmful plumbing products.



For new brass plumbing products, the two currently accepted performance standards designed to protect public health include NSF 61 Section 9 and NSF 61 Section 8 (Table 1). Plumbing products that pass NSF Section 9 have explicit recognition from the EPA in terms of limiting lead leaching to water (*EPA, 2004*). All other brass devices fall under NSF 61 Section 8 (Table 3.1) and are termed “in-line” devices. There is presently no national legal requirement that in-line brass devices meet either NSF 61 Section 8 or Section 9 standards. However, 44 states had legislation requiring conformance to these standards by 2001, and the remaining states had intentions to do so (*ASDWA, 2001*). Of course, enforcing the standards requires continued vigilance and verification. For instance, recent surveys in the state of Pennsylvania have shown that prohibited lead:tin solder are widely available for use in plumbing installations and repairs (Ziegler 2001; Crowell 2002; Hendrix 2004; Wade 2003) and similar issues can be expected for leaded brass devices.

Table 3.1: Comparison of NSF 61 Section 8 and Section 9.

	NSF 61-Section 8	NSF 61-Section 9
Stated Coverage	In-line devices, or devices installed on the service line downstream of the endpoint devices.	Endpoint devices, or devices that typically contact the last liter of the distribution system (e.g., the first draw sample)
Illustrative brass devices covered	Backflow preventor, valves and fittings (e.g., building valves, check valves, compression fittings), corporation stops, meter couplings, meter stops, water meters	Lavatory and kitchen faucets, drinking water fountains, supply stops and endpoint control valves.
Illustrative brass devices specifically exempted	Temperature and pressure relief valves, valves with hose thread outlets	Bath and shower valves, roman tub valves, backflow prevention devices, faucets with a hose tread spout end, faucets that are self-closing, metering or electronically activated.

While many in the drinking water industry are familiar with the general reputation of NSF 61 in certifying plumbing products as safe for drinking water usage, detailed knowledge of the test protocol is not readily accessible or widely understood. Few appreciate that there are important differences between the test protocols for end-point devices such as faucets versus those for in-line devices as detailed by *Hazan et al. (1994)*. In-line devices are tested in two waters henceforth termed the “NSF pH 5” and “NSF pH 10” water. After the devices are exposed to the test waters for up to 14 days conditioning, lead leached to the test water is quantified after a 12-16 hour stagnation period. The measured concentration of lead from the test is then normalized to “*determine the level of contaminants projected “at the tap” based on the level of contaminants identified during laboratory analysis*” (e.g. *NSF, 2000*). If the normalized concentration is less than 15 parts per billion (ppb) with both test waters, the product passes the protocol and can be NSF certified, as long as the product also contains less than 8% lead by weight as specified by law (*EPA, 2004*).

Products that pass the test can be found labeled “*ANSI/NSF 61-8 Clean Water for Our Future*” in the marketplace, and other prominent displays indicate that devices offered for sale have passed the standard (Figure 3.2). A purchaser would be further reassured to read NSF literature which indicates the NSF 61 Section 8 standard was developed by a consortium of: NSF International, The American Water Works Association Research Foundation, the Association of State Drinking Water Administrators, The American Water Works Association with support from The U.S. Environmental Protection Agency under cooperative agreement #CR-812144 (e.g. *NSF, 2000*). In the preface on page v of the original 1988 NSF 61 Standard, it is stated: “*Standard 61 was developed to establish minimum requirements for the control of potential adverse human health effects from products which contact drinking water.*” The key point is that members of the public and the water industry expect that NSF 61 certification prevents public use of products that would release excessive concentrations of lead to drinking water.



Figure 3.2: Photo of public advertisement of NSF Section 8 certified devices.

It is recognized that compromises are necessary in developing a test, and that the actual concentrations of lead measured during the test are controlled by the test protocol. Key factors in the protocol include chemistry of the test water, duration of the test, duration of the contact time of test water and material before sampling, “normalization” (volume adjustment) factors, and reproducibility. Reproducibility is a function of both the water chemistry and laboratory protocol, and also whether or not particulate or colloidal lead could be released randomly or episodically by the material being tested. The experiments conducted in this work focus only on examining the chemistry of the test waters and the “normalization” factors, and how they relate to the practical stringency of the test with respect to lead leaching.

## MATERIALS AND METHODS

Sixteen apparently identical hose bibs were purchased from a local hardware store, each from the same manufacturer and from the same lot. While hose bibs themselves do not normally require NSF 61 Section 8 testing, as they are not specifically intended to produce water for human consumption (Table 3.1), they were convenient for scientifically examining the aggressivity of the test waters. The specific type of hose bib used in these tests had been voluntarily submitted for NSF testing, and they were clearly labeled as NSF certified according to the Section 8 protocol. Later testing also compared these devices to other brass devices passing NSF 61 Section 8, and the performance of the hose bibs was highly representative of lead leaching measured from the other devices.

The hosebibs were covered at one end with a threaded PVC cap and at the other end with a non-threaded cap (Figure 3.3). During testing the hose bibs were set horizontally with the outlet directed up. Twelve identical sections of 12 cm long 1.7 cm inner diameter pure lead pipe were also used to examine the aggressivity of the test solutions to pure lead. One end of each lead pipe was plugged with a rubber stopper that did not leach lead, whereas the other end of the lead was loosely covered to exclude dust from entering the device.



Figure 3.3: Photo of brass hose bib assembly used in experiment.

The leaded samples were rinsed twice with de-ionized water, and then rinsed twice and later filled with water from one of four different solutions:

- 1) NSF pH 5.0 water: 203.25 mg/L  $\text{MgCl}_2$  (51.82 mg/L as Mg) and 347.25 mg/L  $\text{NaH}_2\text{PO}_4$  (77 mg/L as P) with 2 mg/L as  $\text{Cl}_2$ .
- 2) NSF pH 5.0 water without phosphate: same recipe as pH 5 water but without  $\text{NaH}_2\text{PO}_4$ .
- 3) NSF pH 10 water: 476.75 mg/L sodium borate (110.4 mg/L-B) at pH 10 dosed with 2 mg/L as  $\text{Cl}_2$ .
- 4) Aerated NSF pH 10 water: Same recipe as NSF pH 10 water but aerated for an hour, then readjusted to pH 10.

For comparison, the same leaded materials were exposed to a relatively non-aggressive tap water containing 30.5 mg/L alkalinity as  $\text{CaCO}_3$ , pH 8.6, 40 mg/L of  $\text{Cl}^-$  and 50 mg/L of  $\text{SO}_4^{-2}$ . In each case, chlorine was added from fresh solutions of reagent grade sodium hypochlorite (bleach) when fresh solutions were made up weekly. Each condition was tested in triplicate. pH was precisely adjusted to the target value using 1 N HCl or 1 N NaOH.

Water was changed in the devices as per the published ANSI/NSF 61, Section 8 schedule. Basically, after the product is rinsed as described above, the protocol calls for a minimum of 24 hours between water changes and allows up to 10 water changes over a time period up to 14 days. In this work, water in the device was changed every 24 hours, except when samples were taken for lead analysis after the 2<sup>nd</sup>, 9<sup>th</sup>, 25<sup>th</sup> and 58<sup>th</sup> days of exposure. All sampling was after a 16 hour stagnation time. The same schedule was followed for the pure lead pipes except that the experiments were terminated after the 25<sup>th</sup> day. On occasion, samples collected from the pure lead pipes were passed through a 0.45  $\mu\text{m}$  pore size nylon syringe filter to quantify soluble lead.

Another short-term experiment was designed to test the ability of the NSF protocol to detect plumbing products that would pose an obvious lead hazard. For the test, an “in-line device” was made of pure lead that held 6.3 mL of water. This device was then tested according to the NSF protocol using the pH 5 water with only 2 days of exposure, which is allowable under NSF 61 but which maximizes the likelihood a product would fail. Samples were collected from the pipe after a 13 hour dwell time and were preserved with 2% nitric acid and held for at least 28 hours before analysis.

All samples were analyzed for phosphorous, lead, copper, and zinc using a Jobin Yvon Ultima Induced Coupled Plasma-Emission Spectroscopy (ICP-ES) as per standard method 3120 B (*APHA, 1998*).

## **RESULTS AND DISCUSSION**

Results are presented in five sections including: 1) considerations of test water chemistry, 2) effect of the phosphate on leaching propensity of the NSF pH 5.0 water, 3) effect of CO<sub>2</sub> influx on leaching propensity of the NSF pH 10 water, 4) ability of the NSF protocol to detect an obviously flawed product, and 5) retrospective analysis and recommendations.

### **Consideration of Test Water Chemistry.**

Many believe that the two NSF Section 8 test waters were specifically designed to extract a very high amount of lead from a product. To the extent this is true, the test would be more protective, since concentrations of lead leached to the test water would be much higher than would ever be encountered in practice. But close examination of the test water chemistry and methodology reveal potential problems with that belief.

For the NSF pH 5 water, the concern is the presence of 2.5 mM of orthophosphate. This is a level of orthophosphate expressed, in common units, as 77 mg/L as P or 240 mg/L as PO<sub>4</sub>. Orthophosphate is present in the test solution to act as a pH buffer, but it is also specifically added to drinking water to reduce lead leaching (e.g., *Schock et al, 1996*). Nationally, about half of all large public utilities add phosphate corrosion inhibitors to their drinking water (*McNeill & Edwards, 2002*). The concentration of orthophosphate in the NSF pH 5.0 water is between 20-100 times higher than the level of phosphate commonly added to water by utilities to control lead leaching to drinking water.

Solubility models have been useful in predicting changes to lead leaching in response to phosphate inhibitor dosing. The models predict, and field evidence supports, that even low doses of phosphate dramatically reduce lead solubility even at pH 5 (Figure 3.4); therefore, it is expected that the presence of the phosphate would reduce lead leaching to the test solution (*Schock, 1989a; Schock et al, 1996; Edwards et. al., 1999 and 2002a&b*). For example, a water at pH 5 in equilibrium with the atmosphere can hold millions of ppb lead in solution, but the same water with 77 mg P/L orthophosphate present can hold only a few hundred of micrograms per liter (ppb) of lead in solution. This suggests that the NSF pH 5 water may not be as aggressive as is commonly believed, due to the very high concentrations of inhibitor that are present.

Considering the NSF pH 10 water, which is a pure water buffered with a high concentration of borate, confidential discussions with laboratories that conduct such testing revealed that this water is of highly variable aggressiveness. Laboratories observed that generally products fail more easily in “fresh” solutions, whereas they pass more easily in older or “seasoned” pH 10 waters. The test protocol itself does not specify age of the solutions to be used, or the type of containers used (i.e., open or closed to the atmosphere), which could affect CO<sub>2</sub> exchange rates with the water. Some labs use fresh waters while others make up large quantities of water to use over a period of months. If it were proven that this difference in approach caused any variability in results, it would be problematic since the same product might fail in one lab and then pass the test in others. It also has been observed that high concentrations of borate, such as are used in the NSF pH 10 test water, can provide corrosion inhibition through unspecified mechanisms (Butler and Ison, 1966)

The notion that storage of the test water would alter corrosivity is anticipated based on potential dissolution of carbon dioxide from air to the alkaline solution. Lead solubility is extremely sensitive to presence of CO<sub>2</sub> in this pH range. In fact, over a reasonable range of CO<sub>2</sub> that might dissolve into the water in a period of months, solubility models predict that influx of even small amounts of CO<sub>2</sub> to the NSF pH 10 water would dramatically decrease lead leaching (Figure 3.5). This is consistent with water utility experiences, in that high pH and low carbonate waters are known to be highly non-aggressive to lead leaching based on both solubility models and practical data (*Schock, 1980; Schock et al, 1983; Dodrill & Edwards, 1995; Edwards et. al., 1999*). In fact, the high pH and low alkalinity condition is specifically targeted to control lead leaching in many water systems.

Experiments in the following two sections examine the lead leaching ability of the NSF pH 5.0 water and pH 10 waters.



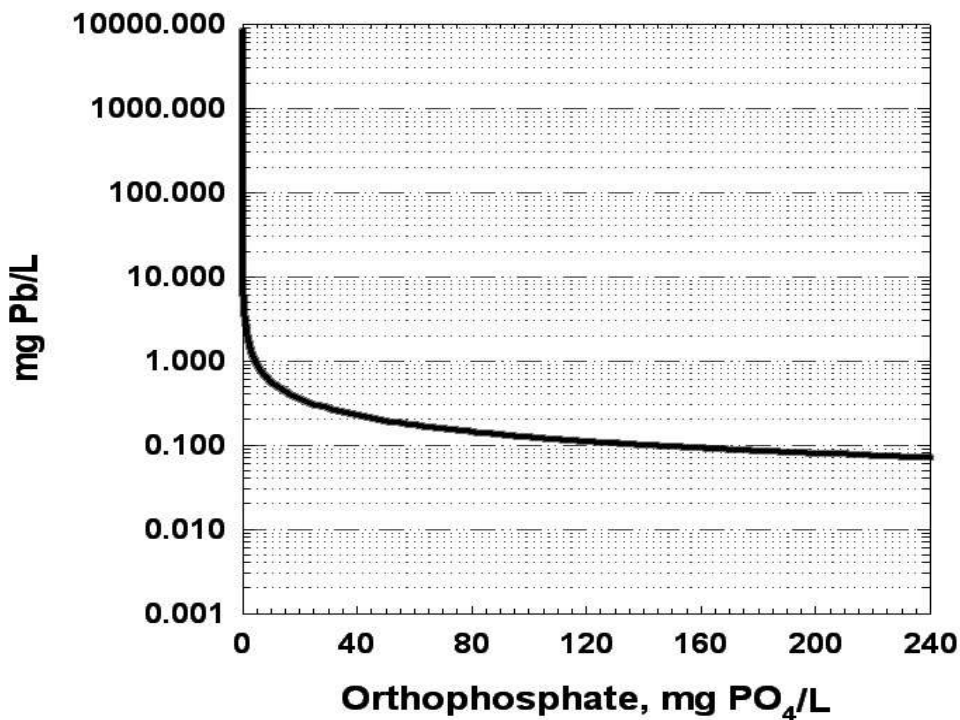


Figure 3.4: Equilibrium solubility of lead as a function of phosphate concentration at pH 5.0. Dissolved inorganic carbon is assumed to be that present at equilibrium with air (0.14 mg/L).

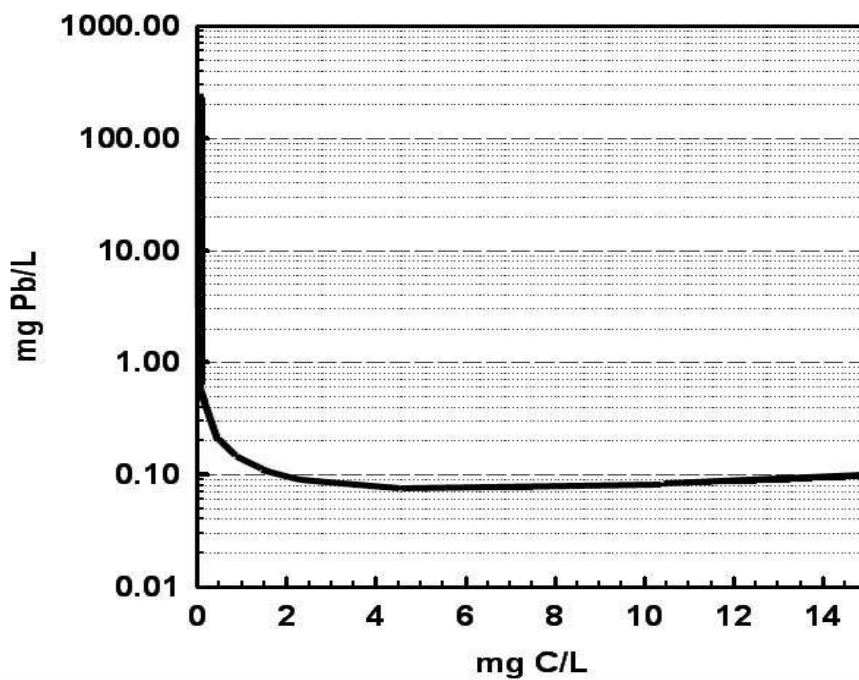


Figure 3.5: Equilibrium solubility of lead as a function of dissolved inorganic carbon (DIC) at pH 10.

### **Effect of Phosphate on Lead Leaching Propensity of the NSF pH 5 Water.**

The concentration of copper, zinc and lead leached from the brass hose bibs and pure lead pipes were studied as a function of time. Results after 9 days of dump and fill exposure are selected as illustrative. The phosphate (i.e., inhibitor) in pH 5 water markedly decreased leaching of lead from both brass (Figure 3.6) and pure lead pipe (Figure 3.7). For instance, for brass on the 9<sup>th</sup> day of exposure, average release from the water without phosphate in brass hose bibs was 0.185 mg/L, consistent with the relatively high aggressiveness of distilled water noted in *Gardels & Sorg (1989)*. In the NSF pH 5 water but with the orthophosphate, lead leaching was 5 times lower at 0.038 mg/L (Figure 3.6). This difference is deemed significant at greater than 99% confidence using a t-test assuming equal variance ( $P = 0.005$ ). As a further point of comparison, leaching of lead to the relatively non-aggressive tap water was 0.16 mg/L. Thus, the non-aggressive tap water actually leached more than 4 times less lead than did the supposedly aggressive NSF pH 5 water. Clearly, the NSF pH 5 is actually not aggressive in the context of lead leaching from leaded brass.

Not surprisingly, levels of lead leached from pure lead pipes during the test were orders of magnitude higher than for brass (Figure 3.7), consistent with the hazardous nature of lead pipe in practical situations. More than 25 times less lead was leached to the NSF pH 5 water relative to the same water without phosphate. The NSF pH 5 water leached 3.5 times less lead than did the non-aggressive tap water at pH 8.5. Most of the lead leached from the pure lead pipes in these tests was particulate, and in the non-aggressive tap water soluble lead was virtually undetectable.

The presence of phosphate in the NSF pH 5 water decreased lead leaching, but its effects on copper were complex in comparison to both field and laboratory experience (*Schock, et al., 1995; Schock & Fox, 2001*). In this test, it increased copper leaching by 14 times relative to the same samples for pH 5 without phosphate buffer (Figure 3.8). This is the result of a complex interaction of low pH with low dissolved inorganic carbon (DIC) concentration, which is consistent with several research studies. The general expectation (*Edwards et. al., 1996 and 2002a; Lytle & Schock, 1996*) is that copper phosphate solids are not predicted to form in low DIC waters at this very low pH, and the phosphate buffer tended to reduce the final pH of water at the end of the test (pH = 5.2) relative to the same water without buffer (pH = 7.77). Since the final pH was lower the phosphate could exert no inhibiting action on copper leaching, and the NSF pH 5.0 water is more aggressive for copper relative to the same water without phosphate (*Edwards et. al., 2002a*). This effect should not be confused with well established benefits from phosphate inhibitors in reducing copper leaching in high alkalinity waters at circa neutral pH.

The effect of test duration was also studied (Figure 3.9). As expected, a higher amount of lead was leached from each device at the start of experiment, and it gradually decreased with time as the sample aged. However, in the presence of phosphate buffer, lead leaching was relatively low even from the very first sample collected and aging was less of an issue. In fact, in the presence of phosphate buffer, lead leaching was less than 0.05 mg/L in just 9 days. The opposite effect was observed for copper in the presence of phosphate. Specifically, with phosphate the copper surface did not passivate, whereas in the absence of phosphate relatively low amounts of copper were leached from the start of the experiment (Figure 3.9). Leaching of zinc from the brass was relatively insensitive to the level of phosphorous, and leaching decreased markedly with exposure time (data not shown).

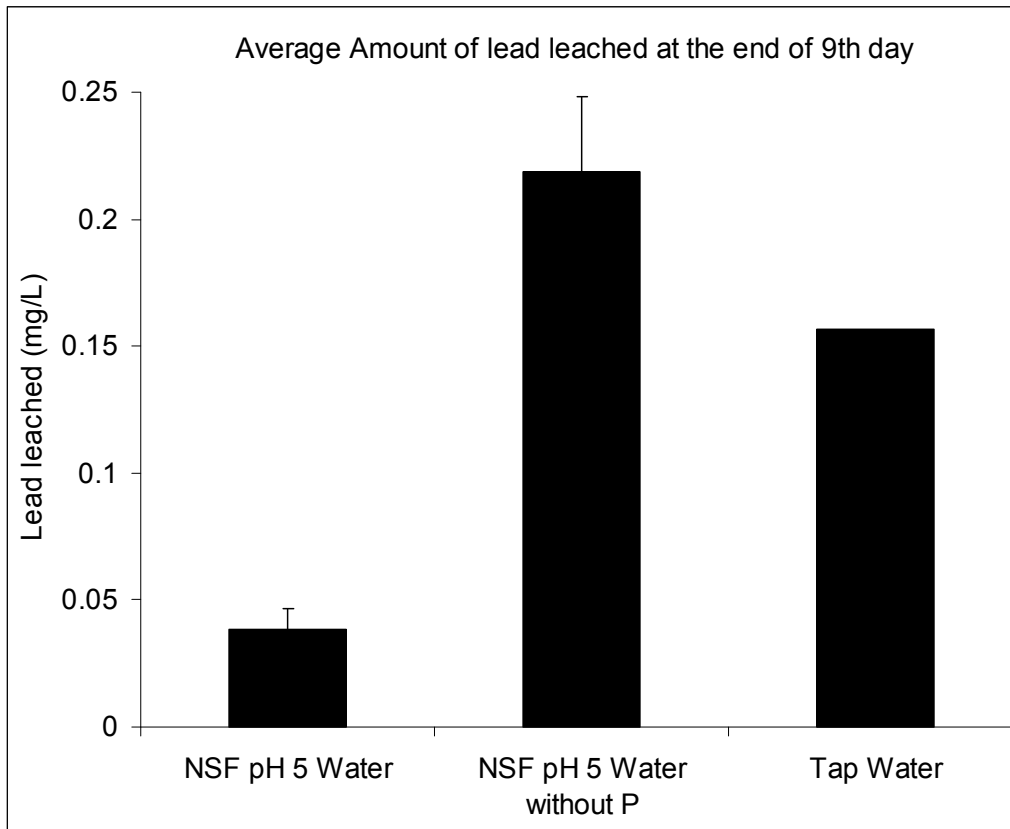


Figure 3.6: Amount of lead leached after an overnight stagnation after 9 days from brass hose bibs. Result is average of triplicate samples. All error bars in this paper denote 90% confidence intervals.

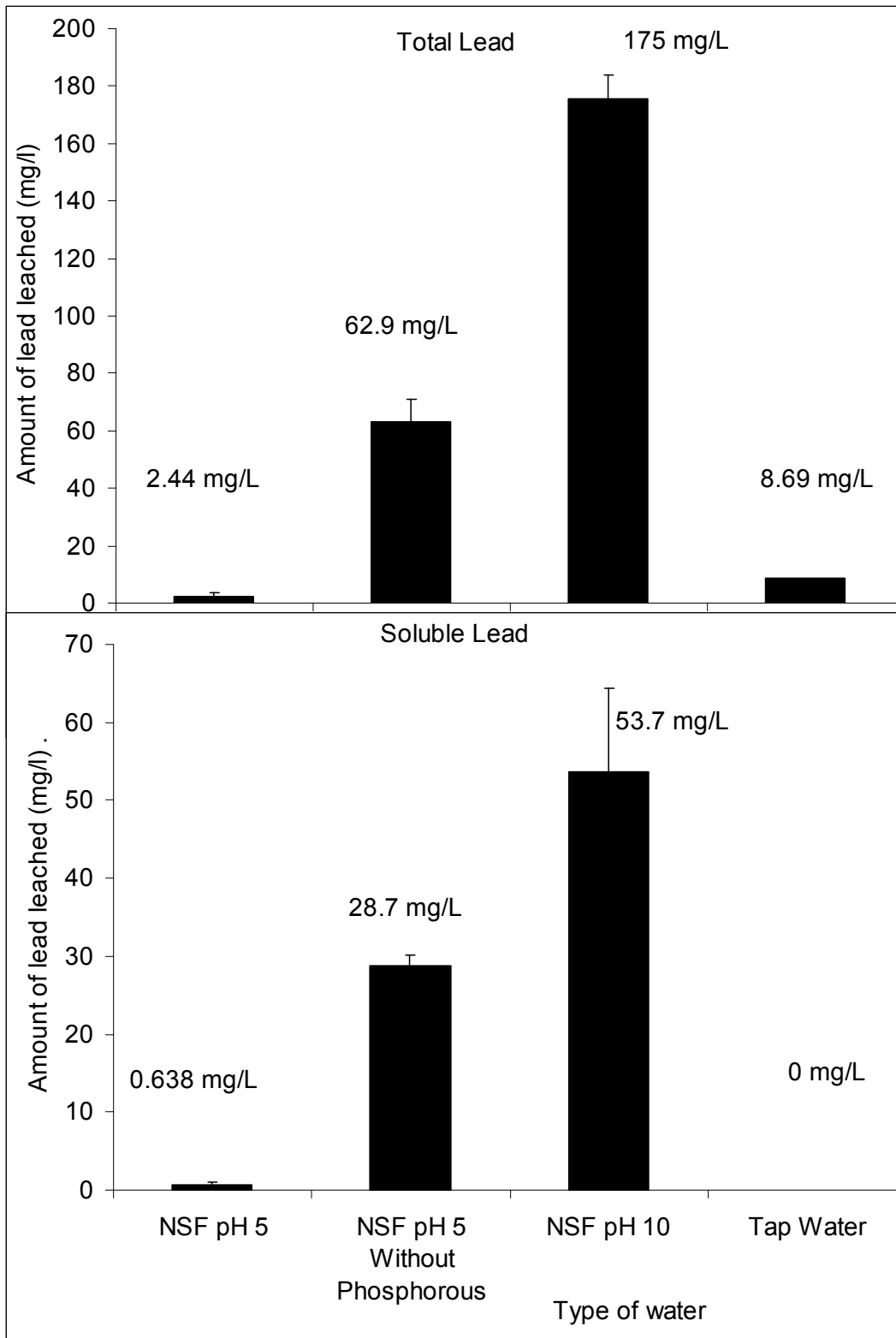


Figure 3.7: Total and soluble lead leached after an overnight stagnation from the pure lead pipes after 9 days of dump and fill.

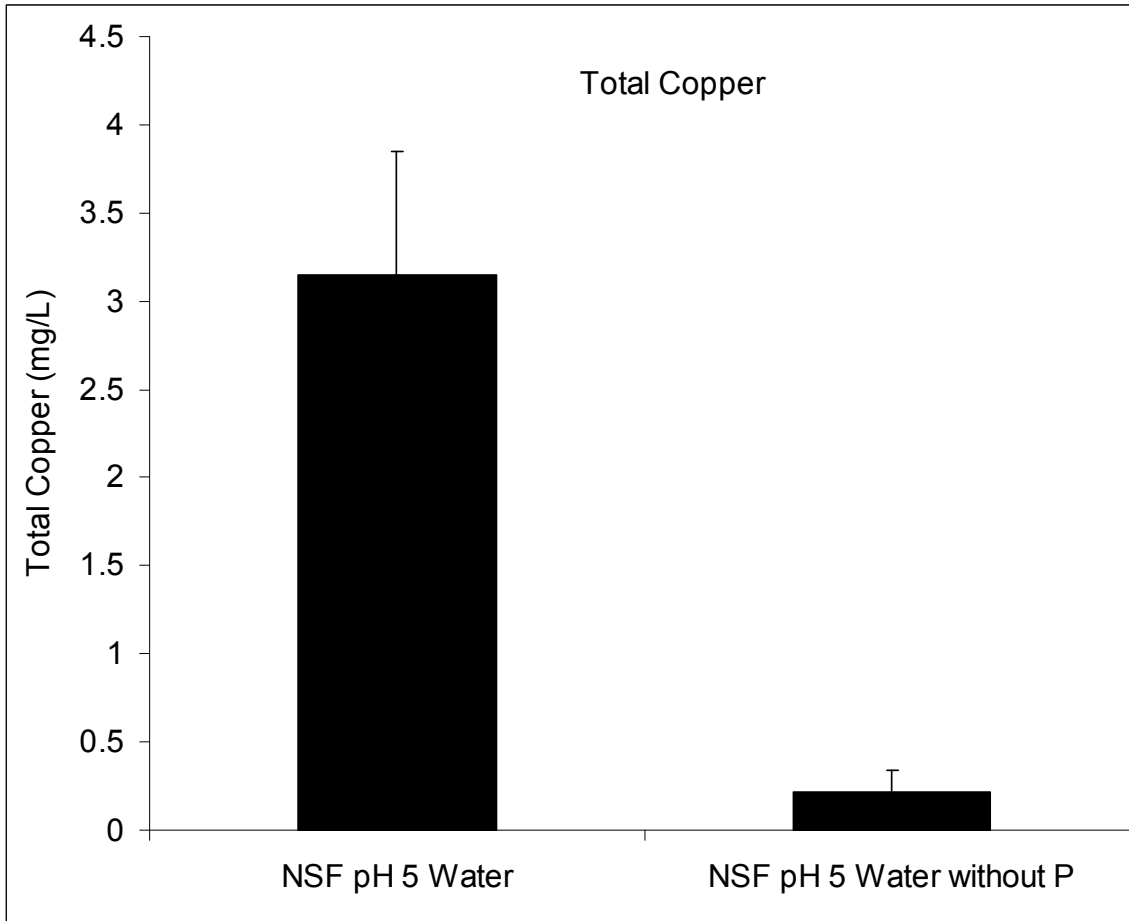


Figure 3.8: Amount of copper leached after an overnight stagnation after 9 days of dump and fill for NSF pH 5 water with and without phosphate.

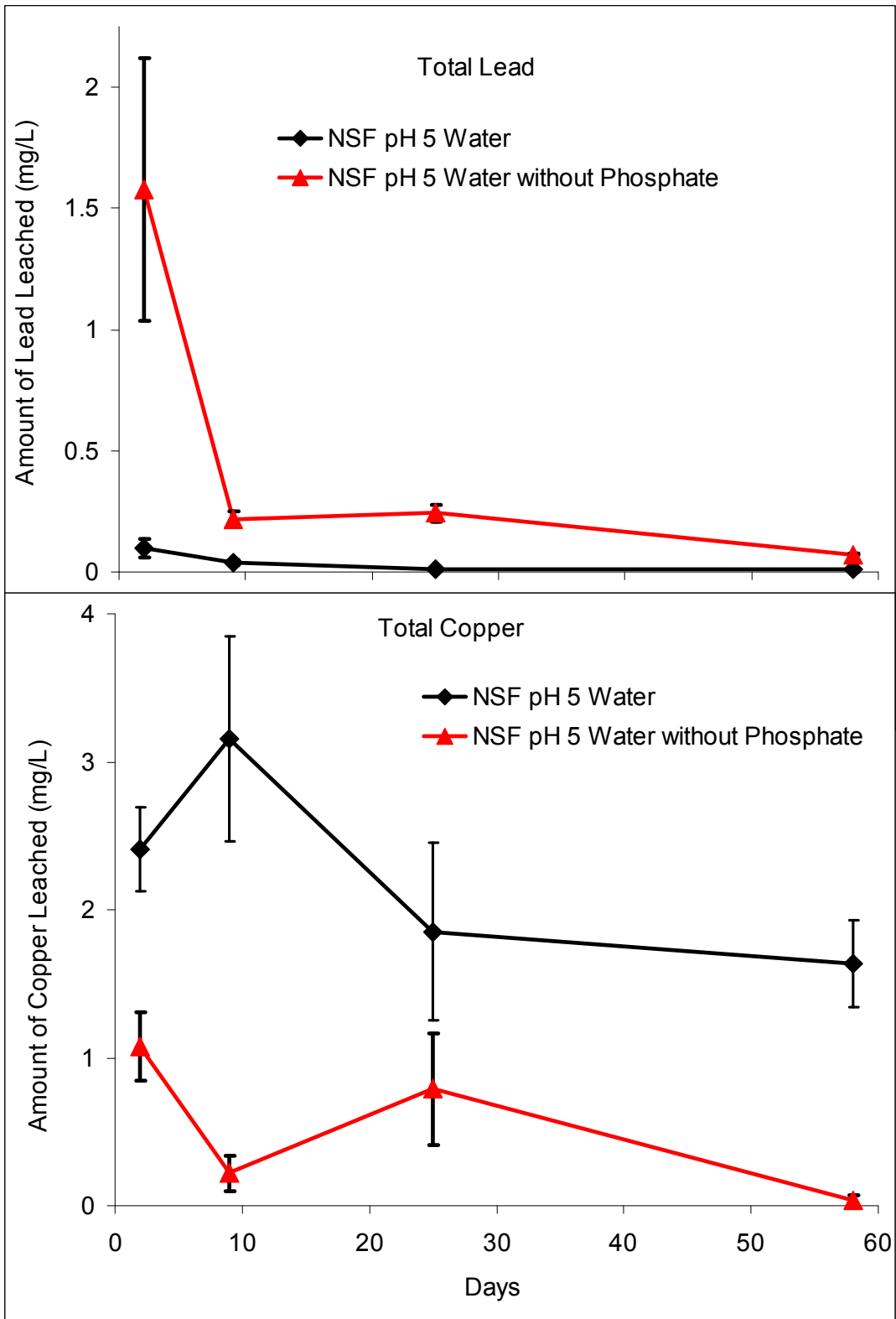


Figure 3.9: Lead and copper leached after an overnight stagnation as a function of time for brass hose bibs.

### **Effect of aeration on Lead Leaching Propensity of the NSF pH 10 Water.**

After one hour of mild aeration, the NSF pH 10 water had a final pH of 9.2 and an inorganic carbon content of 37 mg/L. This is only about 30% of the inorganic carbon expected for a water equilibrated at pH 9.2 CO<sub>2</sub> with the atmosphere, so the water remains highly undersaturated and could have held much more CO<sub>2</sub> (Lytle *et al.*, 1998). This aerated solution was deemed a reasonable compromise between a fresh solution and what might normally be encountered after months of storage in open containers in practice, since the aeration increased the inorganic carbon in this highly buffered solution while only slightly lowering the pH. The pH of this water was re-adjusted back to 10 with freshly prepared NaOH in order to isolate the effect of inorganic carbon alone on the results. The same water prepared without aeration had a pH of 10 and a typical inorganic carbon content of 1.0 mg/L. Solubility curves predict that lead solubility (and therefore soluble lead leaching) would actually be minimized at only 4 mg/L inorganic carbon and maximized at 0 mg/L carbon (Figure 3.10).

Inorganic carbon can have very complex effects on lead leaching as a function of exposure time, since carbonate can form soluble complexes with lead in solution but carbonate can also form highly insoluble lead solids on the surface of the plumbing material. Since it takes time to form the insoluble lead solids, and the kinetics relate to both carbonate and hydroxide ion activities, the presence of inorganic carbon can increase lead leaching for a time before ultimately decreasing lead leaching (Schock & Gardels; 1983; Schock, 1989b; Schock *et al.* 1996; Edwards & McNeill, 2002b). Consistent with that expectation, the first measurement (Figure 8) demonstrated higher lead leaching in the aerated water (high carbonate) relative to the same water without aeration (lower carbonate). But by the 9<sup>th</sup> day of testing the two results were nearly identical, and at every time thereafter the aerated water with higher carbonate contained much less lead. In this case copper showed nearly identical trends to lead (Figure 3.10), as would be expected given short term importance of soluble cupric carbonate complexes relative to the longer term importance of insoluble cupric oxide and hydroxycarbonate solids on the pipe wall (Schock, *et al.*, 1995; Edwards *et al.*, 1996).



As is expected, when pure lead pipes were exposed to aerated and un-aerated water, aeration increased lead solubility for data collected at two days exposure, but at 9 and 25 days soluble lead was much lower in aerated water relative to the same water without aeration (Figure 3.11). This is consistent with utility experiences. Initial dissolved oxygen was the same in all test solutions, so the effect is strictly due to dissolution of CO<sub>2</sub> into the test water.

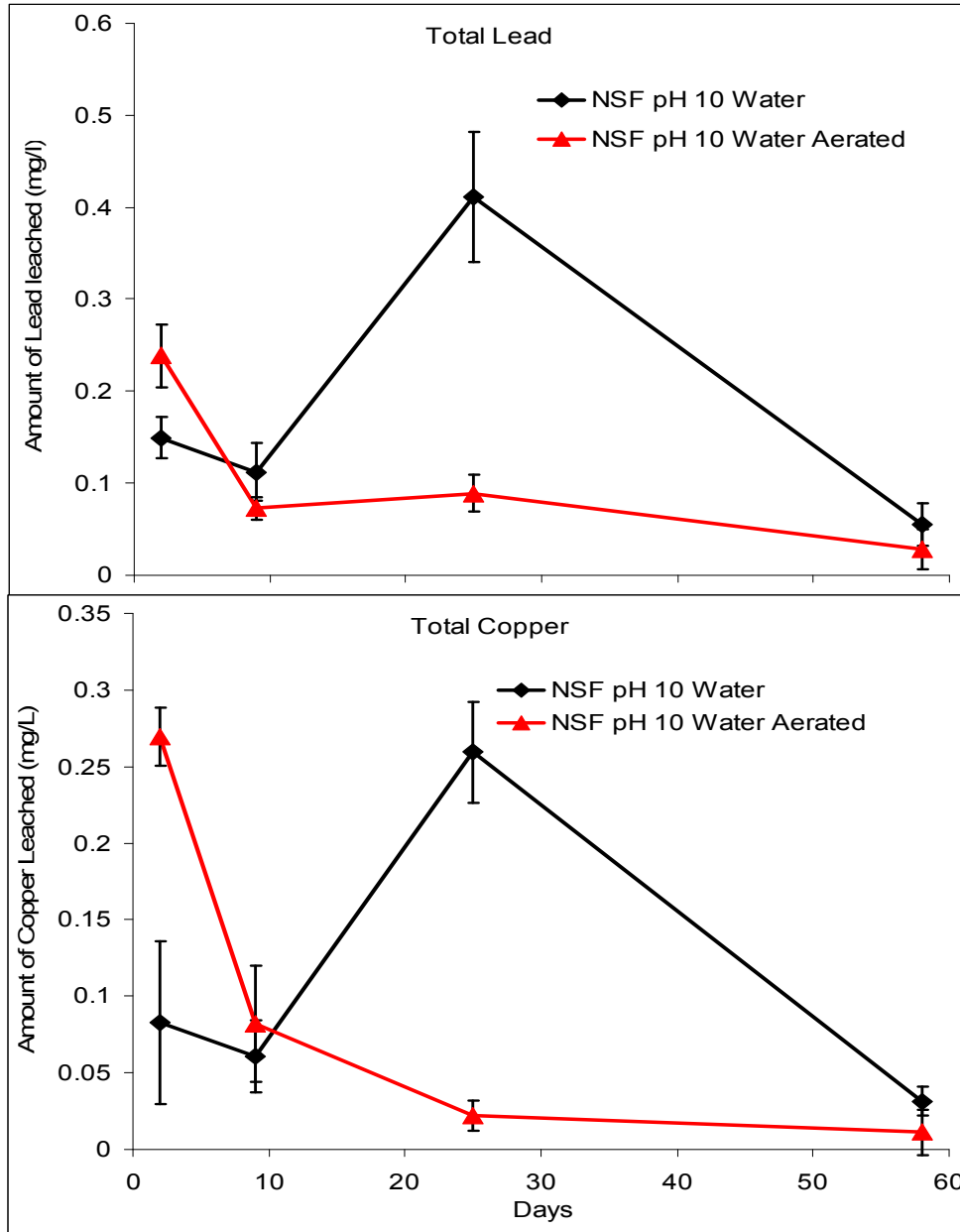


Figure 3.10: Lead and copper leached after an overnight stagnation as a function of days for brass hose bibs.

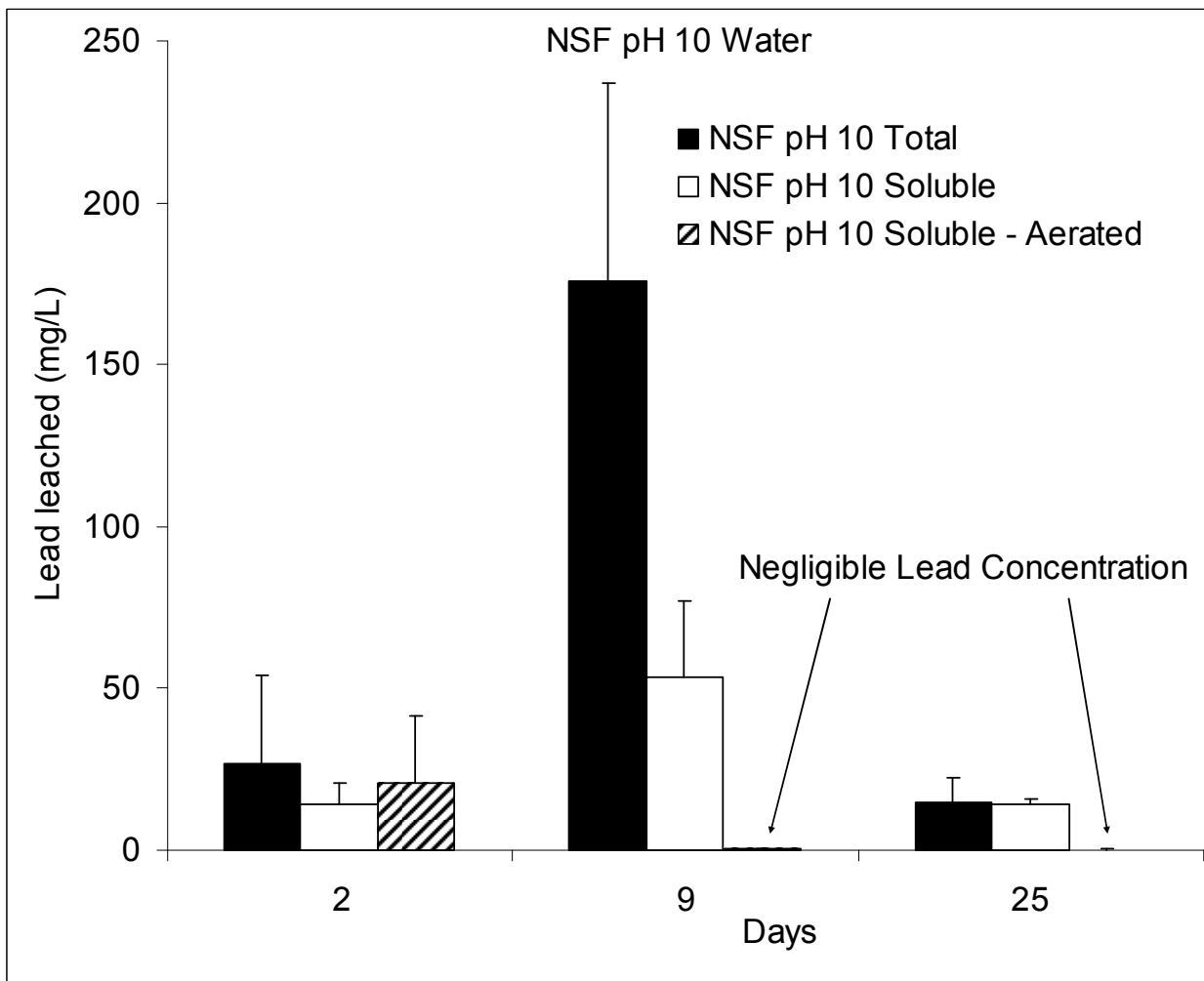


Figure 3.11: Lead leached after an overnight stagnation as a function of time for pure lead pipes.

**Considering the Overall Rigor of the Test.**

It is instructive to consider normalization factors and how they determine whether a device passes the NSF protocol. The normalization factors attempt to take into consideration dispersion of water sitting stagnant within in-line devices as it travels to the tap, the likelihood the water is diluted by collection in a one liter container by the consumer, and a time adjustment factor. For a 13 hour test using a device that holds 6.3 milliliters, the actual lead measured in the water at the end of the test is multiplied by a normalization factor calculated as follows:

$$\text{Normalization factor} = (\text{Dispersion Factor}) \times (\text{Dilution Factor}) \times (\text{Time Factor})$$

Equation 1

For devices that hold up to 1 liter of water, the dilution factor is equal to the amount of water held within the device, divided by 1 liter. For device that holds 6.3 ml water, the dilution factor is therefore 0.0063 (=6.3/1000). Normal stagnation time is assumed to be 12 hours, however if a different time is used in the lab test, the time factor is equal to 12 hours/actual stagnation time. For a 13 hour test, the time factor is therefore 12/13 = 0.92. The dispersion factor is always 0.3333. The net result is that the normalization factor for a 6.3 mL device is:

$$\text{Normalization factor} = 0.3333 \times 0.0063 \times 12/13 = 1.938 \times 10^{-3}$$

Thus, the actual lead concentration measured in the device at the end of the test would be multiplied by  $1.938 \times 10^{-3}$  to project concentrations at the tap.

A test was conducted using pure lead pipes that held 6.3 milliliters of water. After conditioning only 2 days, which is allowed by the protocol and can be only expected to make the product more likely to fail the test when compared to a possible 14 day exposure, the actual concentration of lead leached to the water was 2100 ppb after an overnight stagnation of 13 hours. The normalized lead concentration was therefore 4.2 ppb (= 2100 \* 0.001938). This is far below the threshold of 15 ppb that would fail the device. This pure lead device would therefore pass the leaching part of the NSF test using the pH 5 water, which is the test water most experts thought would be most aggressive to lead. This example clearly illustrates the possible lack of protection offered the public by the NSF test, since it cannot detect a device that would pose an obvious health hazard.

A closer look at the normalization calculation used by NSF for certification reveals that the standard is not actually based on concentration, but rather, the total mass of lead that is leached to the water during the stagnation time. For a 12 hour stagnation time, 45 µg of Pb can leach to water regardless of the size of the device (up to a 1 liter total holding volume). For devices holding small volumes, this means that very high lead concentrations are required to fail the standard, whereas devices holding larger volumes will fail at lower levels of lead (Figure 3.12).

It is worth considering the level of protection offered by the standard in the context of modern regulation and concern about lead in drinking water. A typical residential plumbing system might have between 3 to 10 in-line brass devices between the water main and the consumers tap. There is no upper limit. As the normalization calculation shows, each device can leach up to 45  $\mu\text{g}$  of lead to water in a 12 hour stagnation period and still achieve NSF certification. According to some interpretations, California proposition 65 has legal penalties for manufacturers of devices that could expose consumers to more than 0.5  $\mu\text{g}$  Pb on any day. It seems highly likely that, in a relatively aggressive tap water, that a consumer could someday draw a sample of water that contacted the devices in question during stagnation, and therefore be exposed to much more than 0.5  $\mu\text{g/L}$  Pb.

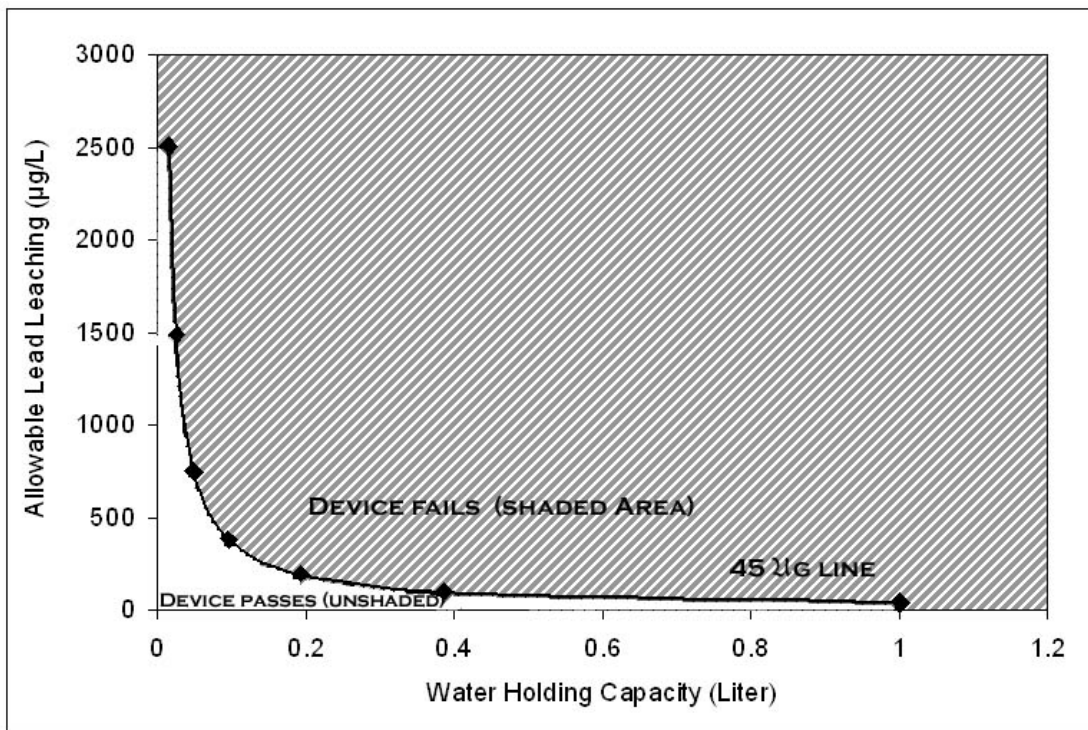


Figure 3.12: Allowable lead leaching from NSF devices as a function of the water holding volume of the product.

### **Retrospective Evaluation and Recommendations.**

Any reasonable test of a product's lead leaching tendency requires significant compromises to be made. Some compromises made in the NSF 61, Section 8 protocol appear to have been problematic. This section retrospectively attempts to document "what went wrong" in the NSF certification process in the context of current problems with LCR compliance and elevated levels of lead in schools. Hopefully, lessons can be learned, and the certification program can be modified, such that the original intent of the testing can be achieved.

As part of the Drinking Water Additives Program, Task Groups were formed by the National Sanitation Foundation in 1986 and 1987 to develop standards for lead and other trace metal contamination from plumbing devices and materials in contact with drinking water (McClelland & Gregorka, 1986; McClelland et al., 1989). One of the issues discussed is the all important identity and nature of the test water. In an internal memo, Schock (1987) stated "*I think it is possibly quite misleading, if not erroneous, to use a buffer system consisting of species which can function as major corrosion inhibitors....*" and "*..the strategy of pH buffering using salts that have a profound effect on metal leaching can not give test results that have any meaning when applied to realistic field situations...*" At that time, the effect of phosphate as an important plumbosolvency inhibitor had already been established by numerous studies (Schock & Wagner, 1985). Also, during this time period, NSF conducted an internal exposure methods study using the original pH 5 and pH 10 proposed solutions, plus a pH 8 water. These tests indicated that the pH 5 water with orthophosphate caused significantly less Pb release upon 24 hours of exposure than either the pH 8 or pH 10 water. Five test waters were later tested without any phosphate whatsoever (Schock, 1989a).

By early 1989, the Mechanical Plumbing Products Task Group of NSF adopted the high alkalinity, pH 8 water as the preferred test water for a new “Section 9” for Mechanical Plumbing Devices. This water met the criteria of being both relatively aggressive towards lead and copper, and also being easier to control in composition which is important given that many laboratories would do testing. Interestingly, the February 1, 1989 draft standard for Section 9 had the following proposed coverage:

*“This section covers the following plumbing devices installed in the water distribution system of a building and components or materials used in devices as follows: kitchen faucets; laundry faucets; lavatory faucets, bar sink faucets; rough, in line control valves; backflow prevention devices; water coolers; drinking fountains; water heaters/storage devices/tanks; water meters and related fittings; supplies and supply stops; drinking water treatment units; ice makers and similar devices as are intended by the manufacturer for drinking and culinary purposes.”*

Clearly, it was originally intended that many in-line devices and water meters, now covered in Section 8, were to have been covered in Section 9. This change may prove to be important given the relatively non-rigorous nature of Section 8 as revealed in this research. Water industry personnel should be made aware of this potential problem.

Representatives of the water industry also expressed serious reservations early on as to the apparent lack of rigor in the developing NSF Section 8 and Section 9 standards. In a letter to NSF dated April 6, 1992, John Sullivan of the American Water Works Association Government Affairs Office wrote the following about the proposed NSF Section 9 standard:

*“I am astounded at the agreement reached by your Ad Hoc Committee... Originally your broad standard was lead (or any other Contaminant) in drinking water from any indirect source...was restricted to a contribution 10 percent of a maximum contaminant level (MCL). Because of objections regarding lead from the Plumbing Manufacturers Institute, this requirement was debated in the drinking water community and AWWA offered the compromise restriction of between 30 and 50 percent of the action level. ...Your agreement allows plumbing fixtures alone to trigger utility action levels through June 1995 and well beyond, depending on stocks available! Allowance of a level of 22 parts per billion for plumbing fixture contributions will cause many utilities to exceed the action level through no fault of the utility. ...This agreement does Not at all address the utilities’ problem of compliance with the law and the real contribution of brass plumbing fixture.... Our previously stated compromise is still firm- we cannot agree to the position of your Ad Hoc Committee.... We are also discussing the entire issue with EPA to try and reach some resolution regarding Compliance or modification of the rule, if that is legally necessary!”*

It is also well known that manufacturers have invested considerable money and effort in producing brass devices that can achieve NSF certification using surface washes or application of coatings. However, there is no guarantee that the techniques reducing lead leaching over a short term exposure in a test water at pH 5 loaded with phosphate inhibitor will have anything to do with reducing lead leaching to real water. The NSF testing protocol does not take into account possible sacrificial behavior of leaded brass when it is galvanically coupled to copper in normal plumbing configurations (Dudi, 2004; Schock, 1989a), thereby enhancing lead leaching relative to a test on a stand alone product. Another important issue to be explored is the higher aggressivity of chloramine versus chlorine in the context of lead leaching (Edwards, 2004a; Edwards et al., 2004b; Dudi, 2004). At a minimum, the NSF Section 8 protocol needs significant revision if it is to meet its intended purpose of protecting public health in real drinking waters.

From a broader perspective, it would also seem desirable to have a standard that is open to public scrutiny and written in a comprehensible manner. Copies of the standard have numerous typos and directions are extremely difficult to follow. It is NSF policy to sell copies of the standard for several hundred dollars per copy, although older versions of the standard are sometimes provided free of charge in some instances, as in the case of this investigation.

It may take years to sort out the public health significance of the problem with leaded brass. Previous researchers attempting to quantify the leaching propensity of leaded brass devices have tended to use more realistic waters regardless of NSF test protocol specifications (*e.g.*, Gardels & Sorg, 1989; Maas *et. al.*, 2002a-e; Patch *et. al.*, 1998). The collective work of Maas and Patch (1997-2002) demonstrates a significant leaching potential for “lead-free” devices, as defined by the Safe Drinking Water Act (EPA, 2004). A dramatic reduction in the allowable lead content of brass products would seem highly desirable relative to experiences to date under the voluntary standards program, unless the testing protocol can be brought more in line with known drinking water treatment chemistry and field experiences with lead sampling and exposure analysis. Future research should address these problems in greater detail.



## CONCLUSIONS

- The use of phosphate buffer in NSF pH 5.0 test waters dramatically reduces lead leaching from brass devices, rendering the water less aggressive for lead than many tap waters. The addition of phosphate to the pH 5 water increases copper leaching relative to the same water without phosphate, making it more aggressive than many tap waters.
- Influx of carbon dioxide to the pH 10 water can dramatically alter its propensity to leach lead. Over the short term, preventing CO<sub>2</sub> influx increases lead solubility by preventing formation of soluble lead carbonate complexes. After about one week exposure time, dramatic reductions in lead leaching are observed, most likely due to formation of lead scales on the device that limit lead solubility. A failure to specify “freshness” of the solutions therefore allows unacceptable variability, and may allow certification of devices that leach excessive lead to water. Use of high levels of borate might also be an issue.
- It has been shown that a small device made of pure lead can pass the NSF leaching test, and would only be prohibited from public sale by the 8% limit under the 1996 amendments to SDWA. The NSF test therefore lacks the rigor necessary to prevent installation of devices that pose an obvious public health hazard.

- The NSF 61 Section 8 standard for brass in-line devices does not appear to offer a stringent level of protection against lead exposure relative to modern regulations such as California's Proposition 65. While potential problems with in-line devices are not always detected through first draw LCR monitoring, there is a potential for devices to contribute to LCR exceedences and to human exposure. Most certainly, leaching of significant lead from new in-line devices is not compatible with the EPA maximum contaminant level goal of 0 ppb. Changing the normalization formula and accounting for multiple devices should be considered. It would also be highly desirable to tie the results of a performance test to at least some field experience, account for more aggressive waters with chloramine, and consider the possible increases to lead leaching from galvanic connections to copper.
- A marked reduction in allowable lead content of brass (from the very high 8% level currently allowed) should be carefully considered.

## ACKNOWLEDGEMENTS

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